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Characterisation of beech wood pyrolysis oil: Chemical and physical properties and decomposition kinetics

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HIGHLIGHTS

- Chemical and physical property data were determined for a beech wood pyrolysis oil.
- Thermo-physical property models were developed for low-temperature conditions.
- Chemical property data were analysed using pilot-scale equilibrium calculations.
- Decomposition kinetics were developed and extrapolated to high heating rates.
- Gauss distributed activation energy models are recommended for extrapolation.

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ABSTRACT

Biogenic and anthropogenic pyrolysis oils can be used as renewable feedstocks in combustion and entrained flow gasification processes. The design, evaluation and scale-up of these processes can be done using process and CFD models. However, this requires comprehensive and consistent data sets for the chemical and thermo-physical properties and the decomposition kinetics. Such data sets have not yet been compiled for research or for commercial pyrolysis oils. Therefore, this study characterised an industrial beech wood pyrolysis oil using (i) proximate, ultimate and heating value analyses, (ii) gas chromatography–mass spectrometry (GC–MS), gel permeation chromatography (GPC) and thermogravimetric (TG) analyses, (iii) vacuum and Engler distillations and (iv) measurements of density, dynamic viscosity, thermal conductivity, specific heat capacity and surface tension under atmospheric-pressure and low-temperature conditions. The chemical analyses demonstrated significant uncertainties in the sampling and the analysis methods, which strongly affect the design and evaluation of pilot-scale entrained flow gasification experiments. The vacuum distillations provided representative samples of the vapourisable and non-vapourisable components to a large extent. The TG analyses showed the superposition of vapourisation and decomposition based on separate analyses of the vacuum distillate and the vacuum distillation residue. Furthermore, thermo-physical property models were developed for the beech wood pyrolysis oil, the vacuum distillate and the vacuum distillation residue. Finally, thermogravimetric kinetics were derived based on multi-reaction Arrhenius law models and multi first-order reaction Gauss distributed activation energy models. Single-particle predictions based on these kinetics indicated that multi first-order reaction Gauss distributed activation energy models should be preferred for extrapolation to high heating rates in the absence of kinetics based on drop-tube reactor experiments.

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Nomenclature			
<i>Latin symbols</i>		eq	equilibrium
C	coefficient	\overline{E}_a	of the Gaussian distribution of the molar activation energy
\hat{C}_p	specific isobaric heat capacity	i	of reaction i
\overline{E}_a	molar activation energy	i	of species i
\overline{E}_a	molar activation energy vector	j	of (mixture) j , in (mixture) j
f	probability density function	m	mass-weighted mean
g	auxiliary function in Merrick model	max	maximum
\dot{H}	enthalpy flow rate	n	number-weighted mean
k_0	pre-exponential factor	ng	of natural gas
\mathbf{k}_0	pre-exponential factor vector	oil	of the beech wood pyrolysis oil
\dot{m}	mass flow rate	op	operating
M	molar mass	part	particle
n	reaction order	slurry	of slurry
\mathbf{n}	reaction order vector	solid	of solid compounds
N	number of parallel reactions	steam	of steam
p	pressure	tot	total
P_{th}	thermal input	vd	of the vacuum distillate
\dot{Q}	heat flow rate	vdr	of the vacuum distillation residue
r	volume fraction	0	initial
\overline{R}	molar gas constant	β	recovered
s	uncertainty	<i>Acronyms</i>	
t	time	bioliq EFG	bioliq Entrained Flow Gasifier
T	temperature	CDF	cumulative distribution function
w	mass fraction	CFD	computational fluid dynamics
\mathbf{w}	mass fraction vector	CGE	cold gas efficiency
X	conversion	DTG	differential thermogravimetric
<i>Greek symbols</i>		EXT I, II or III	external laboratory I, II or III
β	heating rate	FID	flame ionisation detector
η	dynamic viscosity	GC-MS	gas chromatography-mass spectrometry
λ	stoichiometric ratio	GPC	gel permeation chromatography
λ	thermal conductivity	HCR	atomic hydrogen/carbon ratio
μ	expectation	HHV	higher heating value
$\boldsymbol{\mu}$	expectation vector	KIT	Karlsruhe Institute of Technology
ρ	density	KIT I, II or III	KIT laboratory I, II or III
σ	standard deviation	LHV	lower heating value
$\boldsymbol{\sigma}$	standard deviation vector	MFORALM	multi first-order reaction Arrhenius law model
σ	surface tension	MFORGDAEM	multi first-order reaction Gauss distributed activation energy model
φ	parameter in Maxwell mixing rule	MRALM	multi-reaction Arrhenius law model
<i>Subscripts and superscripts</i>		PD	polydispersity
af	on ash-free basis	PDF	probability density function
ash	of ash	SMOD	specific minimum oxygen demand
asr	on as-received basis	TG	thermogravimetric
d	on dry basis	UV	ultraviolet

1. Introduction

Biogenic pyrolysis oils, also known as bio-oils, are the liquid products of the thermal decomposition of biogenic substances in the absence of oxygen [1]. Substances, such as cellulose, hemicellulose and lignin, decompose into numerous liquid and solid components depending on the raw material and the pretreatment process employed [2–7]. Industrial pyrolysis oils are mainly produced using fast pyrolysis processes. These processes are operated at moderate temperatures (~500 K), high heating rates (~10⁴–10⁵ K/s) and short residence times (<2 s) [1] and provide pyrolysis oils that can be applied as alternative feedstocks in both combustion and entrained flow gasification processes. Production processes, experimental characterisation methods and applications of pyrolysis oils have therefore been investigated and reviewed in numerous studies [1,8–13].

1.1. Experimental studies

Biogenic pyrolysis oils are typically characterised through (i) the analysis of elemental, solid, water and ash contents, (ii) the analysis of heating values, flash points, ambient density and ambient dynamic viscosity, (iii) the gas chromatography-mass spectrometry (GC-MS) analysis and (iv) the analysis of long-term and thermal stability and miscibility. The ranges of the chemical and physical properties derived from such analyses are given in Tables 1 and 7.

Measurements of further chemical and physical properties have been conducted less frequently for biogenic pyrolysis oils. In particular, previous studies have rarely measured (i) density and dynamic viscosity at moderate temperatures, (ii) vapour pressure, thermal conductivity, specific heat capacity and refractive index and (iii) distillation curves and molar mass distribution curves. Bakhshi and Adjaye [15] determined

Table 1

Carbon contents (dry) $w_{C,oil,d}$, hydrogen contents (dry) $w_{H,oil,d}$, oxygen contents (dry) $w_{O,oil,d}$, nitrogen contents (dry) $w_{N,oil,d}$, sulphur contents (dry) $w_{S,oil,d}$, ash contents (dry) $w_{ash,oil,d}$, water contents (asr) $w_{H_2O,oil,asr}$ and higher heating values (as received) $HHV_{oil,asr}$ of biogenic pyrolysis oils based on previous studies [8,14].

$\frac{w_{C,oil,d}}{\%}$	$\frac{w_{H,oil,d}}{\%}$	$\frac{w_{O,oil,d}}{\%}$	$\frac{w_{N,oil,d}}{\%}$	$\frac{w_{S,oil,d}}{\%}$	$\frac{w_{ash,oil,d}}{\%}$	$\frac{w_{H_2O,oil,asr}}{\%}$	$\frac{w_{solid,oil,asr}}{\%}$	$\frac{HHV_{oil,asr}}{MJ/kg}$
38.1–62.9	4.6–10.3	29.8–51.4	0–0.2	0–0.01	0–0.2	5–45	0.2–1	16–25

vapour pressure curves as well as atmospheric and vacuum distillation curves of commercial Ensyn pyrolysis oils. Peacocke et al. [16] measured densities, viscosities, thermal conductivities, specific heat capacities and refractive indices of Ensyn pyrolysis oils mainly between 293 K and 343 K under both inert and oxygen-rich conditions to study the impact of ageing. Elliott et al. [17] determined the density and the dynamic viscosity of three biomass fast pyrolysis oils and correlated both properties with the water content.

More efforts (see Table S1) have been made to study the conversion of biogenic pyrolysis oils under inert or combustion conditions. Thermogravimetric (TG) analyses, differential scanning calorimetry (DSC) experiments, batch or drop-tube furnace experiments and single-droplet experiments were employed to investigate decomposition steps, kinetics and products as well as yields, reactivity, morphology and atomisation quality [3–5,18–32]. Specifically, TG analyses were used to assign characteristic temperature ranges to the decomposition steps [3,18]. The vaporisation of light volatiles (e.g. water and acetic acid) and heavy volatiles (e.g. furans and carbohydrates), the formation of secondary char, the low-temperature cracking and the release of gaseous decomposition products (CH_4 , C_xH_y , CO, CO_2 and H_2O) were primarily observed below 600 K [3,18], whereas the heterogeneous combustion of secondary char mainly took place above 600 K in the presence of oxygen [3,18]. In addition, TG analyses were applied to develop decomposition kinetics using multi-reaction Arrhenius law models with 3–8 parallel reactions [4,20,21,24]. The kinetics were derived from TG and DTG curves at various heating rates assuming unique sets of pre-exponential factors, activation energies and reaction orders for each biogenic pyrolysis oil [4,20,21]. However, the kinetics were mainly developed for combustion conditions [4,20,21], i.e. the decomposition was superposed by oxidation. Moreover, TG analyses were combined with DSC experiments, GC–MS analyses and gel permeation chromatography (GPC) analyses [5,21,24]. The results showed that the peaks of the TG and DSC curves can be identified at similar positions (between 683 K and 723 K) in the presence of oxygen [24] and that similar compositions in terms of macro-families (water, monolignols, polar components, sugars, etc.) can be derived from thermogravimetric and molar mass distribution curves by proportionate superposition of the corresponding curves of the macro-families [5].

Furthermore, thermogravimetric analysers, differential scanning calorimeters, batch furnaces and drop-tube furnaces were used to study the yields of gas, condensates and char. The results showed that, with higher reactor temperature, the gas yield increases and the yields of char and condensates decrease, while a higher heating rate increases the condensates yield and decreases the char yield at an almost constant gas yield [26,27,29]. In addition to that, a higher content of vaporisable and a higher pressure increase the char yield [25,31], whereas a higher ash content decreases the gas yield and increases the char yield and also shifts the gas composition to more CO_2 and less CH_4 and CO [29]. Thus, lower temperatures, lower heating rates (due to longer reaction times), higher ash contents and higher pressures (due to higher boiling temperatures) favour the thermal re-polymerisation (typically between 523 K and 773 K) and the production of char. The char yield is between 1 % at high heating rates and atmospheric pressures and 40 % at low heating rates and elevated pressures [26,27,29,32]. In addition, an increase in heating rate from ~ 1 K/min to $\geq 10^5$ K/min reduces the char yield from 30 % to 8 % [26], while an increase in pressure from

1 bar to 40 bar doubles the char yield from 20 % to 40 % in a differential scanning calorimeter [32]. Furthermore, the results showed that the char residues from drop-tube experiments have hollow-spherical structures, compositions similar to graphite, reactivities similar to biomass chars and sizes that are similar to the original droplets [26,27,32]. The char reactivities decrease when exposing chars to higher temperatures [26]. In contrast, chars from thermogravimetric analyses have compact glossy surfaces and high hydrogen and oxygen contents due to pronounced devolatilisation [28]. The decomposition kinetics of the latter chars can be described using four-reaction Arrhenius law models [28].

Previous studies also showed that analysis and measurement results are affected by high uncertainties. This is because of (i) fuel complexity, variability and inhomogeneity, (ii) long-term and thermal fuel instability and (iii) the lack of standardised analysis methods. In particular, the heterogeneous composition of biogenic pyrolysis oils as well as the handling, storage and ageing of samples have challenged the comparability of analysis and measurement results [11,16,27,33]. Therefore, several studies [8,10,11,34] reviewed and standardised the analysis methods, while inter-laboratory round robin tests [35–39] were carried out to investigate the influence of individual laboratory methods on the experimental results. Moreover, Brigdwat et al. [33] provided recommendations for the analysis of elemental and water contents and concluded, based on various test reports, that carbon and hydrogen contents can be reproduced with good accuracy. Furthermore, Harman-Ware and Ferrel [34] recommended GPC analysis for determining the molar mass distributions but suggested improvements to enable the use of GPC analysis for a wide range of biogenic pyrolysis oils.

1.2. Modelling studies

Chemical and physical properties at initial and intermediate conversion states as well as reaction kinetics are essential for describing the conversion of biogenic pyrolysis oils in both combustion and entrained flow gasification processes. However, in the absence of appropriate data and models, the conversion of biogenic pyrolysis oils has mainly been modelled using the surrogate vaporisation approach. Zhang and Kong [40], Saha et al. [41], Sallevet et al. [42], Mahmoudi et al. [43] and Sital [44] defined surrogates with up to ten volatile components based on GC–MS data reported for bio-oils [2,3]. However, major organic components seldom have mass fractions of more than 2 %, and biogenic pyrolysis oils, in contrast to liquid fossil fuels, contain components from various chemical classes. The surrogate vaporisation approach thus strongly simplifies the conversion. Instead of the surrogate vaporisation approach, Hallet and Clark [45] suggested the continuous thermodynamics approach, wherein gamma probability density functions were assumed for acids, aldehydes/ketones, alcohols, water and lignin. It was shown that the probability density functions (in particular of water and lignin) can significantly affect the vaporisation predictions. Furthermore, the surrogate vaporisation approach and the continuous thermodynamics approach were combined with decomposition reaction kinetics. Sital [44] used the mechanism of Houminer et al. [46] for the thermal polymerisation of levoglucosan. Hallet and Clark [45] described the decomposition of lignin using an Arrhenius law model with reaction parameters proposed for cellulose.

The physical property models incorporated in previous studies [40–45] were mainly based on group contribution methods [47–50] and

corresponding-states methods. Specific physical property models were seldom used or developed for biogenic pyrolysis oils. So far, Yang et al. [51] derived empirical equations for the molar enthalpy of formation and the molar physical enthalpy as a function of the H/C and O/C ratios in order to estimate the enthalpy of pyrolysis for bio-oils.

1.3. Objectives

Numerous studies have investigated the chemical and physical properties and the conversion of biogenic pyrolysis oils. However, they have focussed on specific analyses due to the natural origin of bio-oils and the necessary experimental expenditures. For example, Branca et al. [3,4,20,21] conducted proximate, ultimate, GC–MS and TG analyses, whereas Peacocke et al. [16] derived by far the most comprehensive physical property data sets, but without providing the chemical property data. Thus, there is a lack of comprehensive and consistent data sets for (i) the design, evaluation and scale-up of combustion or gasification experiments with biogenic pyrolysis oils using process models and (ii) the mathematical description of atomisation and conversion of biogenic pyrolysis oils using CFD models. As part of the bioliq project [52], biogenic (and anthropogenic) pyrolysis oils are converted to synthesis gas in both laboratory-scale and pilot-scale entrained flow gasifiers at Karlsruhe Institute of Technology (KIT) [53–56]. In addition, flow-sheet models [55,57] and CFD models [58–64] are under development for detailed investigation of sub-processes and for process optimisation and scale-up. Therefore, this study derived chemical and physical property data and decomposition kinetics for an industrial beech wood pyrolysis oil. This bio-oil was produced in the commercial fast pyrolysis plant of proFagus [65] and was used as feedstock in high-pressure entrained flow gasification experiments at the bioliq Entrained Flow Gasifier (bioliq EFG) plant for the production of high-quality synthesis gas and liquid fuels [55,56]. In this context, samples of the beech wood pyrolysis oil were characterised using (i) proximate, ultimate and heating value analyses, (ii) GC–MS, GPC and TG analyses, (iii) vacuum and Engler distillations and (iv) measurements of density, dynamic viscosity, thermal conductivity, specific heat capacity and surface tension. The TG analyses were applied to derive decomposition kinetics based on multi-reaction Arrhenius law models and multi first-order reaction Gauss distributed activation energy models. The vacuum distillations were used to separate the vaporisable from the non-vaporisable components, whereas the Engler distillations were carried out to determine the boiling behaviour. Furthermore, samples of the vacuum distillates were analysed for boiling behaviour, TG behaviour, density, thermal conductivity and specific heat capacity, and samples of the vacuum distillation residues were analysed for TG behaviour and dynamic viscosity. The measured thermo-physical properties of both the beech wood pyrolysis oil and the vacuum distillate were finally used to derive the density, thermal conductivity and specific heat capacity of the vacuum distillation residue. The possible applications of the measured and derived data are summarised in Section 2. Then, the methods and the results of the analyses and measurements are presented in Sections 3 and 4 and are discussed in Section 5. Finally, the conclusions are given in Section 6.

2. Possible applications

This study derived pyrolysis oil data and models for process, single-particle, RANS based and large-eddy simulations in the course of the entrained flow gasification research at KIT. The process simulations are primarily employed for the design, evaluation and scale-up of experiments (see Section 5.1 and [55]). This requires reliable elemental, water and ash contents, and heating values (see Sections 3.2 and 4.1) as well as low-temperature correlations for density and specific heat capacity (see Sections 3.9.2 and 4.8.1). The single-particle simulations, in turn, are applied to develop, test and validate sub-models for describing the conversion of biogenic or anthropogenic (slurry) particles (see

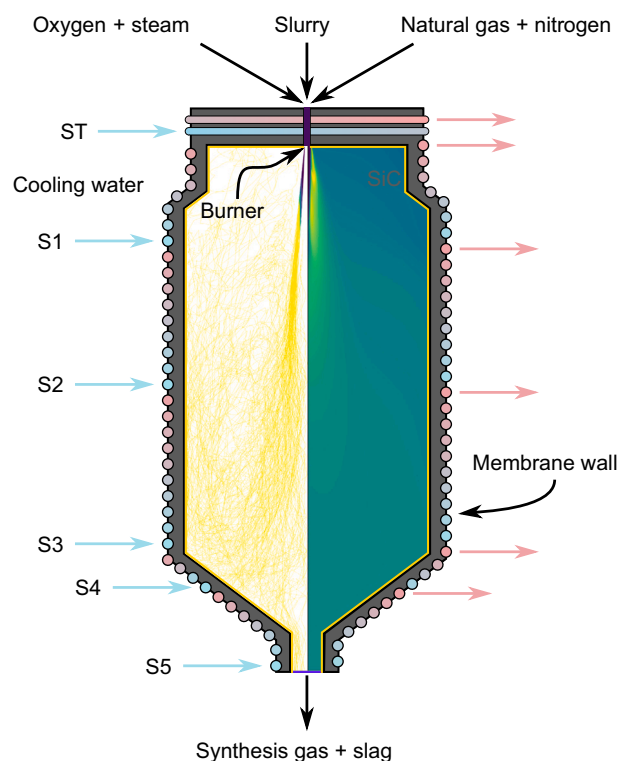


Fig. 1. Schematic cross section of the bioliq EFG reactor with the feed and product streams, with the cooling circuits S1, ..., S5, with particle trajectories of pyrolysis oil droplets (left; coloured by conversion; violet: no conversion, yellow: almost full conversion) and with a gas temperature distribution (right). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Section 5.4 and [63,66]). The compositions of such particles are typically based on the elemental, water and ash contents (see Sections 3.2 and 4.1). In addition, the density, thermal conductivity and heat capacity (see Sections 3.9.2 and 4.8.1) and the thermo-chemical conversion (see Sections 3.8, 4.7 and 5.4) can be described using customised models. Moreover, surrogates (see Section S4) can be defined using GC–MS data (see Sections 3.3 and 4.2), Engler distillation data (see Sections 3.6 and 4.5) and thermo-physical property data of vacuum distillates (see Sections 3.9.2 and 4.8.1). Resolved single-particle-models might also account for the molar mass distribution (see Sections 3.4 and 4.3) and the impact of diffusion based on viscosity models (see Sections 3.9.5, 4.8.3 and S5).

The RANS based simulations (see [59,62,63]) and the large eddy simulations (see [67]) are finally used (i) to describe the local stoichiometry and the local temperatures in entrained flow gasification processes and (ii) to determine heat extraction, local slag behaviour and conversion. Based on the temperature distribution of a bioliq EFG experiment, the possible conversion of pyrolysis oil droplets is shown in Fig. 1. The conversion is described using a multi first-order reaction Arrhenius model (see Section 5.4), while the heat capacity is based on a simplified approach (see Section S3). Large eddy simulations can also be used to describe the atomisation of pyrolysis oils at ambient temperatures (see [58,60]), based on density, viscosity and surface tension data (see Sections 3.9.2, 3.9.4, 3.9.5, 4.8).

3. Methods

This section describes the experimental and mathematical methods used to derive the chemical and physical property data and the thermogravimetric kinetics.

3.1. Preparation

Samples of the beech wood pyrolysis oil, produced by proFagus [65] in 2020, were collected from the storage tanks of the bioliq EFG plant [55,56]. The pyrolysis oil was continuously stirred in these tanks and additionally pumped in closed circuits for intensive mixing. Therefore, the collected samples can be assumed to be homogeneous and representative mixtures of the original charge. After sampling, some samples were sent to external laboratories, while the other samples were stored in glass bottles of 1 l and kept refrigerated at temperatures below 258 K to suppress composition changes due to ageing and vapourisation. Before their use in internal laboratory experiments, each bottle was warmed up in a water bath at room temperature and was homogenised through stirring the sample.

3.2. Chemical analyses

Chemical analyses were used to determine elemental, ash and water contents as well as lower and higher heating values of the beech wood pyrolysis oil.

The elemental, ash and water contents of the beech wood pyrolysis oil were determined at the internal laboratories KIT I, KIT II and KIT III as well as the external laboratories EXT I and EXT II. In the absence of specific standards for biogenic pyrolysis oils, the analyses of carbon, hydrogen, nitrogen, ash and water contents were conducted using the standards that were suggested by the laboratories and are summarised in Tables S3 and S4. The oxygen contents were determined by difference, while the ash contents were obtained using an ashing temperature of 823 K at the laboratory EXT I or using an ashing temperature of 1088 K at the laboratories KIT I and KIT III. The lower ashing temperature was suggested in accordance with the standards for biomass, whereas the higher ashing temperature is more realistic for ashing under entrained flow gasification conditions. The water contents were determined using Karl-Fischer titration at the laboratories EXT I, EXT II and KIT II and using xylene distillation at the laboratories KIT I and KIT III.

The lower heating values and the higher heating values of the beech wood pyrolysis oil were determined at the laboratories KIT I, KIT II, KIT III and EXT I according to DIN 51900-2:2003 [68]. Moreover, higher heating values were calculated using the elemental and water contents and the Boie correlation [69]. The ratios of the calculated higher heating values to the measured higher heating values provided the Boie ratios. Following previous studies [55,70], these ratios were used to evaluate the accuracy of the chemical analysis data for process calculations (see Section 5.1), where ratios around 100 % can indicate superior chemical property data.

Furthermore, reproducibility limits were extracted for the carbon, hydrogen and nitrogen contents from DIN 51732:2007 [71], for the water content from DIN 51777:2020 [72] and for the higher heating value from DIN 51900-1:2000 [73]. Assuming rectangular probability distributions, these limits were used to determine uncertainties s for various variables Y in the course of process calculations (see Section 5.1), i.e. the equilibrium temperature T_{eq} and the equilibrium species mole fractions $x_{CO,eq}$, $x_{CO_2,eq}$, $x_{H_2,eq}$ and $x_{H_2O,eq}$. The uncertainties s_Y are given by

$$s_Y = \left(\sum_{i=C,H,H_2O} \left(\frac{dY}{dw_{i,asr}} s_{w_{i,asr}} \right)^2 + \left(\frac{dY}{dHHV_{asr}} s_{HHV_{asr}} \right)^2 \right)^{0.5} \quad (1)$$

where $s_{w_{C,asr}} = 0.0185/\sqrt{3}$, $s_{w_{H,asr}} = 0.004/\sqrt{3}$ and $s_{w_{H_2O,asr}} = 0.067 w_{H_2O,asr}/\sqrt{3}$ are the uncertainties of the mass fractions and $s_{HHV_{asr}} = 400/\sqrt{3}$ kJ/kg is the uncertainty of the higher heating value [71–73].

3.3. GC–MS analyses

GC–MS/FID analyses were used to investigate the contents of the vapourisable components of the beech wood pyrolysis oil. Two

measurements were carried out using a commercial gas chromatograph system (Agilent 6890 with a VF-1701ms column (60 m × 0.25 mm, ID × 0.25 mm)) at the laboratory EXT II. The initial oven temperature of 318 K was held for 4 min and was then increased to 553 K at a heating rate of 3 K/min. The final oven temperature was held constant for 20 min. The maximum injection temperature of the FID was 523 K with a split mode of 15:1. The mass fractions of the components were quantified through a comparison with calibration lines.

3.4. GPC analyses

GPC analyses were conducted to determine the molar mass distribution of the beech wood pyrolysis oil using the principle of size exclusion chromatography. Two measurements were performed using a commercial liquid chromatograph system (Agilent 1100 Series with an Agilent PolarGel-LGuard pre-column (50 mm × 7.5 mm) and two Varian PolarGel-L columns (300 mm × 7.5 mm)) at the laboratory EXT II. The UV detector had a wavelength of 254 nm. Nine polyethylene glycol standards (with molar masses of 194 g/mol, 420 g/mol, 615 g/mol, 1010 g/mol, 1970 g/mol, 3930 g/mol, 7920 g/mol, 12140 g/mol and 21030 g/mol) were used for the calibration. The injection volumes of the samples were 100 μl. The number-weighted mean molar mass M_n , the mass-weighted mean molar mass M_m and the polydispersity PD were derived from each molar mass distribution. The polydispersity PD is a measure of the width of the molar mass distribution and is given by

$$PD = \frac{M_m}{M_n} \quad (2)$$

3.5. Vacuum distillations

Vacuum distillations were used to separate the beech wood pyrolysis oil into vapourisable and non-vapourisable components. The laboratory setup consisted of (i) an electrically heated round bottom flask with a volume of 1000 ml, (ii) a Vigreux column with a length of 300 mm, (iii) a reflux condenser at the top of the separation column, (iv) a condenser with a connection to a vacuum pump and (v) a second flask for collecting the distillate. The beech wood pyrolysis oil sample was continuously homogenised with a stirring bar during the vacuum distillation, while a high reflux ratio of the condenser and a long separation column ensured the separation of the volatile components according to their boiling points. Two type K thermocouples tracked the liquid and gas temperatures. One thermocouple was placed at the bottom of the round bottom flask, while the other was positioned at the condenser inlet and the top of the separation column. Both condensers were operated at 293 K. The absolute operating pressure was 40 mbar, which was the lowest value that ensured constant pressure throughout the distillation process and kept the loss of the volatile components to a minimum.

The temperature in the flask could be increased up to 523 K, while white fumes indicated thermal decomposition reactions at higher temperatures. 523 K was therefore used to separate the vapourisable from the non-vapourisable components and to produce vacuum distillates of the beech wood pyrolysis oil for Engler distillations (see Sections 3.6 and 4.5), TG analyses (see Sections 3.7 and 4.6) and measurements of thermo-physical properties (see Sections 3.9 and 4.8). Furthermore, the batch distillations were stopped at four temperatures (373 K, 423 K, 473 K, 508 K) below 523 K (i) to determine the recovered mass fractions at different liquid temperatures and (ii) to obtain different vacuum distillation residues (see Sections 3.9.5 and 4.8.3). Each distillation was performed three times. The recovered fractions at specific temperatures are reported as mean values with corresponding standard deviations.

3.6. Engler distillations

Engler distillations were conducted to determine the boiling-point curves of both the beech wood pyrolysis oil and the vacuum distillate. Three measurements each were carried out following ASTM D86-20a [74] and using modified temperature measurements. The default

mercury thermometer was replaced by two type J thermocouples based on previous recommendations [75,76] in order to track both the liquid temperature and the gas temperature. Both thermocouples were calibrated in the temperature range between 273 K and 673 K. The initial sample volumes in the Engler flask and the recovered distillate volumes were recorded at 293 K to ensure reliable and accurate measurement data. The measured temperatures were finally used to determine mean values and standard deviations for the boiling-point curves.

3.7. TG analyses

TG analyses of the beech wood pyrolysis oil, the vacuum distillate and the vacuum distillation residue were performed using a commercial device (Netzsch TG 209 F1). The analyses of the beech wood pyrolysis oil were carried out using constant heating rates of 2 K/min, 5 K/min, 10 K/min, 20 K/min and 50 K/min, while the analyses of the vacuum distillate and the vacuum distillation residue were conducted using a constant heating rate of 20 K/min only. The initial sample masses were between 70 mg and 100 mg. The temperature was measured using a thermocouple positioned in the gas phase below the sample crucible. In contrast to previous recommendations to use the position close to the sample bottom [3,20], this was performed in accordance with the fixed setup of the analytical instrument. Nitrogen was applied as inert gas using volume flow rates of approximately 100 ml/min. Concentrations of the decomposition products were not measured, whereas TG and DTG curves, representing the relative mass loss w and the derivative of the relative mass loss dw/dt , were mainly determined three times (only twice for the beech wood pyrolysis oil at 50 K/min). The measured TG and DTG curves of each heating-rate condition were averaged using linear interpolation.

3.8. TG kinetics

TG kinetics were derived from the averaged TG and DTG curves of the beech wood pyrolysis oil using either multi-reaction Arrhenius law models or multi-reaction distributed activation energy models. For both modelling approaches, the temperature T , the mass fraction w , the time derivative of the mass fraction dw/dt and the temperature derivative of the mass fraction dw/dT are given by [4,20,21,77]

$$T = \begin{cases} T_0 + \beta t, & \text{if } 0 \leq t \leq \frac{T_{\max} - T_0}{\beta} \\ T_{\max}, & \text{if } t > \frac{T_{\max} - T_0}{\beta} \end{cases}, \quad (3)$$

$$w = 1 - \sum_{i=1}^N w_{i,0} + \sum_{i=1}^N w_i, \quad (4)$$

$$\frac{dw}{dt} = \sum_{i=1}^N \frac{dw_i}{dt}, \quad (5)$$

$$\frac{dw}{dT} = \sum_{i=1}^N \frac{dw_i}{dT}, \quad (6)$$

where T_0 is the initial and ambient temperature, β is the constant heating rate, t is the time, T_{\max} is the maximum temperature, N is the number of parallel reactions, w_i is the mass fraction of reaction i and $w_{i,0}$ is the initial mass fraction of reaction i . The latter is given by [4,20,21]

$$w_{i,0} = w_i|_{t=0} = w_i|_{T=T_0}. \quad (7)$$

3.8.1. Multi-reaction Arrhenius law models

Multi-reaction Arrhenius law models, as used in this study, are defined by

$$\frac{dw_i}{dt} = -k_{0,i} \exp\left(-\frac{\bar{E}_{a,i}}{RT}\right) w_i^{n_i}, \quad (8)$$

where $k_{0,i}$ is the pre-exponential factor of reaction i , $\bar{E}_{a,i}$ is the molar activation energy of reaction i , \bar{R} is the molar gas constant and n_i is the order of reaction i . In order to determine approximations for the pre-exponential factors $k_0 = (k_{0,i})_{i=1,\dots,N}$, the molar activation energies $\bar{E}_a = (\bar{E}_{a,i})_{i=1,\dots,N}$, the orders $n = (n_i)_{i=1,\dots,N}$ and the initial mass fractions $w_0 = (w_{i,0})_{i=1,\dots,N}$, regressions of the averaged TG and DTG curves were performed using Eqs. (3)–(8) as well as the *least_squares* and *solve_ivp* methods of SciPy [78,79]. The differential equations were solved using the LSODA (Adams/BDF) method [80,81].

3.8.2. Multi-reaction distributed activation energy models

Multi-reaction distributed activation energy models can be developed using various probability distributions and assuming either unity or non-unity reaction orders [77]. Preliminary tests showed that Gaussian distributions and unity reaction orders provide the best approximations for the measured TG and DTG data. Multi-reaction distributed activation energy models were therefore combined with Gaussian distributions and unity reaction orders. Multi-reaction distributed activation energy models, as used in this study, are defined by [77]

$$w_i = \int_0^\infty \exp\left(-\int_{T_0}^T \frac{k_i(\bar{E}_a, \tilde{T})}{\beta} d\tilde{T}\right) f_i(\bar{E}_a) d\bar{E}_a, \quad (9)$$

$$\frac{dw_i}{dt} = \beta \frac{dw_i}{dT}, \quad (10)$$

$$\frac{dw_i}{dT} = \int_0^\infty \frac{k_i(\bar{E}_a, T)}{\beta} \exp\left(-\int_{T_0}^T \frac{k_i(\bar{E}_a, \tilde{T})}{\beta} d\tilde{T}\right) f_i(\bar{E}_a) d\bar{E}_a, \quad (11)$$

where

$$k_i(\bar{E}_a, T) = k_{0,i} \exp\left(-\frac{\bar{E}_a}{RT}\right), \quad (12)$$

is the rate constant and $f_i(\bar{E}_a)$ is the probability density function, each of reaction i . The probability density function $f_i(\bar{E}_a)$ is given by

$$f_i(\bar{E}_a) = \frac{1}{\sqrt{2\pi}\sigma_{\bar{E}_{a,i}}} \exp\left(-\frac{\bar{E}_a - \mu_{\bar{E}_{a,i}}}{2\sigma_{\bar{E}_{a,i}}^2}\right), \quad (13)$$

where $\mu_{\bar{E}_{a,i}}$ and $\sigma_{\bar{E}_{a,i}}$ are the expectation and the standard deviation of the Gaussian distribution for the molar activation energy \bar{E}_a of reaction i . In order to determine appropriate approximations for the pre-exponential factors $k_0 = (k_{0,i})_{i=1,\dots,N}$, the expectations $\mu_{\bar{E}_a} = (\mu_{\bar{E}_{a,i}})_{i=1,\dots,N}$, the standard deviations $\sigma_{\bar{E}_a} = (\sigma_{\bar{E}_{a,i}})_{i=1,\dots,N}$ and the initial mass fractions $w_0 = (w_{i,0})_{i=1,\dots,N}$, regressions of the averaged TG and DTG curves were carried out using Eqs. (3)–(7) and (9)–(13) as well as the *trapz*, *quadgk*, *fminsearch* and *fmincon SPQ* methods of Matlab [82]. The *trapz* method (trapezoidal quadrature) with 100 equally spaced intervals was applied to the outer integrals, while the *quadgk* method (Gauss–Kronrod quadrature) was used for the inner integrals. The percentiles at 0.0001 and 0.9999 of the Gaussian distributions were used as limits of the outer integrals. The *fminsearch* was used to obtain appropriate initial parameters for the final optimisation using the *fmincon SPQ* method. In the final optimisation, constraints were applied to ensure that the mass fraction w is described properly for $T \rightarrow \infty$.

3.9. Thermo-physical properties

Density, thermal conductivity and specific heat capacity were determined for the beech wood pyrolysis oil (see Section 3.9.2), the vacuum distillate (see Section 3.9.2) and the vacuum distillation residue

(see Section 3.9.3) under low-temperature conditions. In addition, the surface tension of the beech wood pyrolysis oil was measured under ambient conditions (see Section 3.9.4). Furthermore, the dynamic viscosity of the beech wood pyrolysis oil and three different vacuum distillation residues were determined under low-temperature conditions (see Section 3.9.5). The standards of the experimental methods are summarised in Table S5.

3.9.1. Challenges

The vaporisation of light volatiles, the thermal polymerisation and the decomposition affect measurements under low-temperature conditions. Therefore, three measures were taken to avoid composition changes and ensure reliable and accurate measurement data. Firstly, all measurements were conducted well below 600 K (see Sections 3.9.2 and 3.9.5). Secondly, comparative measurements were carried out using either different heating behaviour or different set-ups (see Sections 3.9.2 and 3.9.5). Thirdly, some measurements of density, thermal conductivity and specific heat capacity were carried out under pressures of 6 bar to impede the vaporisation of light volatiles (see Section 3.9.2). Possible impacts of the pressurised conditions on the measured data were neglected as pressure effects are considerably smaller than temperature and composition effects for liquids if pressures are moderate and conditions are not close to critical conditions [83].

3.9.2. Density, thermal conductivity and specific heat capacity of the beech wood pyrolysis oil and the vacuum distillate

The density, the thermal conductivity and the specific heat capacity of both the beech wood pyrolysis oil and the vacuum distillate were determined between 293 K and 453 K at the laboratory EXT III. The measurements below 373 K were carried out at atmospheric pressure and, for temperatures above 373 K, at 6 bar. The density was measured according to DIN EN ISO 1183-1:2019 [84] with minor adaptations. The Mohr balance was calibrated using standard calibration substances. The thermal conductivity was obtained using a commercial thermal conductivity meter (flucon LAMBDA) based on the hot wire method according to ASTM D-7896-19 [85]. The measurements were performed using temperature ramps, while stopping at 17 temperatures between 293 K and 453 K and executing each measurement after reaching thermal equilibrium. The specific heat capacity was measured using continuously stirred sample volumes of 100 ml and an adiabatic calorimeter following ASTM D2766-95 [86].

Furthermore, the thermal conductivity and specific heat capacity of the beech wood pyrolysis oil were measured at 373 K and 453 K with fresh samples in single runs to investigate the heating effects. Finally, the density was also determined following ASTM D4052-18a [87] at both KIT and the laboratory EXT I. At KIT, the measurements were conducted between 293 K and 333 K using a commercial density meter (Anton Paar DMA 400). At EXT I, the measurements were carried out at 288 K using an U-shaped oscillating sample tube.

3.9.3. Density, thermal conductivity and specific heat capacity of the vacuum distillation residue

The density, the thermal conductivity and the specific heat capacity of the vacuum distillation residue were derived from the data measured for the beech wood pyrolysis oil and the vacuum distillate. The density of the vacuum distillation residue ρ_{vdr} and the specific heat capacity of the vacuum distillation residue $\hat{C}_{p,\text{vdr}}$ were determined by

$$\rho_{\text{vdr}} = \frac{1 - w_{\text{vd,oil}}}{\frac{1}{\rho_{\text{oil}}} - \frac{w_{\text{vd,oil}}}{\rho_{\text{vd}}}}, \quad (14)$$

$$\hat{C}_{p,\text{vdr}} = \frac{\hat{C}_{p,\text{oil}} - w_{\text{vd,oil}} \hat{C}_{p,\text{vd}}}{1 - w_{\text{vd,oil}}}, \quad (15)$$

where $w_{\text{vd,oil}}$ is the recovered mass fraction of the vacuum distillate at the maximum liquid temperature, ρ_{oil} is the density of the beech wood

pyrolysis oil, ρ_{vd} is the density of the vacuum distillate, $\hat{C}_{p,\text{oil}}$ is the specific heat capacity of the beech wood pyrolysis oil and $\hat{C}_{p,\text{vd}}$ is the specific heat capacity of the vacuum distillate. The thermal conductivity of the vacuum distillation residue λ_{vdr} was calculated using the mass-weighted mixing rule by

$$\lambda_{\text{vdr}} = \frac{\lambda_{\text{oil}} - w_{\text{vd,oil}} \lambda_{\text{vd}}}{1 - w_{\text{vd,oil}}} \quad (16)$$

and using the Maxwell mixing rule by

$$\lambda_{\text{vdr}} = \frac{2 \lambda_{\text{vd}}^2 (1 - \varphi) - \lambda_{\text{oil}} \lambda_{\text{vd}} (2 + \varphi)}{\lambda_{\text{oil}} (1 - \varphi) - \lambda_{\text{vd}} (1 + 2 \varphi)}, \quad (17)$$

where λ_{oil} is the thermal conductivity of the beech wood pyrolysis oil, λ_{vd} is the thermal conductivity of the vacuum distillate and $\varphi = 1 - w_{\text{vd,oil}} \frac{\rho_{\text{oil}}}{\rho_{\text{vdr}}}$.

3.9.4. Surface tension

The surface tension of the beech wood pyrolysis oil was measured at 293 K using a commercial tensiometer (Krüss K20 force) based on the Du Noüy ring method.

3.9.5. Dynamic viscosity

The dynamic viscosity of the beech wood pyrolysis oil and three vacuum distillation residues (obtained after reaching liquid temperatures of 373 K, 423 K and 473 K; see Sections 3.5 and 4.4) were determined between 293 K and 373 K using a commercial rheometer (Anton Paar MCR 302). A concentric cylinder geometry cell was used for the beech wood pyrolysis oil, while a parallel plate setup was applied to the vacuum distillation residues due to their high viscosities and the difficult sample handling. For each measurement point, three measurements were conducted using a shear rate of 40 s^{-1} . For comparison, the dynamic viscosity of the beech wood pyrolysis oil was measured at 293 K, 313 K and 343 K according to DIN EN ISO 3219:1994 [88] at the laboratory EXT I.

4. Results

This section presents the experimental and numerical results of the characterisation of the beech wood pyrolysis oil.

4.1. Chemical analyses

The elemental, ash and water contents of the beech wood pyrolysis oil are given in Tables S6 and S7. The contents range from 0.569 to 0.585 for carbon and from 0.054 to 0.073 for hydrogen. In addition, the nitrogen, sulphur, chlorine and ash contents are below 0.001, and the water contents are between 0.052 and 0.083. The water contents are thus below those that are typical for pyrolysis oils. Moreover, the carbon, hydrogen and nitrogen contents are primarily inside the respective reproducibility limits of ± 0.0185 , ± 0.0040 and ± 0.0017 [71], respectively, whereas the water contents are partially outside the reproducibility limits of $\pm 0.067 w_{\text{H}_2\text{O,asr}}$ [72]. Overall, all contents are subject to higher uncertainties and cannot be reproduced with good accuracy, in contrast to previous conclusions [33].

The lower heating values and the higher heating values of the beech wood pyrolysis oil, based on both measurements and calculations, are given in Table S8. The higher heating values on dry basis are between 25.53 MJ/kg and 26.38 MJ/kg and partially outside the reproducibility limits of $\pm 400 \text{ kJ/kg}$ [73]. Thus, similarly to carbon, hydrogen and water contents, the heating values are afflicted with higher uncertainties than should be expected.

Furthermore, the higher heating values based on the Boie correlation [69] as well as the Boie ratios are presented in Table S9. The Boie ratios are close to 100 % for the analysis results of KIT III and EXT I and deviate from 100 % to a greater extent for the analysis results of KIT I

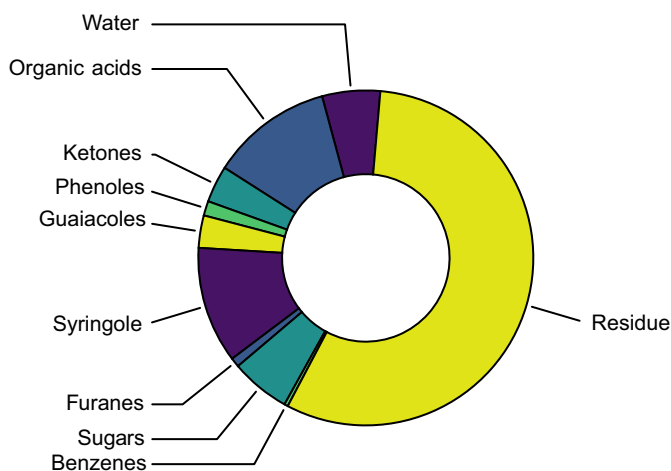


Fig. 2. Composition of the beech wood pyrolysis oil based on the GC–MS analyses.

and KIT II. As values around 100% indicate superior fuel data for process calculations [55,70], the analysis results of KIT III and EXT I are likely superior (see Section 5.1). The analysis results of KIT I and KIT II could deviate due to erroneous sampling and analysis methods if the fuel variability has been low due to intensive mixing (see Section 3.1).

4.2. GC–MS analyses

The GC–MS analyses of the beech wood pyrolysis oil provided repeatable results (see Section S2) and identified 48 organic components from different chemical classes, including acids, non-aromatic ketones, furans, benzenes, lignin derived phenols, methoxy phenols, dimethoxy phenols and carbohydrates. The contents are depicted in Fig. 2 and are listed in Table S10. On average, 44.5% of the sample mass (including a water content of 5.6%) could be itemised, where 36.5% of the total mass was assigned to specific organic components, and 2.4% of the total mass was linked with an unspecific anhydrosugar. Such values are fairly typical for pyrolysis oils (for example, see [7]) as GC–MS analyses can only detect components that are sufficiently volatile to pass through the injector and the GC column.

Furthermore, organic acids (11.8% of the sample mass) as well as phenol and phenol derivatives (16.0% of the sample mass) were identified as major components of the beech wood pyrolysis oil. Thus, in comparison with previous results [2,3,89,90], the beech wood pyrolysis oil is characterised by high mass fractions of the decomposition products of lignin. Furthermore, the mass fractions of sugars (6.0%) and ketones (3.7%), derived from carbohydrates, are quite small for the beech wood pyrolysis oil.

4.3. GPC analyses

The molar mass distributions of the beech wood pyrolysis oil are shown using probability density functions (PDFs) and cumulative distribution functions (CDFs) in Fig. 3. The probability density functions are characterised by a first increase up to a molar mass of 30 g/mol, a strong peak at a molar mass of 60 g/mol, a broad peak between molar masses of 94 g/mol and 210 g/mol, a third peak at a molar mass of 300 g/mol and a largely continuous decrease up to a molar mass of $3 \cdot 10^4$ g/mol. The molar mass distributions up to a molar mass of 210 g/mol are in agreement with the GC–MS data. The first increase can mainly be attributed to the water content, while the first peak is due to the contents of organic acids (acetic acid and propionic acid) and ketones (acetol and 2-cyclopenten-1-one). Moreover, the second peak is due to the high contents of phenol and phenol derivatives. Furthermore, 54.1% of the pyrolysis oil is characterised by molar masses of up to 210 g/mol, 25.3%

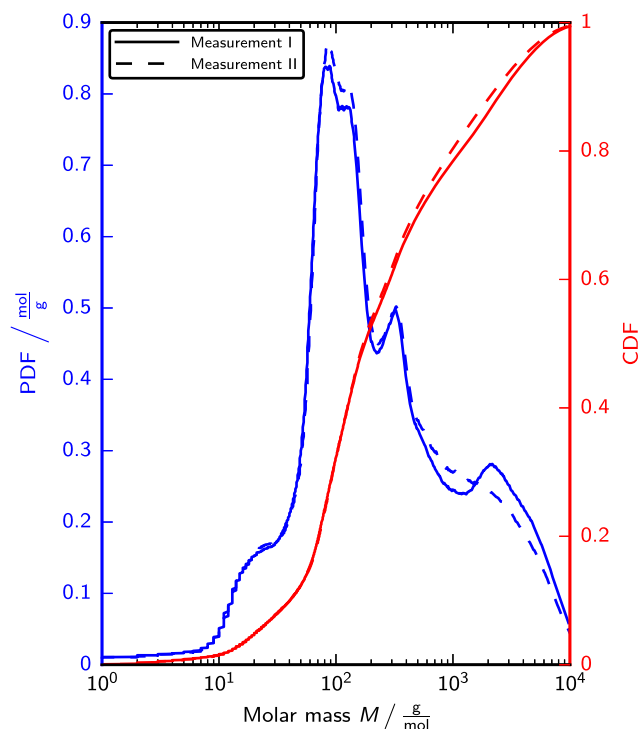


Fig. 3. Molar mass distributions of the beech wood pyrolysis oil based on the GPC analyses: probability density function (PDF) and cumulative distribution function (CDF) for two single measurements.

Table 2

Mass-weighted molar masses M_m , number-weighted molar masses M_n and polydispersities PD of the beech wood pyrolysis oil based on the GPC analysis results.

Measurement	M_m g/mol	M_n g/mol	PD
I	902	71	12.70
II	811	71	11.42

of the pyrolysis oil by molar masses between 210 g/mol and 1000 g/mol, and 20.3% of the pyrolysis oil by molar masses between 1000 g/mol and $3 \cdot 10^4$ g/mol. The latter contents can be due to oligomeric components derived from lignin or carbohydrates [7], recalling that dimers and trimers have typical molar masses between 210 g/mol and 1000 g/mol.

The characteristic values of both molar mass distributions are shown in Table 2. The beech wood pyrolysis oil has a mean mass-weighted molar mass M_m of 860 g/mol, a mean number-weighted molar mass M_n of 71 g/mol and a mean polydispersity PD of 12. In comparison with previous results [7,34,89,90], the number-weighted molar mass M_n is lower due to higher contents of water and acetic acid, whereas the mass-weighted molar mass M_m is higher due to the broad distribution of molar masses between 18 g/mol and $3 \cdot 10^4$ g/mol. This results in fairly high polydispersities PD compared to typical polydispersities PD of between 1 and 3 for biogenic pyrolysis oils from a wide range of feedstocks and pyrolysis processes [34].

4.4. Vacuum distillations

The vacuum distillations were stopped at five different liquid temperatures. The recovered mass fractions at these temperatures are shown in Table 3. Most of the volatiles, such as phenolic derivatives, were accordingly separated at liquid temperatures between 423 K and 473 K,

Table 3

Recovered mass fractions of the vacuum distillates at different liquid temperatures.

Liquid temperature / K	Gas temperature / K	Recovered mass fraction / %	
		Total	Differential
293	273	0	0
373	314	9.4 ± 0.7	9.4
423	368	16.4 ± 0.6	7.0
473	433	42.5 ± 0.3	26.1
508	461	55.3 ± 0.2	12.8
523	471	57.7 ± 0.1	2.4

while 57.7% of the sample mass was recovered at the maximum liquid temperature of 523 K. Furthermore, 91% of the sample mass was retrieved as vacuum distillate or vacuum distillation residue, while 9% of the sample mass was lost. It is expected that the losses are rather escaped volatiles than uncollected solid residues. Therefore, up to 66.7% of the sample mass should have been recovered as vacuum distillate at the maximum liquid temperature of 523 K under ideal conditions (see Section 5.2).

4.5. Engler distillations

The Engler distillation curves were determined for both the beech wood pyrolysis oil and the vacuum distillate. The mean gas and mean liquid temperatures are plotted over the recovered volume fraction in Fig. 4. The temperatures are only depicted up to a volume fraction of 60% in the case of the beech wood pyrolysis oil and up to a volume fraction of 90% in the case of the vacuum distillate, as decomposition reactions were observed at higher volume fractions.

The gas temperatures of the beech wood pyrolysis oil are largely congruent with those of the vacuum distillate. The initial boiling temperatures are approximately 373 K due to the transition of water into vapour, and the final boiling temperatures are approximately 550 K. However, the gas temperature curves are distorted due to the different contents and compositions of the volatiles (see Section 4.4), given that the fraction of vapourisable components at ambient conditions is 60% in volume fractions and 60.4% in mass fractions.

The liquid temperatures are significantly higher than the gas temperatures and increase to approximately 650 K with increasing recovered volume fraction. In addition, the liquid temperature curves of the beech wood pyrolysis oil and the vacuum distillate diverge above recovered volume fractions of 15% due to the deviating contents and compositions of the volatiles. The liquid temperature curve of the vacuum distillate also gets quite steep at the end of the Engler distillation as the sample mass in the flask decreased and the constant heat supply could have falsified the measured data. Furthermore, solid organic residues were formed during the Engler distillation of the vacuum distillate. This indicates that vacuum distillation up to 523 K separated some components that decompose rather than vaporise under atmospheric-pressure conditions (see Section 5.2).

4.6. TG analyses

The TG and DTG curves that were obtained for the beech wood pyrolysis oil at five heating rates between 303 K and 1273 K are shown in Fig. 5. Firstly, the curves exhibit similar shapes indicating similar decomposition behaviour at the various heating rates. The mass decrease shifts to higher temperatures with an increase in heating, while the total mass decrease (up to 90%) increases with faster heat-up. Secondly, the mass mainly decreases between 373 K and 723 K, where the maximum mass decrease is between 470 K and 600 K. Above 723 K, the mass varies only slightly. The mass decreases are in qualitative agreement with previous studies [2,3,18,26,29] (see Section 5.3) and the results obtained through vacuum distillation and Engler distillation (see Section 5.2). Thirdly, the mass decrease at lower temperatures was due to the vaporisation

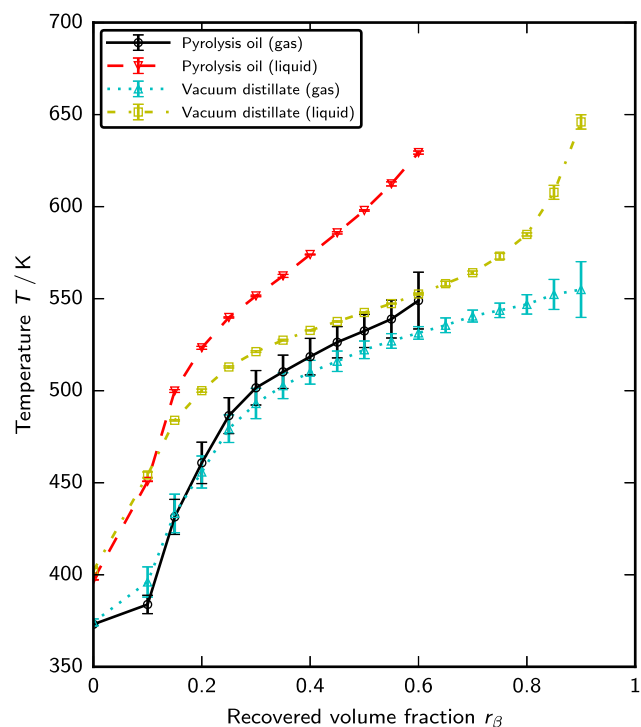


Fig. 4. Engler distillation curves of the beech wood pyrolysis oil and the vacuum distillate.

of light volatiles, while the mass decrease at higher temperatures was due to the vaporisation of heavy volatiles and the release of gases. At the heating rate of 2 K/min, water and very light components (15% of the mass) evaporated below 423 K, while heavy volatiles vaporised between 423 K and 523 K. About 60% of the mass was lost at the peak of 473 K. In addition, gaseous decomposition products were released from the non-vaporisable residue at temperatures above 523 K.

The TG and DTG curves of both the vacuum distillate and the vacuum distillation residue, determined at the heating rate of 20 K/min, are compared with the corresponding TG and DTG curves of the beech wood pyrolysis oil in Fig. 6. The TG and DTG curves of both the vacuum distillate and the vacuum distillation residue were weighted by their mass fractions (as determined by vacuum distillation up to the maximum liquid temperature) to demonstrate the contributions of the vaporisable and the non-vaporisable fractions to the thermogravimetric conversion of the beech wood pyrolysis oil. The TG curves of the vacuum distillate and the vacuum distillation residue show that the mass of the vacuum distillate was almost completely converted between 350 K and 650 K, whereas the mass of the vacuum distillation residue started to decrease at 520 K. About 25% of the initial mass of the vacuum distillation residue remained at the end, which is in agreement with the residues of approximately 10% observed in the TG analyses of the beech wood pyrolysis oil. In addition, the DTG curves of the vacuum distillate and the vacuum distillation residue demonstrate the superposition of vaporisation and decomposition in the conversion of the beech wood pyrolysis oil between 500 K and 650 K.

Furthermore, cumulated TG and DTG curves were obtained from the respective curves of the vacuum distillate and the vacuum distillation residue. These curves are shown in Fig. 6 and are in good agreement with the curves of the beech wood pyrolysis oil (see Section 5.2).

4.7. TG kinetics

The approximations of the TG and DTG curves using multi-reaction Arrhenius law models with reaction orders bounded between 0.1

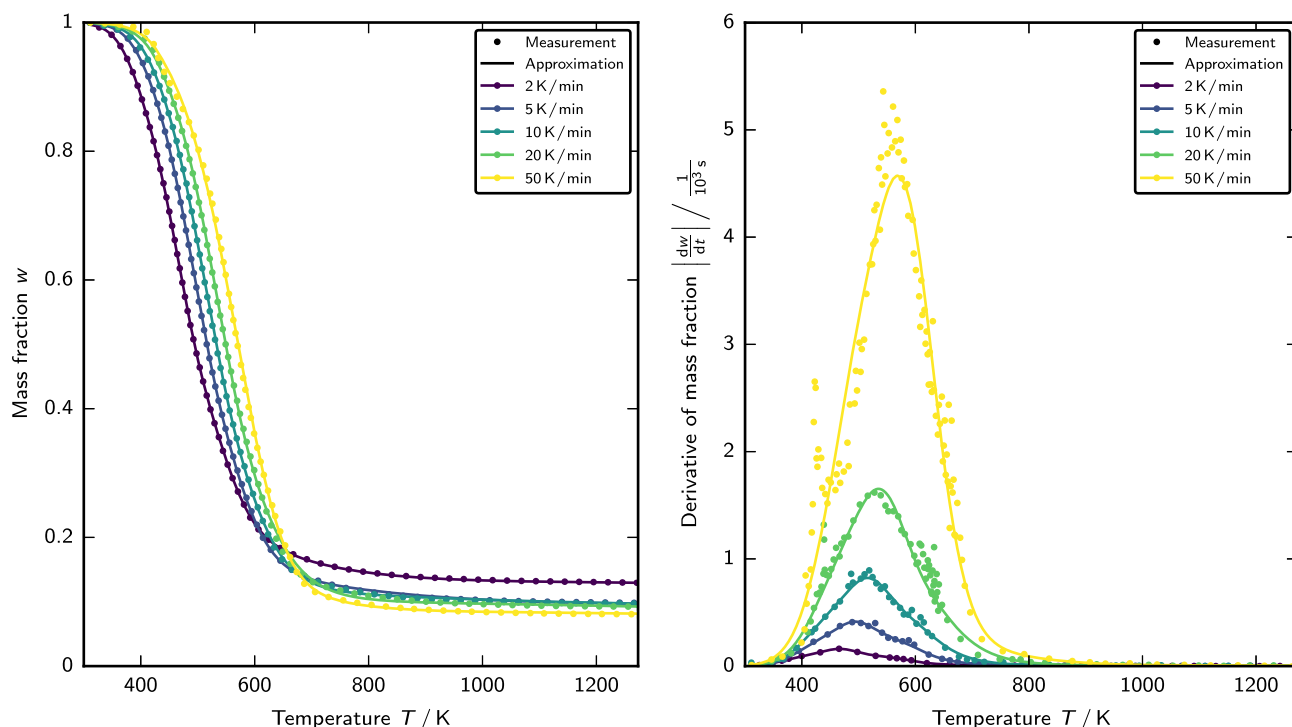


Fig. 5. TG and DTG curves of the beech wood pyrolysis oil: comparison of measurement data with numerical approximations based on the multi-reaction Arrhenius law model.

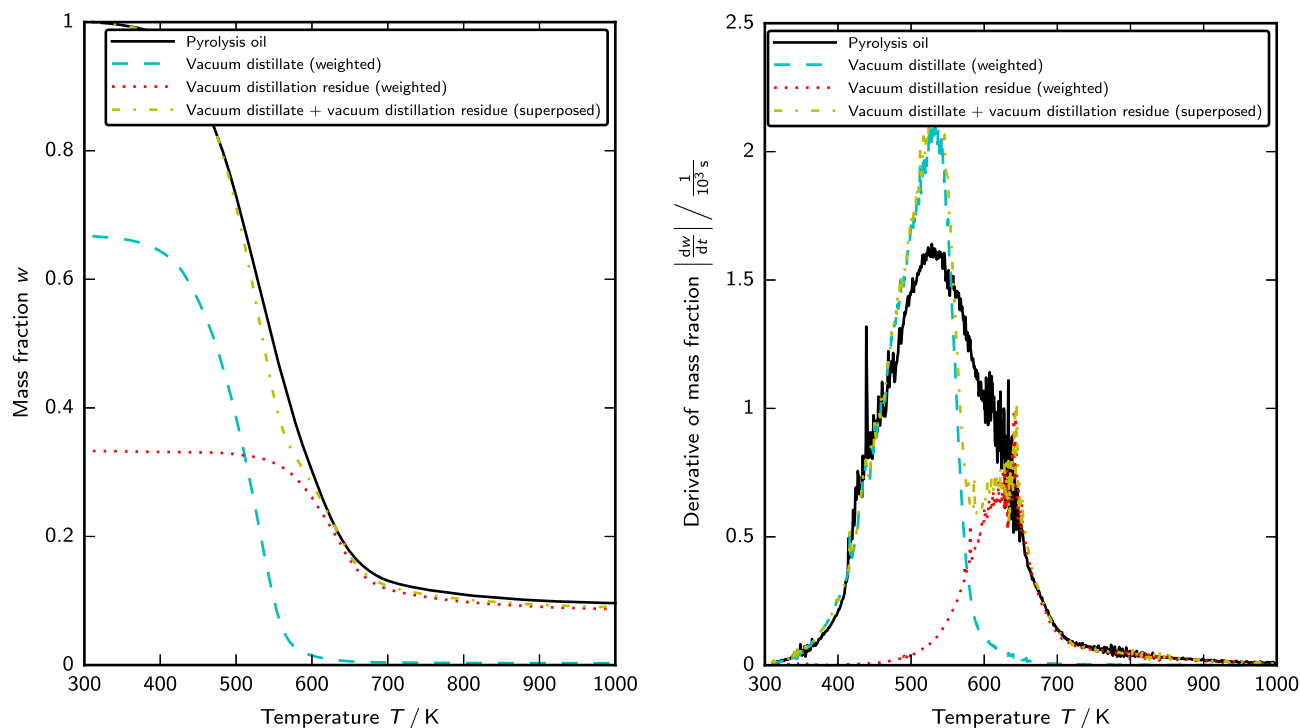


Fig. 6. TG and DTG curves of the beech wood pyrolysis oil, the vacuum distillate and the vacuum distillation residue.

and 2 are shown in Fig. 5, while the approximations using multi first-order reaction Arrhenius law models are depicted in Fig. 7. In addition, the approximations using multi first-order reaction Gauss distributed activation energy models are shown in Fig. 8. The parameters of the models are given in Tables 4, 5 and 6. The approximations of all three models

are in good agreement with the measurement data. However, the multi-reaction Arrhenius law models provide slightly superior approximations compared to the multi first-order reaction Gauss distributed activation energy models and could provide better predictions at low heating rates (see Section 5.3).

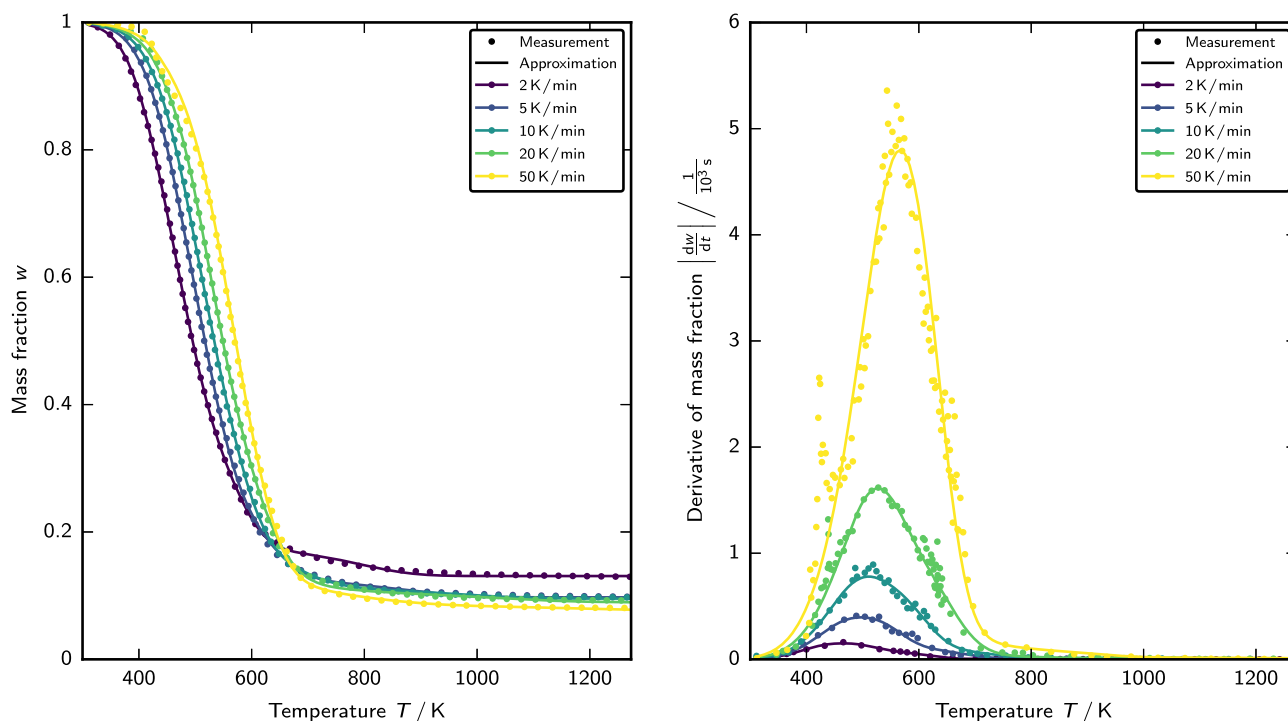


Fig. 7. TG and DTG curves of the beech wood pyrolysis oil: comparison of measurement data with numerical approximations based on the multi first-order reaction Arrhenius law model.

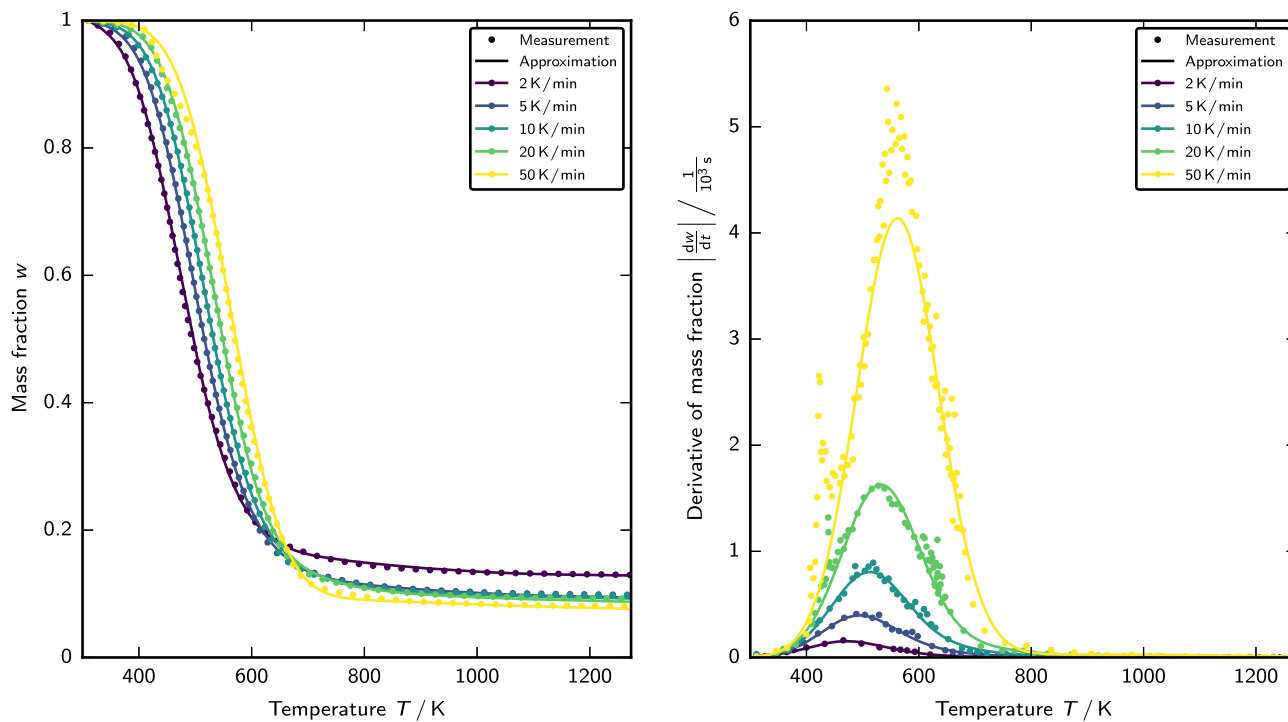


Fig. 8. TG and DTG curves of the beech wood pyrolysis oil: comparison of measurement data with numerical approximations based on the multi first-order reaction Gauss distributed activation energy model.

4.8. Thermo-physical properties

The thermo-physical properties of the beech wood pyrolysis oil under ambient conditions are compared with ranges of values obtained in previous studies [8,11,12,14,16,91] in Table 7.

The measured density, the measured dynamic viscosity and the measured surface tension of the beech wood pyrolysis oil are in the respective ranges of previously measured values, whereas the measured specific heat capacity and the measured thermal conductivity are

Table 4

Parameters for the calculation of the mass loss w and the derivative of the mass loss dw/dt for the beech wood pyrolysis oil using the multi-reaction Arrhenius law model based on Eqs. (3)–(8).

i	$\frac{k_{0,i}}{1/s}$	$\frac{\bar{E}_{a,i}}{J/mol}$	n_i	$w_{0,i}$				
				$2 \frac{K}{min}$	$5 \frac{K}{min}$	$10 \frac{K}{min}$	$20 \frac{K}{min}$	$50 \frac{K}{min}$
1	$4.134 \cdot 10^3$	$4.452 \cdot 10^4$	2.000	$1.861 \cdot 10^{-1}$	$1.787 \cdot 10^{-1}$	$1.947 \cdot 10^{-1}$	$2.170 \cdot 10^{-1}$	$2.769 \cdot 10^{-1}$
2	$1.535 \cdot 10^3$	$5.394 \cdot 10^4$	1.482	$4.072 \cdot 10^{-1}$	$4.593 \cdot 10^{-1}$	$4.954 \cdot 10^{-1}$	$5.452 \cdot 10^{-1}$	$6.254 \cdot 10^{-1}$
3	3.788	$3.728 \cdot 10^4$	2.000	$5.801 \cdot 10^{-2}$	$3.796 \cdot 10^{-2}$	$1.861 \cdot 10^{-2}$	$1.183 \cdot 10^{-2}$	$9.053 \cdot 10^{-3}$
4	$2.530 \cdot 10^5$	$8.189 \cdot 10^4$	2.000	$2.200 \cdot 10^{-1}$	$2.299 \cdot 10^{-1}$	$1.987 \cdot 10^{-1}$	$1.390 \cdot 10^{-1}$	$1.355 \cdot 10^{-2}$

Table 5

Parameters for the calculation of the mass loss w and the derivative of the mass loss dw/dt for the beech wood pyrolysis oil using the multi first-order reaction Arrhenius law model based on Eqs. (3)–(8).

i	$\frac{k_{0,i}}{1/s}$	$\frac{\bar{E}_{a,i}}{J/mol}$	n_i	$w_{0,i}$				
				$2 \frac{K}{min}$	$5 \frac{K}{min}$	$10 \frac{K}{min}$	$20 \frac{K}{min}$	$50 \frac{K}{min}$
1	7.440	$3.653 \cdot 10^4$	1	$3.818 \cdot 10^{-1}$	$5.139 \cdot 10^{-1}$	$5.289 \cdot 10^{-1}$	$4.342 \cdot 10^{-1}$	$3.237 \cdot 10^{-2}$
2	$1.842 \cdot 10^1$	$3.449 \cdot 10^4$	1	$1.414 \cdot 10^{-1}$	$1.687 \cdot 10^{-1}$	$2.658 \cdot 10^{-1}$	$4.373 \cdot 10^{-1}$	$8.531 \cdot 10^{-1}$
3	2.209	$3.858 \cdot 10^4$	1	$3.033 \cdot 10^{-1}$	$1.925 \cdot 10^{-1}$	$9.171 \cdot 10^{-2}$	$2.187 \cdot 10^{-2}$	$2.927 \cdot 10^{-2}$
4	1.259	$5.387 \cdot 10^4$	1	$4.275 \cdot 10^{-2}$	$2.745 \cdot 10^{-2}$	$1.828 \cdot 10^{-2}$	$1.720 \cdot 10^{-2}$	$7.817 \cdot 10^{-3}$

Table 6

Parameters for the calculation of the mass loss w and the derivative of the mass loss dw/dt for the beech wood pyrolysis oil using the multi first-order reaction Gauss distributed activation energy model based on Eqs.(3)–(7) and (9)–(13).

i	$\frac{k_{0,i}}{1/s}$	$\frac{\mu \bar{E}_{a,i}}{J/mol}$	$\frac{\sigma \bar{E}_{a,i}}{J/mol}$	$w_{0,i}$				
				$2 \frac{K}{min}$	$5 \frac{K}{min}$	$10 \frac{K}{min}$	$20 \frac{K}{min}$	$50 \frac{K}{min}$
1	$7.736 \cdot 10^{-3}$	$1.056 \cdot 10^5$	$2.917 \cdot 10^4$	$4.708 \cdot 10^{-2}$	$3.825 \cdot 10^{-2}$	$2.595 \cdot 10^{-2}$	$2.519 \cdot 10^{-2}$	$2.160 \cdot 10^{-2}$
2	7.778	$3.961 \cdot 10^4$	$5.998 \cdot 10^3$	$4.819 \cdot 10^{-1}$	$3.541 \cdot 10^{-1}$	$2.305 \cdot 10^{-1}$	$1.185 \cdot 10^{-1}$	0
3	$1.147 \cdot 10^4$	$6.371 \cdot 10^4$	$7.014 \cdot 10^3$	$3.424 \cdot 10^{-1}$	$5.136 \cdot 10^{-1}$	$6.510 \cdot 10^{-1}$	$7.693 \cdot 10^{-1}$	$9.034 \cdot 10^{-1}$

Table 7

Density ρ_{oil} , specific heat capacity $\hat{C}_{p,oil}$, thermal conductivity λ_{oil} , dynamic viscosity η_{oil} and surface tension σ_{oil} of the beech wood pyrolysis oil under ambient conditions in comparison with ranges of values obtained in previous studies [8,11,12,14,16,91].

	$\frac{\rho_{oil}}{kg/m^3}$	$\frac{\hat{C}_{p,oil}}{J/(kg K)}$	$\frac{\lambda_{oil}}{W/(m K)}$	$\frac{\eta_{oil}}{Pa s}$	$\frac{\sigma_{oil}}{N/m}$
Beech wood pyrolysis oil	1201	2062	0.1887	1.19	23.43
Literature values	1100–1300	2600–3500	0.35–0.45	0.02–10	22–37

significantly lower than the literature values. However, comparative data for these thermo-physical properties is scarce and depends on the feedstock and the pyrolysis process. Given that the density and the viscosity of bio-oils decrease with an increase in water content [17], the water content could strongly affect heat capacity and thermal conductivity. When considering the thermo-physical properties of water, it is expected that the heat capacity and the thermal conductivity of bio-oils increase with an increase in water content. Thus, if the literature data for heat capacity and thermal conductivity have been determined for pyrolysis oils with water contents between 20% and 35% (see [3]), the data measured for the beech wood pyrolysis oil are in a reasonable agreement with the literature data.

4.8.1. Density, thermal conductivity and specific heat capacity of the beech wood pyrolysis oil and the vacuum distillate

The measured densities ρ , the measured thermal conductivities λ and the measured specific heat capacities \hat{C}_p of both the beech wood pyrolysis oil and the vacuum distillate are shown in Figs. 9–11.

In Fig. 9, the densities of both the beech wood pyrolysis oil and the vacuum distillate decrease linearly by about 12% when the temperature is increased from 293 K to 453 K. The density of the vacuum distillate is always lower than that of the beech wood pyrolysis oil, as the vacuum distillate only consists of light components. Moreover, the density

of the beech wood pyrolysis oil changes by $54 kg/m^3$ between 293 K and 353 K, which is in agreement with previous data [16] for Ensyn pyrolysis oil samples (albeit with higher water contents). Furthermore, the densities of the beech wood pyrolysis oil that were measured between 293 K and 343 K at KIT or at 287 K at EXT I are shown in Fig. 9. The measured data of KIT are in excellent agreement with the data of EXT III, whereas the measured data of EXT I is 2% lower and could be erroneous. Comparative measurements are thus recommended for future studies.

In Fig. 10, the thermal conductivities of both the beech wood pyrolysis oil and the vacuum distillate decrease by 16% and 12%, respectively, when increasing the temperature from 293 K to 453 K. The thermal conductivity of the vacuum distillate decreases linearly, whereas that of the beech wood pyrolysis oil decreases more strongly at higher temperatures than at lower ones. The decrease in the thermal conductivity with increasing temperature is in agreement with literature data for water and extracted bio-oils [92], while previous findings for Ensyn pyrolysis oil samples [16] have suggested a slight increase between 303 K and 333 K for thoroughly mixed samples.

In Fig. 11, the specific heat capacities of both the beech wood pyrolysis oil and the vacuum distillate increase linearly by 24% and 30%, respectively, when increasing the temperature from 293 K to 453 K. Due to the higher water content, the measured heat capacities are higher for the vacuum distillate than for the beech wood pyrolysis oil. Moreover,

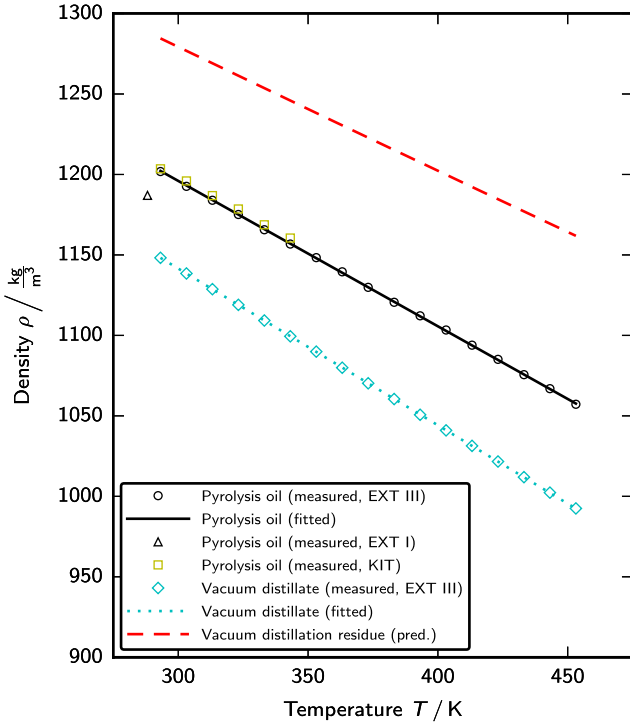


Fig. 9. Densities of the beech wood pyrolysis oil, the vacuum distillate and the vacuum distillation residue: comparison of measurement data with numerical approximations. Note the abbreviation: pred.: predicted.

the beech wood pyrolysis oil exhibits a smaller increase in heat capacity between 303 K and 333 K compared to Ensyn pyrolysis oil samples [16], recalling that previous data varied strongly between 2600 J/(kg K) and 3800 J/(kg K) due to various measurement challenges, such as the vapourisation and decomposition of pyrolysis oil components [16].

Furthermore, the measured single-run data of EXT III are shown in Figs. 10 and 11. These single-run values are in good agreement with the previously measured data of EXT III. Thus, heating did not significantly affect the measurements.

The density ρ , the thermal conductivity λ and the specific heat capacity \hat{C}_p were finally approximated by

$$\rho_j = \left(\sum_{i=1}^2 C_{i,j} \left(\frac{T}{K} \right)^{i-1} \right) \frac{\text{kg}}{\text{m}^3}, \quad (18)$$

$$\lambda_j = \left(\sum_{i=1}^3 C_{i,j} \left(\frac{T}{K} \right)^{i-1} \right) \frac{\text{W}}{\text{mK}}, \quad (19)$$

$$\hat{C}_{p,j} = \left(\sum_{i=1}^3 C_{i,j} \left(\frac{T}{K} \right)^{i-1} \right) \frac{\text{J}}{\text{kgK}}, \quad (20)$$

where $j = \text{oil, vd}$ refers to the beech wood pyrolysis oil and the vacuum distillate, respectively, C_1 , C_2 and C_3 are coefficients and T is the temperature. The coefficients C_1 , C_2 and C_3 are given in Tables 8 and 9. The approximations are in good agreement with the measured data.

4.8.2. Density, thermal conductivity and specific heat capacity of the vacuum distillation residue

The derived density ρ , the derived thermal conductivity λ and the derived specific heat capacity \hat{C}_p of the vacuum distillation residue are shown in Figs. 9, 10 and 11. The density of the vacuum distillation

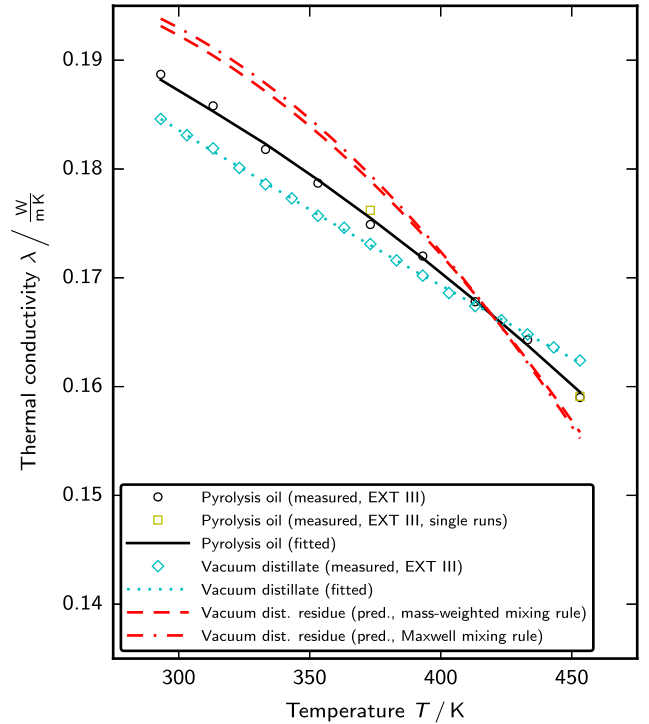


Fig. 10. Thermal conductivities of the beech wood pyrolysis oil, the vacuum distillate and the vacuum distillation residue: comparison of measurement data with numerical approximations. Note the abbreviations: dist.: distillation; pred.: predicted.

residue is thus higher than that of the beech wood pyrolysis oil under low-temperature conditions, while the specific heat capacity of the vacuum distillation residue is lower than the specific heat capacity of the beech wood pyrolysis oil. Moreover, the thermal conductivity of the vacuum distillation residue is higher than that of the beech wood pyrolysis oil at temperatures of up to 420 K and lower than the thermal conductivity of the beech wood pyrolysis oil at higher temperatures. This is in agreement with the deviating slopes of the thermal conductivities of the beech wood pyrolysis oil and the vacuum distillate. In addition, both the mass-weighted mixing rule and the Maxwell mixing rule provide fairly similar predictions for the thermal conductivity of the vacuum distillation residue. The impact of the mixing rule on the derived data is thus rather low. Furthermore, the specific heat capacity of the vacuum distillation residue $\hat{C}_{p,\text{vdr}}$ was approximated using the Einstein/Merrick model with two characteristic temperatures [93] in order to enable a reasonable extrapolation to higher temperatures. The approximation is given by

$$\hat{C}_{p,\text{vdr}} = (1 - w_{\text{ash,oil}}) \hat{C}_{p,\text{vdr,af}} + w_{\text{ash,oil}} \hat{C}_{p,\text{ash}}, \quad (21)$$

$$\hat{C}_{p,\text{vdr,af}} = \left(C_1 \left(g \left(C_2 \frac{\text{K}}{T} \right) + 2g \left(C_3 \frac{\text{K}}{T} \right) \right) \right) \frac{\text{J}}{\text{kgK}}, \quad (22)$$

$$\hat{C}_{p,\text{ash}} = \left(754 + 0.586 \left(\frac{T}{\text{K}} - 273.15 \right) \right) \frac{\text{J}}{\text{kgK}}, \quad (23)$$

where C_1 , C_2 and C_3 are coefficients, given in Table 9, and g is an auxiliary function that is defined by [93]

$$g(z) = \frac{\exp(z)}{((\exp(z) - 1)/z)^2}. \quad (24)$$

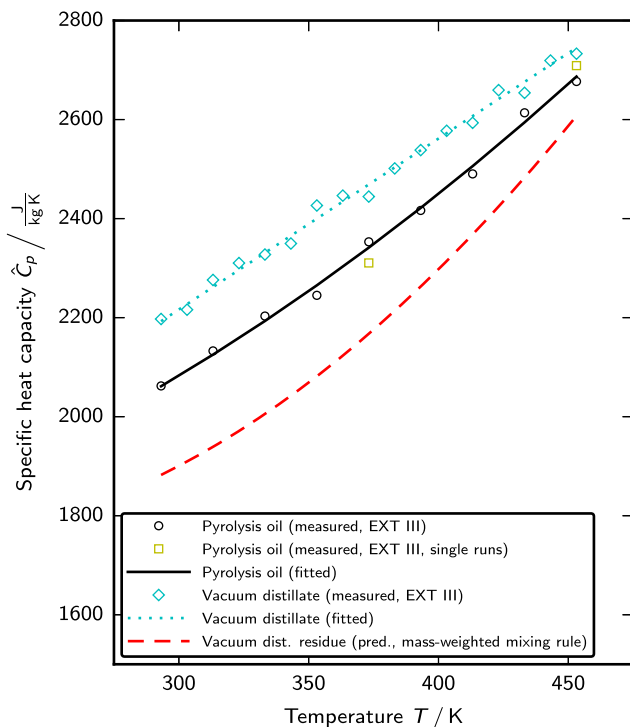


Fig. 11. Specific heat capacities of the beech wood pyrolysis oil, the vacuum distillate and the vacuum distillation residue: comparison of measurement data with numerical approximations. Note the abbreviations: dist.: distillation; pred.: predicted.

Table 8

Coefficients for the calculation of the density ρ_{oil} using Eq. (18), the calculation of the thermal conductivity λ_{oil} using Eq. (19) and the calculation of the specific heat capacity $\hat{C}_{p,oil}$ using Eq. (20), each of the beech wood pyrolysis oil.

i	C_i		
	ρ_{oil}	λ_{oil}	$\hat{C}_{p,oil}$
1	$1.466068 \cdot 10^{-3}$	$2.174394 \cdot 10^{-1}$	$1.672170 \cdot 10^3$
2	$-9.008656 \cdot 10^{-1}$	$-4.402192 \cdot 10^{-5}$	$-2.935937 \cdot 10^{-1}$
3	–	$-1.848268 \cdot 10^{-7}$	$5.582648 \cdot 10^{-3}$

Table 9

Coefficients for the calculation of the density of the vacuum distillate ρ_{vd} using Eq. (18), the calculation of the thermal conductivity of the vacuum distillate λ_{vd} using Eq. (19), the calculation of the specific heat capacity of the vacuum distillate $\hat{C}_{p,vd}$ using Eq. (20) and the calculation of the specific heat capacity of the vacuum distillation residue $\hat{C}_{p,vdr}$ using Eqs. (21)–(24).

i	C_i			
	ρ_{vd}	λ_{vd}	$\hat{C}_{p,vd}$	$\hat{C}_{p,vdr}$
1	$1.433500 \cdot 10^3$	$2.342043 \cdot 10^{-1}$	$1.202392 \cdot 10^3$	$1.007613 \cdot 10^2$
2	$-9.733561 \cdot 10^{-1}$	$-1.881592 \cdot 10^{-4}$	3.393910	$4.272600 \cdot 10^2$
3	–	–	$6.470100 \cdot 10^{-8}$	$2.322618 \cdot 10^3$

4.8.3. Dynamic viscosity

The measured dynamic viscosities of the beech wood pyrolysis oil η_{oil} are shown in Fig. 12. The dynamic viscosity decreases with an increase in temperature and asymptotically approaches a minimum value at high temperatures. Furthermore, the measurement data are in agreement with the data measured at the laboratory EXT I. However, in comparison with the literature data [11], the measured dynamic viscosities are higher due to the lower water content and the higher fraction of large molecules (see Section 4.3). An accurate approximation is

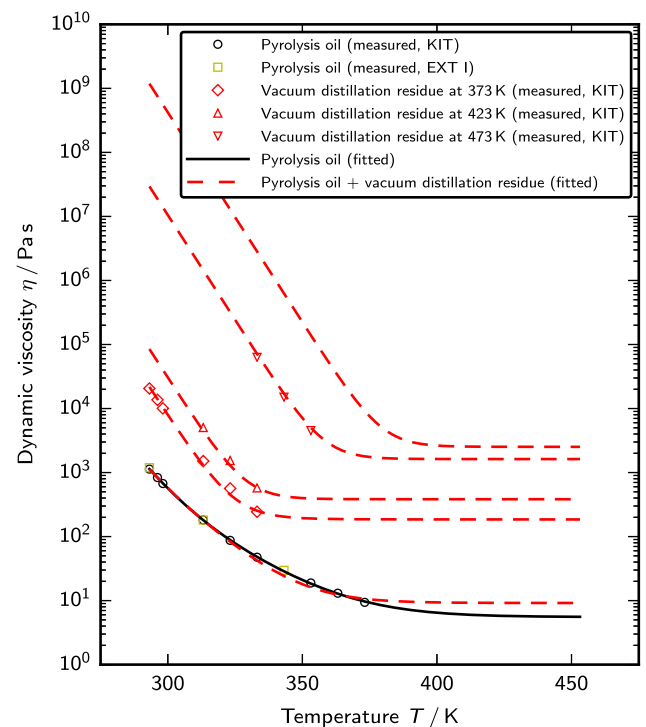


Fig. 12. Dynamic viscosity of the beech wood pyrolysis oil and four vacuum distillation residues: comparison of measurement data with numerical approximations.

Table 10

Coefficients for the calculation of the dynamic viscosity of the beech wood pyrolysis oil using Eq. (25) and the calculation of the dynamic viscosity of the beech wood pyrolysis oil and the vacuum distillation residues using Eq. (26).

i	C_i	
	η_{oil}	η_{vdr}
1	$4.463692 \cdot 10^1$	$1.373277 \cdot 10^{-2}$
2	$1.295787 \cdot 10^{-1}$	3.104976
3	$2.220811 \cdot 10^1$	5.463751
4	$5.572887 \cdot 10^{-2}$	6.768664
5	5.550941	$2.050511 \cdot 10^1$
6	–	$8.516608 \cdot 10^{-1}$
7	–	$9.938904 \cdot 10^{-1}$
8	–	-1.275005
9	–	$2.929994 \cdot 10^1$
10	–	$2.498487 \cdot 10^2$
11	–	$-2.738196 \cdot 10^3$
12	–	$7.705428 \cdot 10^{-2}$
13	–	9.169229
14	–	$1.326153 \cdot 10^3$
15	–	$5.811586 \cdot 10^3$

given by

$$\eta_{oil} = \exp\left(C_1 - C_2 \left(\frac{T}{K}\right)\right) + \exp\left(C_3 - C_4 \left(\frac{T}{K}\right)\right) + C_5, \quad (25)$$

where C_1 , C_2 , C_3 , C_4 and C_5 are coefficients, given in Table 10.

The measured dynamic viscosities of the vacuum distillation residues, obtained at 373 K, 423 K and 473 K (see Sections 3.5 and 4.4), are shown in Fig. 12. These data were mainly obtained at higher temperatures, as the samples were usually too viscous at lower ones. Furthermore, the dynamic viscosity increases with increasing fraction of non-vaporisable components, while the temperature dependency differs for the various vacuum distillation residues.

Table 11

Characteristic operating parameters of the bioliq EFG experiment V105: slurry, thermal input P_{th} , operating pressure p_{op} , ash/slurry mass flow rate ratio $\dot{m}_{ash}/\dot{m}_{slurry}$, steam/slurry mass flow rate ratio $\dot{m}_{steam}/\dot{m}_{slurry}$, oxygen/slurry mass flow rate ratio $\dot{m}_{O_2}/\dot{m}_{slurry}$ and nitrogen/slurry mass flow rate ratio $\dot{m}_{N_2}/\dot{m}_{slurry}$.

Experiment	Slurry	$\frac{P_{th}}{MW}$	$\frac{p_{op}}{bar}$	$\frac{\dot{m}_{ash}}{\dot{m}_{slurry}}$	$\frac{\dot{m}_{steam}}{\dot{m}_{slurry}}$	$\frac{\dot{m}_{O_2}}{\dot{m}_{slurry}}$	$\frac{\dot{m}_{N_2}}{\dot{m}_{slurry}}$
V105	Beech wood pyrolysis oil + glass beads	4.9	40	0.045	0.36	0.94	0.26

Several approximations of the measured dynamic viscosities of the beech wood pyrolysis oil and the vacuum distillation residues were tested in this study. The best possible approximation, which provides both accurate results and reasonable extrapolation behaviour, is shown in Fig. 12 and is given by

$$\eta_{vdr} = (C_1 + C_2 w_\beta) \exp\left(C_3 + C_4 w_\beta + C_5 w_\beta^2 - C_6 \left(\frac{T}{K}\right)\right) + (C_7 + C_8 w_\beta) \exp\left(C_9 + C_{10} w_\beta + C_{11} w_\beta^2 - C_{12} \left(\frac{T}{K}\right)\right) + (C_{13} + C_{14} w_\beta + C_{15} w_\beta^2), \quad (26)$$

where C_1, \dots, C_{15} are coefficients, given in Table 10, and w_β is the recovered mass fraction, which is used to include the effect of distillation progress corresponding to the distillation temperature (see Table 3). The approximation slightly overestimates the dynamic viscosity at higher temperatures and may be revised in future studies.

5. Discussion

This section discusses (i) the chemical analysis data in connection with process calculations, (ii) the separation of vaporisable and non-vaporisable components using vacuum distillations, (iii) the TG data and (iv) the extrapolation of the TG kinetics to high-temperature and high-heating-rate conditions.

5.1. Chemical analyses

Chemical analyses conducted at five laboratories provided scattered data mainly within the reproducibility limits of DIN 51732:2007 [71], DIN 51777:2020 [72] and DIN 51900-1:2000 [73]. Process calculations were therefore applied to investigate the impact of the chemical analysis results on the design and the evaluation of the bioliq EFG experiment V105. This experiment was conducted at the bioliq EFG plant [55,56,94] with a total thermal input of 4.9 MW and a total pressure of 40 bar. Oxygen and steam were used as gasification media, glass beads were supplied to ensure slag deposition on the refractory material of the cooling screen, and natural gas was used for ignition and flame stabilisation (see [55]). The characteristic operating parameters are given in Table 11, whereas the averaged mass flow rates and corresponding enthalpy flow rates of the feed streams are given in Tables 12 and S11. The total heat extraction was balanced to 652 kW, while peripheral heat losses were neglected following previous assumptions [55]. The molar H/C ratios HCR_{slurry} , the minimum specific oxygen demands $SMOD_{slurry}$, the stoichiometric ratios λ , the equilibrium compositions in mole fractions x_{eq} , the equilibrium temperatures T_{eq} and the equilibrium cold-gas efficiencies CGE_{eq} were determined using the chemical analysis results of the laboratories¹, the measured mass flow rates, temperatures and pressures, and the equilibrium model for the bioliq EFG [55].

The molar H/C ratios HCR_{slurry} and the specific minimum oxygen demands $SMOD_{slurry}$ based on the five chemical analysis results are given in Table 13. The molar H/C ratios are between 1.1 and 1.5, while the specific minimum oxygen demands $SMOD_{slurry}$ are between 1.68

Table 12

Feed data of the bioliq EFG experiment V105: mass flow rate of slurry \dot{m}_{slurry} , mass flow rate of natural gas \dot{m}_{ng} , mass flow rate of steam \dot{m}_{steam} , mass flow rate of O_2 \dot{m}_{O_2} and mass flow rate of N_2 \dot{m}_{N_2} based on measurements.

Experiment	$\frac{\dot{m}_{slurry}}{kg/h}$	$\frac{\dot{m}_{ng}}{kg/h}$	$\frac{\dot{m}_{steam}}{kg/h}$	$\frac{\dot{m}_{O_2}}{kg/h}$	$\frac{\dot{m}_{N_2}}{kg/h}$
V105	743.9	37.5	267.6	702.5	195.2

Table 13

Molar H/C ratios HCR_{slurry} , minimum specific oxygen demands $SMOD_{slurry}$, stoichiometric ratios λ and equilibrium cold gas efficiencies CGE_{eq} , based on different chemical analysis results, for the bioliq EFG experiment V105.

Laboratory	$\frac{HCR_{slurry}}{mol/mol}$	$\frac{SMOD_{slurry}}{kg/kg}$	λ	$\frac{CGE_{eq}}{\%}$
KIT I	1.28	1.61	0.525	59.39
KIT II	1.40	1.61	0.525	60.22
KIT III	1.42	1.69	0.503	64.79
EXT I	1.46	1.68	0.506	63.81
EXT II	1.65	1.71	0.496	64.63

and 1.79. This, in turn, suggests a wide range of stoichiometric ratios λ between 0.496 and 0.525 (based on the specific minimum oxygen demands $SMOD_{slurry}$ and the mass flow rates \dot{m}_{slurry} and \dot{m}_{O_2}).

The equilibrium compositions in mole fractions $x_{eq} = (x_{i,eq})$ and the equilibrium temperatures T_{eq} based on the five chemical analysis results are shown in Fig. 13. The equilibrium concentrations of H_2 and H_2O and the equilibrium temperature are thus very sensitive to the chemical analysis results, whereas this applies less to the equilibrium concentrations of CO , CO_2 and N_2 . Moreover, the uncertainties (see Section 3.2) are shown in Fig. 13. The uncertainties of the equilibrium temperatures are up to ± 151 K if the deviations of the analysis results are inside the reproducibility limits (in particular of the carbon and hydrogen contents). Moreover, the uncertainties of the equilibrium concentrations of H_2 and H_2O are up to ± 0.021 , whereas those of the equilibrium concentrations of CO , CO_2 and N_2 are much smaller. Note that the uncertainties of the equilibrium concentrations reflect both the impact of the uncertainties of the elemental contents and the impact of the adjusted equilibrium temperature. The former impact is based on the reproducibility limits, whereas the latter is due to the water–gas shift reaction (see [55]). The uncertainties of the equilibrium concentrations due to the shift of the equilibrium temperature only are up to ± 0.013 .

The equilibrium cold gas efficiencies CGE_{eq} are compared in Table 13. The equilibrium cold gas efficiency CGE_{eq} is in a broad range between 59% and 65%. However, similar values were obtained based on the analysis results of the laboratories KIT III, EXT I and EXT II, i.e. the analysis data with Boie ratios of approximately 100%. This is in agreement with previous recommendations to use fuel data with a Boie ratio close to 100% for process calculations [55,70].

In summary, uncertain chemical beech wood pyrolysis oil data strongly affect both the design and the evaluation of entrained flow gasification experiments. This is primarily because the elemental and water contents are strongly linked with the stoichiometries of both slurry and feed. In addition, both the elemental and water contents, and the heating value influence the flow rate, composition and temperature of the

¹ Heating values were not determined at the laboratory EXT II and were therefore based on the Boie correlation [69].

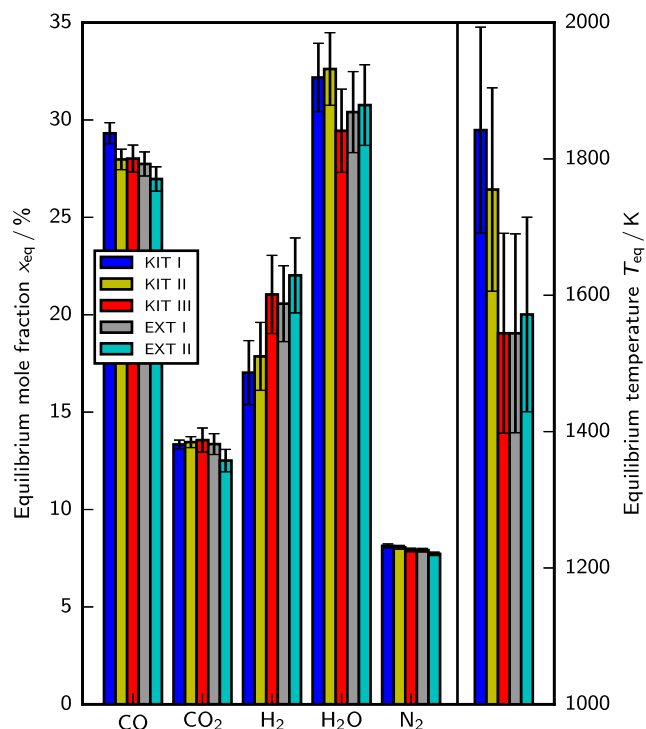


Fig. 13. Equilibrium compositions in mole fractions x_{eq} and equilibrium temperature T_{eq} based on different chemical analysis results, for the bioliq EFG experiment V105.

synthesis gas in the equilibrium model. In order to reduce the uncertainties of both the carbon, hydrogen and water contents and the heating values (see Section 4.1) and eventually improve the design and evaluation of technical processes, future studies should enhance the sampling and the analysis methods for the chemical properties of pyrolysis oils.

5.2. Vacuum distillations

Vacuum distillations at 40 mbar were applied to separate the beech wood pyrolysis oil into vaporisable and non-vaporisable components, assuming that the vacuum distillate and the vacuum distillation residue can represent the volatile and the non-volatile components of the beech wood pyrolysis oil. However, some comments and comparisons are needed to substantiate this approach:

1. The GC-MS data indicates a lower mass fraction of volatiles (44.5%) compared to both the vacuum distillation data (57.7%) and the Engler distillation data (60.4%). This is reasonable because the GC-MS analyses did not (fully) detect low-volatile components with boiling temperatures above 523 K (see Sections 3.3 and 4.2). Thus, both vacuum distillates and Engler distillates are better representatives of the vaporisable components than mixtures based on GC-MS data (see also Section S4).
2. The mass fraction of the Engler distillate (60.4%) is greater than the mass fraction of the vacuum distillate (57.7%) and less than the maximum possible mass fraction of the vacuum distillate (66.7%). This is because some volatiles were lost during vacuum distillation (see Section 4.4). In addition to that, some volatiles that decompose rather than vaporise under atmospheric-pressure conditions were released during vacuum distillation (see Section 4.4). Therefore, the vacuum distillate differs from the Engler distillate and is not fully representative of the vaporisable

components under atmospheric-pressure conditions. The Engler distillate could be superior to the vacuum distillate.

3. The Engler distillation residue cannot be used for further analysis based on the authors' experiences. Thus, the vacuum distillation residue is likely the most appropriate basis for investigating the chemical and physical properties of the non-vaporisable components.
4. The TG data demonstrates that the TG and DTG curves for the beech wood pyrolysis oil are largely consistent with the mass fraction-weighted and superposed TG and DTG curves of the vacuum distillate and the vacuum distillation residue. Thus, the vacuum distillate and the vacuum distillation residue can reflect the TG behaviour of the beech wood pyrolysis oil.

In summary, vacuum distillation can provide representative samples of the vaporisable and non-vaporisable components to a large extent. Therefore, the thermo-physical properties of the vacuum distillate and the vacuum distillation residue were measured and used to describe the vaporisable and non-vaporisable fractions of the beech wood pyrolysis oil. Future studies may improve upon this approach.

5.3. TG analyses

TG analyses have been conducted for a wide range of biogenic pyrolysis oils. For example, TG curves were determined for four commercial wood pyrolysis oils in the presence of oxygen at a heating rate of 5 K/min and a maximum temperature of 600 K [3]. These oils were derived in the pyrolysis plants of BTG, Dynamotive, Ensyn and Pyrovac, respectively, and exhibited water contents of 30.4% (BTG), 21.1% (Dynamotive), 20.3% (Ensyn) and 15.7% (Pyrovac) [3]. The TG curves of these four oils are reproduced in Fig. 14 and are compared with the TG data of the (proFagus) beech wood pyrolysis oil for 5 K/min. First, note that the TG curves were determined using different setups. In this study, the temperature was measured below the sample crucible (see Section 3.7),

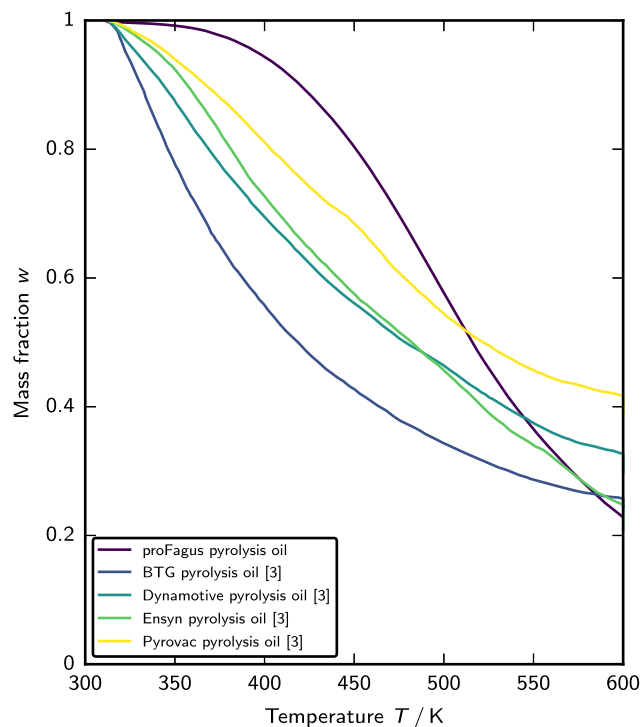


Fig. 14. TG curves of the BTG, Dynamotive, Ensyn and Pyrovac pyrolysis oils at 5 K/min [3] in comparison with the TG data of the (proFagus) beech wood pyrolysis oil.

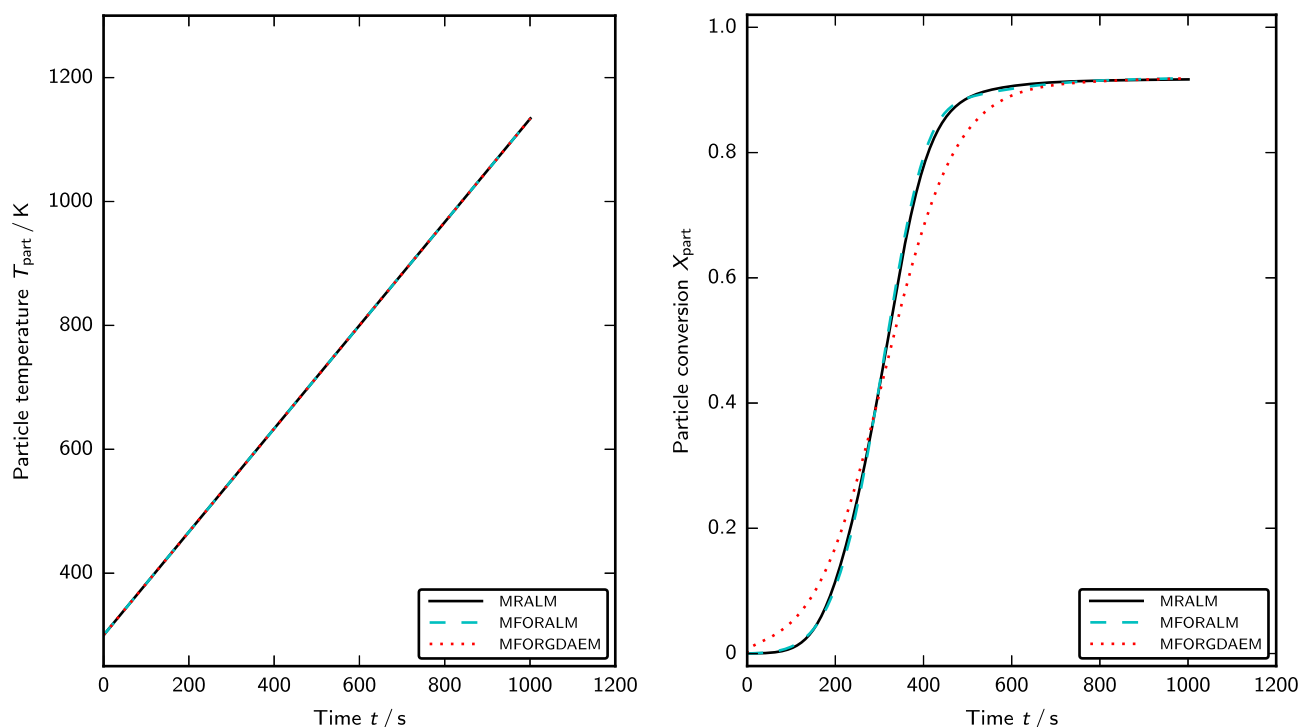


Fig. 15. Assumed particle temperatures T_{part} (left) and predicted particle conversions X_{part} (right) using the multi-reaction Arrhenius law model (MRALM), the multi first-order reaction Arrhenius law model (MFORALM) and the multi first-order reaction Gauss distributed activation energy model (MFORGDAEM) for test case 1.

whereas the thermocouple was previously positioned close to the sample bottom [3]. This could limit the comparability of the TG data (see [20]). Then, despite a qualitative agreement, the TG curves differ clearly from each other. The volatiles of the proFagus pyrolysis oil were mainly released between 350 K and 600 K, whereas the sample masses of the other pyrolysis oils mainly decreased between 300 K and 550 K. Moreover, between 300 K and 400 K, the mass decreased more strongly for the BTG pyrolysis oil with the highest water content than for the other oils with lower water contents. The water content thus strongly determines the thermogravimetric conversion, while the impact of other volatiles is less pronounced, as the pyrolysis oils with similar water contents (Dynamotive and Ensyn) have shown similar mass decreases. This is also in line with TG analyses of other proFagus pyrolysis oil charges with slightly different water contents. Furthermore, 23%–45% of the initial sample masses were retrieved as residues at 600 K. The residues were similar for the proFagus, the Ensyn and the BTG pyrolysis oil, while larger residues were obtained for the Dynamotive and the Pyrovac pyrolysis oil. This reflects different contents of (light and heavy) volatiles. In summary, the TG data of the (proFagus) beech wood pyrolysis oil are in accordance with its water content. Therefore, the TG data should not be adopted for other pyrolysis oils with higher water contents. However, future studies may use the TG data for pyrolysis oils with similar water contents in the absence of experimental data.

5.4. TG kinetics

TG kinetics were derived for the beech wood pyrolysis oil using multi-reaction Arrhenius law models (MRALM), multi first-order reaction Arrhenius law models (MFORALM) and multi first-order reaction Gauss distributed activation energy models (MFORGDAEM). Zero-dimensional particle simulations were subsequently performed using an in-house software in Python to compare the kinetics. Two test cases were considered in this study.

In test case 1, a non-moving spherical droplet with an initial temperature of 300 K and an initial diameter of 100 μm is heated up using a constant heating rate of 50 K/min in an inert non-moving gas. The particle temperature T_{part} was thus prescribed, as shown in Fig. 15 (left), while differential equations were solved for the particle conversion X_{part} using constant time steps of 1 s and assuming constant particle diameters. The simulated particle conversions X_{part} are shown in Fig. 15 (right). The multi-reaction Arrhenius law model and the multi first-order reaction Arrhenius law model provide similar predictions, whereas the conversion based on the multi first-order reaction Gauss distributed activation energy model is initially faster and then slows down in accordance with the numerical approximations (see Section 4.6).

In test case 2, a non-moving spherical droplet with the same initial temperature of 300 K and the same initial diameter of 100 μm is assumed in a non-moving gas consisting of nitrogen with a gas temperature of 1673 K and a gas pressure of 1 bar. Differential equations were solved for the particle temperature T_{part} and the particle conversion X_{part} using constant time steps of 10^{-4} s, assuming constant particle diameters and with an empirical approach for the particle heat capacity (see Section S3). Furthermore, the initial mass fractions $w_0 = (w_i)$ were adjusted for high-heating-rate conditions based on previous observations [29] and SEM images of cenospheres collected in atmospheric-pressure drop-tube reactor experiments and bioliq EFG experiments (see Fig. 16). The adjustment is depicted for the multi first-order reaction Gauss distributed activation energy model in Fig. 17. The initial mass fractions w_0 for high heating rates are given in Table S12.

The simulated particle temperatures T_{part} are shown in Fig. 18 (left) and differ clearly from each other, as the particle temperatures T_{part} are linked with the particle conversion X_{part} through the correlation of the particle heat capacity (see Section S3). The simulated particle conversions X_{part} are shown in Fig. 18 (right). The kinetics provide full conversion at about 0.3 s (MFORGDAEM), 1.6 s (MRALM) and 3.5 s (MFORALM), respectively. First of all, this is in line with the adjusted

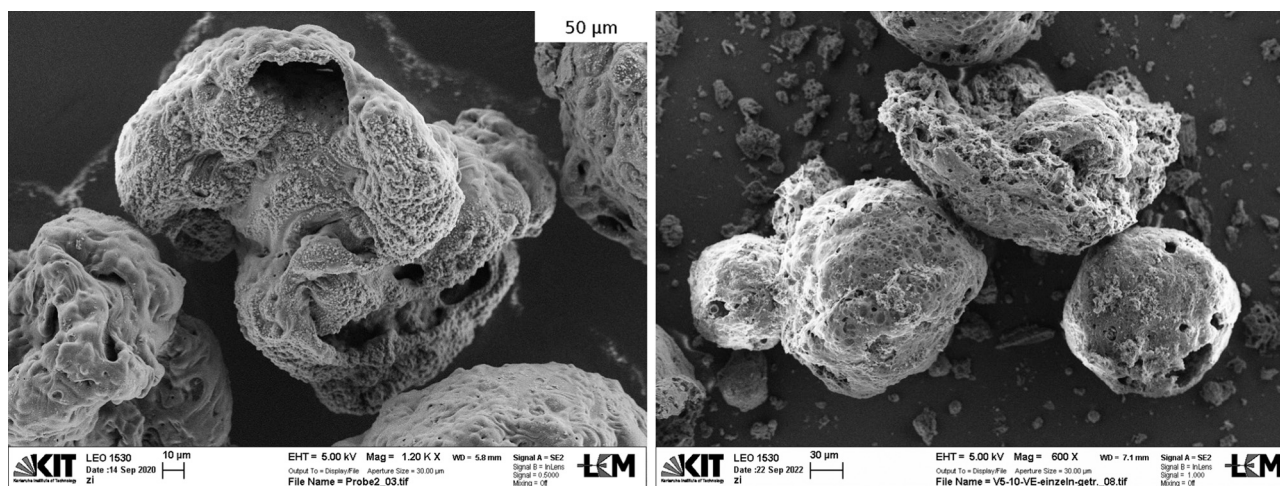


Fig. 16. SEM images of cenospheres collected in an atmospheric-pressure drop-tube reactor experiment (1273 K, 1 bar, left) and in a bioliq EFG experiment (1433 K, 40 bar, right), each with (proFagus) beech wood pyrolysis oil.

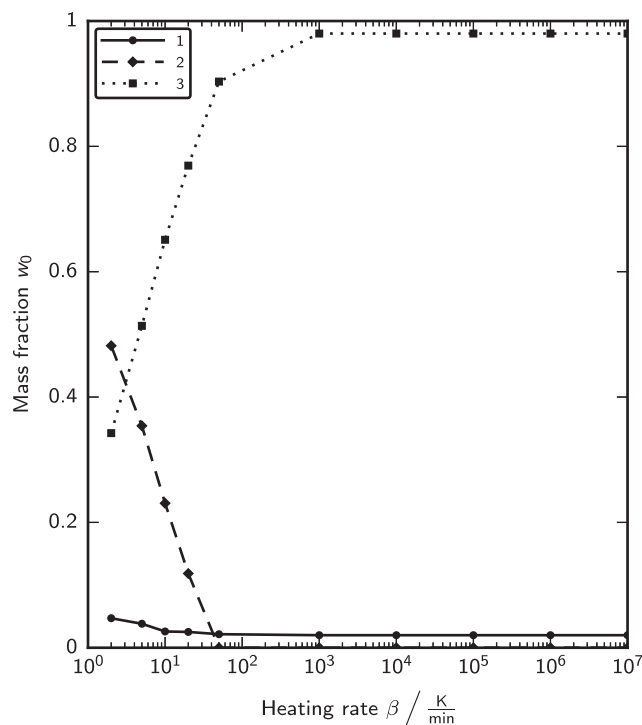


Fig. 17. Extrapolation of the initial mass fractions $w_{0,1}$, $w_{0,2}$ and $w_{0,3}$ to high heating rates for the multi first-order reaction Gauss distributed activation energy model. Note that the labels refer to the indices of the initial mass fraction w_0 .

initial mass fractions w_0 . Then, the multi first-order reaction Gauss distributed activation energy model provides faster conversion than the multi-reaction Arrhenius law models. This can also be observed for both smaller and larger particles (see Figs. S1 and S2). Moreover, both multi-reaction Arrhenius law models provide deviating predictions. Recalling that the kinetics were derived at low heating rates of between 2 K/min and 50 K/min, this indicates inconsistent extrapolation behaviour of the multi-reaction Arrhenius law models. It also shows that extrapolation of TG kinetics can result in unreliable predictions at high heating rates. Therefore, kinetics from drop-tube reactor experiments should be

preferred over TG kinetics for simulations with rapid heating processes. However, in the absence of kinetics based on elaborative drop-tube reactor experiments, kinetics may be developed using the steps described below:

1. TG analyses under inert conditions at heating rates of 2 K/min, 5 K/min, 10 K/min, 20 K/min and 50 K/min up to a maximum temperature of 1273 K
2. Numerical approximation of experimental TG curves under constraints using multi-reaction Gauss distributed activation energy models
3. Numerical extrapolation of TG and DTG curves to heating rates of 10^3 K/min, 10^4 K/min, 10^5 K/min and 10^6 K/min applying multi-reaction Gauss distributed activation energy models with the parameters from the previous numerical approximation but with adjusted initial mass fractions (corresponding to the expected minimum remaining mass fractions at high heating rates)
4. Calculation of numerical TG and DTG curves at 2 K/min, 5 K/min, 10 K/min, 20 K/min, 50 K/min, 10^3 K/min, 10^4 K/min, 10^5 K/min and 10^6 K/min using multi first-order reaction Gauss distributed activation energy models
5. Numerical approximation using multi-reaction Arrhenius law models or multi first-order reaction Arrhenius law models

In summary, decomposition kinetics for high heating rates may be derived using multi-reaction Arrhenius law models from TG and DTG curves predicted by multi-reaction Gauss distributed activation energy models, where the latter models should be based on experimental TG and DTG curves. This is recommended because (i) multi-reaction Gauss distributed activation energy models could provide better extrapolation behaviour (see [66,95]) and (ii) decomposition kinetics based on multi-reaction Arrhenius law models are beneficial for CFD simulations of combustion and entrained flow gasification processes due to lower computing times.

The numerical approximations of the numerical TG and DTG curves using multi-reaction Arrhenius law models with unity and non-unity reaction orders are shown in Fig. 19. The approximations based on the multi-reaction Arrhenius law model and non-unity reaction orders are thus slightly superior for high heating rates compared to the approximations based on the multi first-order reaction Arrhenius law model. The parameters of the approximations for the heating rate of 10^6 K/min are presented in Tables 14 and 15.

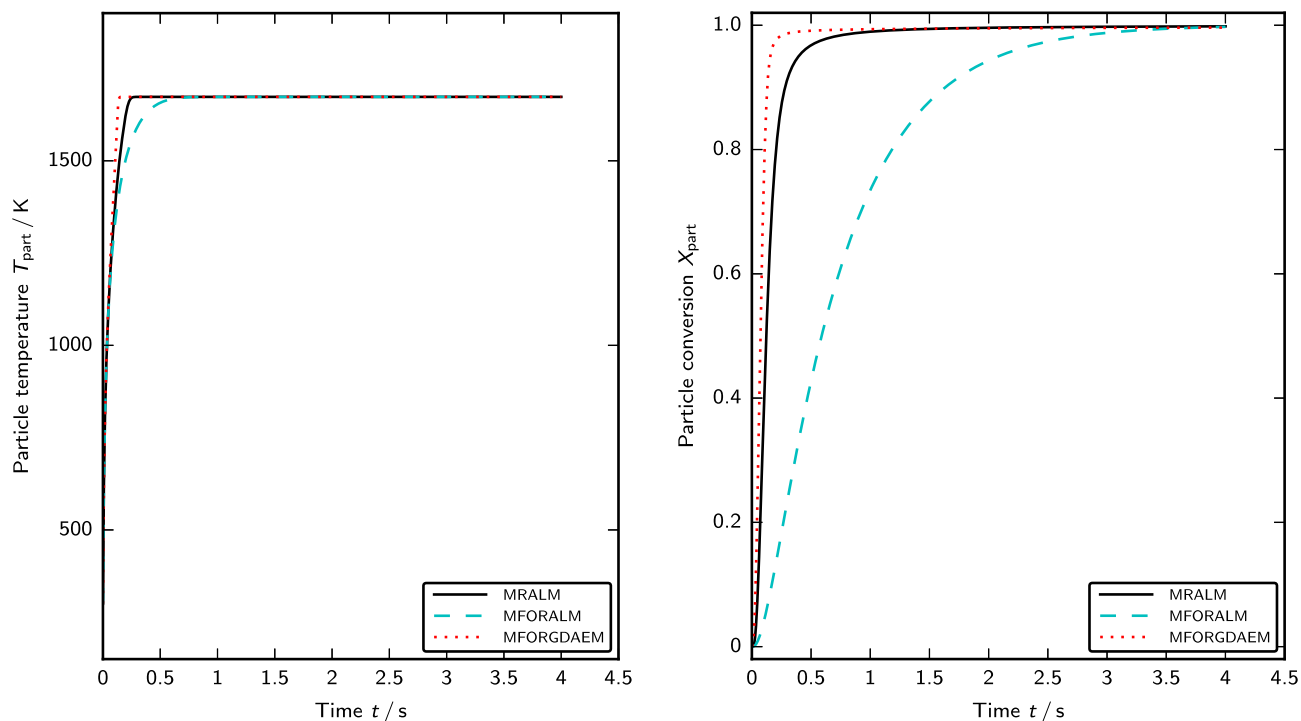


Fig. 18. Predicted particle temperatures T_{part} (left) and predicted particle conversions X_{part} (right) using the multi-reaction Arrhenius law model (MRALM), the multi first-order reaction Arrhenius law model (MFORALM) and the multi first-order reaction Gauss distributed activation energy model (MFORGDAEM) for test case 2.

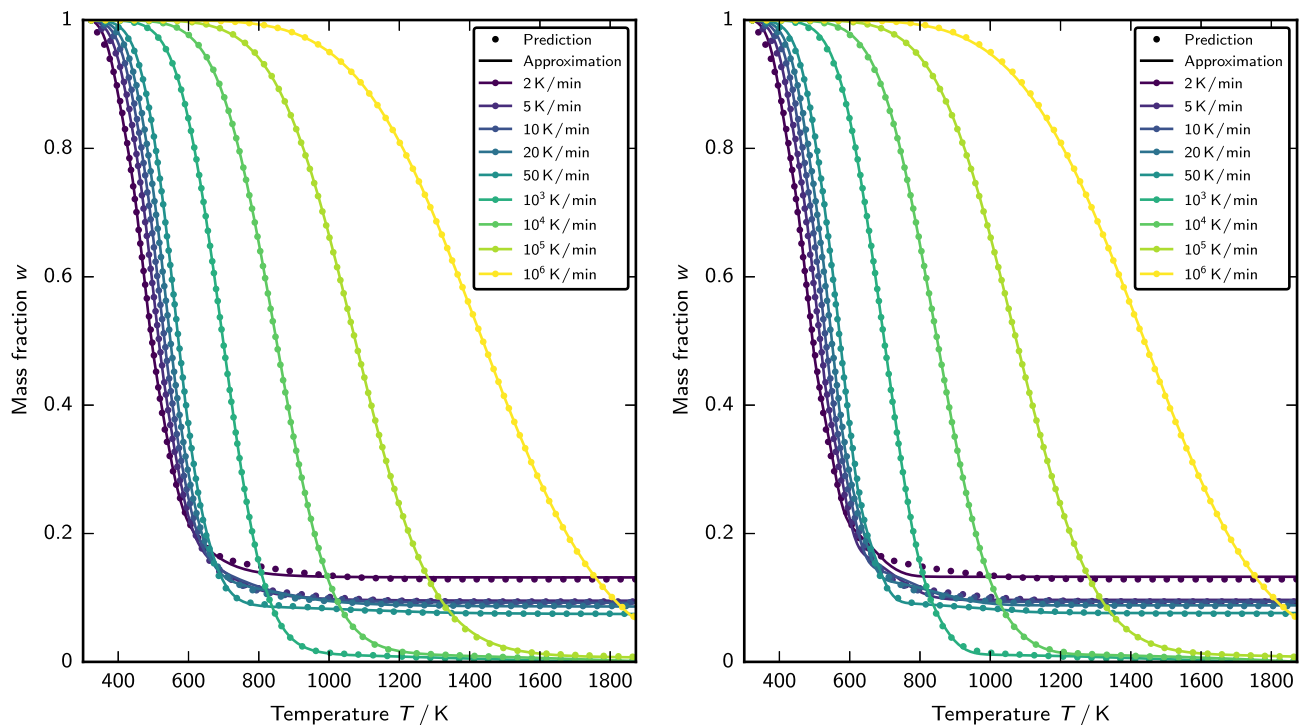


Fig. 19. TG curves of the beech wood pyrolysis oil: comparison of predicted data based on the multi first-order reaction Gauss distributed activation energy model with numerical approximations based on the multi-reaction Arrhenius law model (left) and the multi first-order reaction Arrhenius law model (right).

Table 14

Parameters for the calculation of the mass loss w and the derivative of the mass loss dw/dt for the beech wood pyrolysis oil using the multi-reaction Arrhenius law model based on Eqs. (3)–(8).

i	$\frac{k_{0,i}}{1/s}$	$\frac{\bar{E}_{a,i}}{J/mol}$	n_i	$\frac{w_{0,i}}{10^6 \frac{K}{min}}$
1	$1.089 \cdot 10^5$	$7.951 \cdot 10^4$	1.552	$8.758 \cdot 10^{-11}$
2	$3.363 \cdot 10^3$	$4.697 \cdot 10^4$	1.228	$3.211 \cdot 10^{-1}$
3	$1.849 \cdot 10^2$	$5.481 \cdot 10^4$	2	$2.215 \cdot 10^{-7}$
4	$1.077 \cdot 10^4$	$6.132 \cdot 10^4$	1.281	$6.982 \cdot 10^{-1}$

Table 15

Parameters for the calculation of the mass loss w and the derivative of the mass loss dw/dt for the beech wood pyrolysis oil using the multi first-order reaction Arrhenius law model based on Eqs. (3)–(8).

i	$\frac{k_{0,i}}{1/s}$	$\frac{\bar{E}_{a,i}}{J/mol}$	n_i	$\frac{w_{0,i}}{10^6 \frac{K}{min}}$
1	$6.394 \cdot 10^3$	$6.115 \cdot 10^4$	1	$4.839 \cdot 10^{-1}$
2	$6.721 \cdot 10^3$	$7.172 \cdot 10^4$	1	0
3	$4.609 \cdot 10^3$	$5.026 \cdot 10^4$	1	$4.951 \cdot 10^{-1}$
4	1.259	$4.390 \cdot 10^4$	1	0

6. Conclusions

Chemical and physical property data, thermo-physical property models and decomposition kinetics were determined for an industrial beech wood pyrolysis oil with a low water content and a high oligomer content. The investigation included (i) proximate, ultimate, heating value, gas chromatography–mass spectrometry (GC–MS), gel permeation chromatography (GPC) and thermogravimetric (TG) analyses, (ii) vacuum and Engler distillations and (iii) measurements of density, dynamic viscosity, thermal conductivity, specific heat capacity and surface tension. The data and the models can be used for the design and scale-up of combustion or entrained flow gasification processes using both process and CFD models. The conclusions based on the evaluation of the measured and derived data are summarised below:

1. The uncertainties of the sampling and chemical analysis methods strongly affect the design and the performance evaluation of technical processes.
2. The vaporisable and non-vaporisable fractions of pyrolysis oils can be separated through vacuum distillation to a large extent.
3. The TG data of the vacuum distillate and the vacuum distillation residue can show the superposition of vaporisation and decomposition.
4. The thermal conductivity data and the heat capacity data of pyrolysis oils strongly depend on the water content.
5. Multi-reaction Arrhenius law models have provided slightly superior approximations of the TG data of the beech wood pyrolysis oil compared to multi first-order reaction Gauss distributed activation energy models. The latter models, however, are recommended for the extrapolation to high heating rates in the absence of kinetics based on drop-tube reactor experiments.

Future studies should enhance the sampling and the analysis methods for the chemical properties of pyrolysis oils, including the carbon, hydrogen, oxygen and water contents and the heating values. In the absence of enhanced methods, the chemical analysis data could be assessed using the Boie correlation [69] and the Boie ratio (see [55]), or using measured and balanced process data from laboratory-scale or pilot-scale experiments (see [55]). Due to fuel complexity and variability and the impact of the water content, the chemical and physical property data and kinetics derived in this study could only be used to describe beech wood pyrolysis oils with water contents around 5%–10%. Therefore, future

studies may also focus on the comprehensive characterisation of biogenic pyrolysis oils with water contents between 10% and 30% and of anthropogenic pyrolysis oils. Such an investigation may analyse whether pyrolysis oils on dry basis exhibit similar thermo-physical properties. Future studies may also determine the decomposition rates at low and high heating rates as well as under atmospheric- and high-pressure conditions. In addition, gaseous and solid decomposition products may be characterised regarding their chemical and physical properties, as the products determine the temperature distribution and the conversion in technical processes (see [53,54,63]). Finally, future studies may incorporate the data and the models for the beech wood pyrolysis oil in detailed combustion or entrained flow gasification models. The chemical analysis data and the thermo-physical property models can be used to describe the chemical and physical properties of pyrolysis oil droplets, while the extrapolated kinetics can be applied to describe the droplet conversion.

CRedit authorship contribution statement

Maximilian Dammann: Writing – review & editing, Writing – original draft, Visualisation, Validation, Supervision, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualisation. **Fabian Hüsing:** Writing – review & editing, Writing – original draft, Visualisation, Validation, Methodology, Investigation, Formal analysis, Conceptualisation. **Ulrike Santo:** Writing – review & editing, Writing – original draft, Visualisation, Validation, Methodology, Investigation, Formal analysis. **David Böning:** Validation, Software, Methodology, Investigation, Formal analysis. **Marco Mancini:** Supervision, Writing – review & editing. **Thomas Kolb:** Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Most of the data is included in this article or in the supplementary data. Further data will be made available on request.

Supplementary data

Supplementary data related to this article can be found online at <https://doi.org/10.1016/j.fuel.2025.134897>.

References

- [1] Mohan D, Pittman CU, Steele PH. Pyrolysis of wood/biomass for bio-oil: a critical review. *Energy Fuels* 2006;20(3):848–89. <https://doi.org/10.1021/ef0502397>.
- [2] Branca C, Giudicianni P, Di Blasi C. GC/MS characterization of liquids generated from low-temperature pyrolysis of wood. *Ind Eng Chem Res* 2003;42(14):3190–202. <https://doi.org/10.1021/ie030066d>.
- [3] Branca C, Di Blasi C, Elefante R. Devolatilization and heterogeneous combustion of wood fast pyrolysis oils. *Ind Eng Chem Res* 2005;44(4):799–810. <https://doi.org/10.1021/ie049419e>.

- [4] Branca C, Di Blasi C. Multistep mechanism for the devolatilization of biomass fast pyrolysis oils. *Ind Eng Chem Res* 2006;45(17):5891–99. <https://doi.org/10.1021/ie060161x>.
- [5] García-Pérez M, Chaala A, Pakdel H, Kretschmer D, Roy C. Characterization of bio-oils in chemical families. *Biomass Bioenergy* 2007;31(4):222–42. <https://doi.org/10.1016/j.biombioe.2006.02.006>.
- [6] García-Pérez M, Adams TT, Gudrum JW, Geller DP, Das KC. Production and fuel properties of pine chip bio-oil/biodiesel blends. *Energy Fuels* 2007;21(4):2363–72. <https://doi.org/10.1021/ef060533e>.
- [7] Hassan E-BM, Steele PH, Ingram L. Characterization of fast pyrolysis bio-oils produced from pretreated pine wood. *Appl Biochem Biotechnol* 2008;154(1–3):3–13. <https://doi.org/10.1007/s12010-008-8445-3>.
- [8] Czernik S, Bridgwater AV. Overview of applications of biomass fast pyrolysis oil. *Energy Fuels* 2004;18(2):590–98. <https://doi.org/10.1021/ef034067u>.
- [9] Fagernäs L. Chemical and physical characterisation of biomass-based pyrolysis oils. *Tech. Rep.* 1706. Espoo, Finland: VTT Technical Research Centre of Finland; 1995, Dec. <https://cris.vtt.fi/en/publications/chemical-and-physical-characterisation-of-biomass-based-pyrolysis>.
- [10] Oasmaa A, Leppämäki E, Koponen P, Levander J, Tapola E. Physical characterisation of biomass-based pyrolysis liquids: application of standard fuel oil analyses. *Tech. Rep.* 306. Espoo, Finland: VTT Technical Research Centre of Finland; 1997. <https://cris.vtt.fi/en/publications/physical-characterisation-of-biomass-based-pyrolysis-liquids-appl>.
- [11] Oasmaa A, Peacocke C. A guide to physical property characterisation of biomass-derived fast pyrolysis liquids. *Tech. Rep.* 450. Espoo, Finland: VTT Technical Research Centre of Finland; 2001. <https://cris.vtt.fi/en/publications/a-guide-to-physical-property-characterisation-of-biomass-derived>.
- [12] Lu Q, Li W-Z, Zhu X-F. Overview of fuel properties of biomass fast pyrolysis oils. *Energy Convers Manag* 2009;50(5):1376–83. <https://doi.org/10.1016/j.enconman.2009.01.001>.
- [13] Staš M, Kubička D, Chudoba J, Pospíšil M. Overview of analytical methods used for chemical characterization of pyrolysis bio-oil. *Energy Fuels* 2014;28(1):385–402. <https://doi.org/10.1021/ef402047y>.
- [14] Dammann M, Santo U, Böning D, Knoch H, Eberhard M, Kolb T. Characterisation of beech wood pyrolysis oil: chemical and physical property data (internal notes); 2022.
- [15] Bakhshi NN, Adjaye JD. Properties and characteristics of Ensyn bio-oil. In: *Proceedings of the Biomass Pyrolysis Oil Properties and Combustion Meeting*, 26–28 September 1994; Estes Park, CO, USA; 1994. p. 54–66.
- [16] Peacocke GVC, Russell PA, Jenkins JD, Bridgwater AV. Physical properties of flash pyrolysis liquids. *Biomass Bioenergy* 1994;7(1–6):169–77. [https://doi.org/10.1016/0961-9534\(94\)00056-y](https://doi.org/10.1016/0961-9534(94)00056-y).
- [17] Elliott DC, Meier D, Oasmaa A, van de Beld B, Bridgwater AV, Marklund M. Results of the International Energy Agency round robin on fast pyrolysis bio-oil production. *Energy Fuels* 2017;31(5):5111–19. <https://doi.org/10.1021/acs.energyfuels.6b03502>.
- [18] Vitolo S, Ghetti P. Physical and combustion characterization of pyrolytic oils derived from biomass material upgraded by catalytic hydrogenation. *Fuel* 1994;73(11):1810–12. [https://doi.org/10.1016/0016-2361\(94\)90175-9](https://doi.org/10.1016/0016-2361(94)90175-9).
- [19] Wornat MJ, Porter BG, Yang NYC. Single droplet combustion of biomass pyrolysis oils. *Energy Fuels* 1994;8(5):1131–42. <https://doi.org/10.1021/ef00047a018>.
- [20] Branca C, Di Blasi C, Russo C. Devolatilization in the temperature range 300–600 K of liquids derived from wood pyrolysis and gasification. *Fuel* 2005;84(1):37–45. <https://doi.org/10.1016/j.fuel.2004.07.007>.
- [21] Branca C, Blasi CD, Elefante R. Devolatilization of conventional pyrolysis oils generated from biomass and cellulose. *Energy Fuels* 2006;20(5):2253–61. <https://doi.org/10.1021/ef0601059>.
- [22] García-Pérez M, Lappas P, Hughes P, Dell L, Chaala A, Kretschmer D, et al. Evaporation and combustion characteristics of biomass vacuum pyrolysis oils. *IFRR Combust J*. 2006;200601. <https://ifrr.net/research/archive/evaporation-and-combustion-characteristics-of-biomass-vacuum-pyrolysis-oils/>.
- [23] Calabria R, Chiariello F, Massoli P. Combustion fundamentals of pyrolysis oil based fuels. *Exp Therm Fluid Sci* 2007;31(5):413–20. <https://doi.org/10.1016/j.expthermflusc.2006.04.010>.
- [24] Li L, Yin X, Wu C, Ma L, Zhou Z. Kinetic studies on the pyrolysis and combustion of bio-oil. In: *Proceedings of the ISES World Congress 2007*, 18–21 September 2007; Beijing, China; 2007.
- [25] Ramachandran RPB, van Rossum G, van Swaaij WPM, Kersten SRA. Evaporation of biomass fast pyrolysis oil: evaluation of char formation. *Environmental Progress & Sustainable Energy* 2009;28(3):410–17. <https://doi.org/10.1002/ep.10388>.
- [26] van Rossum G. Steam reforming and gasification of pyrolysis oil: reactor and process development for syngas production from biomass [Ph.D. Thesis]. Enschede, The Netherlands: College voor Promoties, University of Twente; 2009. <https://doi.org/10.3990/1.9789036528894>.
- [27] van Rossum G, Güell BM, Ramachandran BRP, Seshan K, Lefferts L, Van Swaaij WPM, et al. Evaporation of pyrolysis oil: product distribution and residue char analysis. *AIChE J* 2010;2200–10. <https://doi.org/10.1002/aic.12126>.
- [28] Branca C, Di Blasi C. Combustion kinetics of secondary biomass chars in the kinetic regime. *Energy Fuels* 2010;24(10):5741–50. <https://doi.org/10.1021/ef100952x>.
- [29] Chhiti Y, Salvador S, Commandré J-M, Broust F. Thermal decomposition of bio-oil: focus on the products yields under different pyrolysis conditions. *Fuel* 2012;102:274–81. <https://doi.org/10.1016/j.fuel.2012.06.098>.
- [30] Beran M, Axelsson L-U. Development and experimental investigation of a tubular combustor for pyrolysis oil burning. *J Eng Gas Turbines Power* 2015;137(3):031508. <https://doi.org/10.1115/1.4028450>.
- [31] Stoesser P, Ruf J, Gupta R, Djordjevic N, Kolb T. Contribution to the understanding of secondary pyrolysis of biomass-based slurry under entrained-flow gasification conditions. *Energy Fuels* 2016;30(8):6448–57. <https://doi.org/10.1021/acs.energyfuels.6b00935>.
- [32] Stösser P. Investigation of solid-phase processes during the conversion of biogenic slurry in entrained-flow gasifiers [Ph.D. Thesis]. Karlsruhe, Germany: Fakultät für Chemieingenieurwesen und Verfahrenstechnik, Karlsruher Institut für Technologie; 2020, Mar.
- [33] Bridgwater AV, editor. *Progress in thermochemical biomass conversion*. Oxford, UK: Wiley; 2001. <https://doi.org/10.1002/9780470694954>.
- [34] Harman-Ware AE, Ferrell JR. Methods and challenges in the determination of molecular weight metrics of bio-oils. *Energy Fuels* 2018;32(9):8905–20. <https://doi.org/10.1021/acs.energyfuels.8b02113>.
- [35] Oasmaa A, Meier D. Norms and standards for fast pyrolysis liquids. *J Anal Appl Pyrolysis* 2005;7(3(2)):323–34. <https://doi.org/10.1016/j.jaap.2005.03.003>.
- [36] Elliott DC, Oasmaa A, Preto F, Meier D, Bridgwater AV. Results of the IEA round robin on viscosity and stability of fast pyrolysis bio-oils. *Energy Fuels* 2012;26(6):3769–76. <https://doi.org/10.1021/ef300384t>.
- [37] Elliott DC, Oasmaa A, Meier D, Preto F, Bridgwater AV. Results of the IEA round robin on viscosity and aging of fast pyrolysis bio-oils: long-term tests and repeatability. *Energy Fuels* 2012;26(12):7362–66. <https://doi.org/10.1021/ef301607v>.
- [38] McKinley JW, Overend RP, Elliott DC. The ultimate analysis of biomass liquefaction products: the results of the IEA round robin. In: *Proceedings of the Biomass Pyrolysis Oil Properties and Combustion Meeting*, 26–28 September 1994; Estes Park, CO, USA; 1994. p. 34–53.
- [39] Meier D. New methods for chemical and physical characterization and round robin testing. In: Czernik S, Diebold J, Meier D, Oasmaa A, Peacocke C, Piskorz J, Radlein D, Bridgwater AV, editors. *Fast pyrolysis of biomass: a handbook*. Newbury, UK: CPL Press; 1999. p. 92–101.
- [40] Zhang L, Kong S-C. Multicomponent vaporization modeling of bio-oil and its mixtures with other fuels. *Fuel* 2012;95:471–80. <https://doi.org/10.1016/j.fuel.2011.12.009>.
- [41] Saha K, Abu-Ramadan E, Li X. Multicomponent evaporation model for pure and blended biodiesel droplets in high temperature convective environment. *Appl Energy* 2012;93:71–79. <https://doi.org/10.1016/j.apenergy.2011.05.034>.
- [42] Sallevelt JLHP, Pozarlik AK, Brem G. Numerical study of pyrolysis oil combustion in an industrial gas turbine. *Energy Convers Manag* 2016;127:504–14. <https://doi.org/10.1016/j.enconman.2016.09.029>.
- [43] Mahmoudi AH, Pozarlik AK, van der Weide E, Kersten SRA, Luding S, Brem G. Effect of char on the combustion process of multicomponent bio-fuel. *Chem Eng Sci* 2018;175:286–95. <https://doi.org/10.1016/j.ces.2017.09.053>.
- [44] Sital C. Pyrolysis oil evaporation including liquid phase polymerization reaction [Master's thesis]. Delft, The Netherlands: Faculty of Mechanical, Maritime and Materials Engineering, Process & Energy Department, Delft University of Technology; 2018, Oct. <http://resolver.tudelft.nl/uuid:0f355e41-1dab-4369-b83e-f4f5e7379a6c>.
- [45] Hallett WLH, Clark NA. A model for the evaporation of biomass pyrolysis oil droplets. *Fuel* 2006;85(4):532–44. <https://doi.org/10.1016/j.fuel.2005.08.006>.
- [46] Houminer Y, Patai S. Thermal polymerization of levoglucosan. *J Polym Sci A1* 1969;7(10):3005–14. <https://doi.org/10.1002/pol.1969.150071020>.
- [47] Joback KG. A unified approach to physical property estimation using multivariate statistical techniques [Ph.D. Thesis]. Cambridge, MA, USA: Department of Chemical Engineering, Massachusetts Institute of Technology; 1984, Jun. <http://hdl.handle.net/1721.1/15374>.
- [48] Joback KG, Reid RC. Estimation of pure-component properties from group-contributions. *Chem Eng Commun* 1987;57(1–6):233–43. <https://doi.org/10.1080/00986448708960487>.
- [49] Constantinou L, Gani R. New group contribution method for estimating properties of pure compounds. *AIChE J* 1994;40(10):1697–710. <https://doi.org/10.1002/aic.690401011>.
- [50] Růžička V, Domalski ES. Estimation of the heat capacities of organic liquids as a function of temperature using group additivity. I. Hydrocarbon compounds. *J Phys Chem Ref Data* 1993;22(3):597–618. <https://doi.org/10.1063/1.555923>.
- [51] Yang H, Kudo S, Kuo H-P, Norinaga K, Mori A, Mašek O, et al. Estimation of enthalpy of bio-oil vapor and heat required for pyrolysis of biomass. *Energy Fuels* 2013;27(5):2675–86. <https://doi.org/10.1021/ef400199z>.
- [52] Karlsruhe Institute of Technology. *bioliq*; 2021. <https://www.bioliq.de>.
- [53] Fleck S, Santo U, Hotz C, Jakobs T, Eckel G, Mancini M, et al. Entrained flow gasification. Part 1: gasification of glycol in an atmospheric-pressure experimental rig. *Fuel* 2018;217:306–19. <https://doi.org/10.1016/j.fuel.2017.12.077>.
- [54] Haas M, Dammann M, Fleck S, Kolb T. Entrained flow gasification: impact of fuel spray distribution on reaction zone structure. *Fuel* 2023;334:126572. <https://doi.org/10.1016/j.fuel.2022.126572>.
- [55] Dammann M, Santo U, Böning D, Knoch H, Eberhard M, Kolb T. Entrained flow gasification: pilot-scale experimental, balancing and equilibrium data for model validation. *Fuel* 2025;382:132809. <https://doi.org/10.1016/j.fuel.2024.132809>.
- [56] Eberhard M, Santo U, Michelfelder B, Günther A, Weigand P, Matthes J, et al. The bioliq® entrained flow gasifier: a model for the German Energiewende. *ChemBioEng Rev* 2020;7(4):106–18. <https://doi.org/10.1002/cben.202000006>.
- [57] Santo U, Böning D, Eberhard M, Schmid H, Kolb T. Entrained flow gasification: experiments and balancing for design and scale-up. In: *Proceedings of the 30th Deutscher Flammentag: für nachhaltige Verbrennung*, 28–29 September 2021; Hannover-Garbsen, Germany: Deutsche Vereinigung für Verbrennungsforschung und Die Combustion Institute Deutsche Sektion; 2021. <https://doi.org/10.5445/IR/1000139705>.

- [58] Müller T, Sängler A, Habisreuther P, Jakobs T, Trimis D, Kolb T, et al. Simulation of the primary breakup of a high-viscosity liquid jet by a coaxial annular gas flow. *Int J Multiphase Flow* 2016;87:212–28. <https://doi.org/10.1016/j.ijmultiphaseflow.2016.09.008>.
- [59] Mancini M, Alberti M, Dammann M, Santo U, Eckel G, Kolb T, et al. Entrained flow gasification. Part 2: mathematical modeling of the gasifier using RANS method. *Fuel* 2018;225:596–611. <https://doi.org/10.1016/j.fuel.2018.03.100>.
- [60] Zhang F, Zirwes T, Müller T, Wachter S, Jakobs T, Habisreuther P, et al. Effect of elevated pressure on air-assisted primary atomization of coaxial liquid jets: basic research for entrained flow gasification. *Renew Sustain Energy Rev* 2020;134:110411. <https://doi.org/10.1016/j.rser.2020.110411>.
- [61] Dammann M, Mancini M, Weber R, Kolb T. Entrained flow gasification: mathematical modelling based on RANS for design and scale-up. In: Proceedings of the 30th Deutscher Flammentag: für nachhaltige Verbrennung, 28–29 September 2021; Germany: Deutsche Vereinigung für Verbrennungsforschung und The Combustion Institute Deutsche Sektion; 2021. <https://doi.org/10.5445/IR/1000140359>.
- [62] Dammann M, Mancini M, Kolb T, Weber R. Thermal radiation at high-temperature and high-pressure conditions: comparison of models for design and scale-up of entrained flow gasification processes. *Therm Sci Eng Prog* 2023;40:101772. <https://doi.org/10.1016/j.tsep.2023.101772>.
- [63] Dammann M. Numerical modelling and simulation of atmospheric entrained flow gasification of surrogate fuels [Ph.D. Thesis]. Karlsruhe, Germany: Fakultät für Chemieingenieurwesen und Verfahrenstechnik, Karlsruher Institut für Technologie; 2024. <https://doi.org/10.5445/IR/1000172116>.
- [64] Wachter S, Jakobs T, Kolb T. Effect of solid particles on droplet size applying the time-shift method for spray investigation. *Appl Sci* 2020;10(21):7615. <https://doi.org/10.3390/app10217615>.
- [65] profagus. 2021. <https://profagus.de>.
- [66] Dammann M, Walker SC, Mancini M, Kolb T. Devolatilisation of beech wood char: kinetics from thermogravimetric and drop-tube reactor experiments. *Fuel* 2024;375:131967. <https://doi.org/10.1016/j.fuel.2024.131967>.
- [67] Eckel G, Le Clercq P, Kathrotia T, Saenger A, Fleck S, Mancini M, et al. Entrained flow gasification. Part 3: insight into the injector near-field by large eddy simulation with detailed chemistry. *Fuel* 2018;223:164–78. <https://doi.org/10.1016/j.fuel.2018.02.176>.
- [68] DIN Deutsches Institut für Normung. DIN 51900-2:2003-03. Prüfung fester und flüssiger Brennstoffe. Bestimmung des Brennwertes mit dem Bomben-Kalorimeter und Berechnung des Heizwertes. Teil 2: Verfahren mit isoperibolem oder static-jacket Kalorimeter; 2003, Mar.
- [69] Boie W. Vom Brennstoff zum Rauchgas: feuerungstechnisches Rechnen mit Brennstoffkenngrößen und seine Vereinfachung mit Mitteln der Statistik. Leipzig, Germany: Teubner; 1957.
- [70] Higman C, van der Burgt M. Gasification. 2nd ed. Burlington, MA, USA: Gulf Professional Publishing; 2008. <https://doi.org/10.1016/b978-0-7506-8528-3.x0001-6>.
- [71] DIN Deutsches Institut für Normung. DIN 51732:2007-08. Prüfung fester Brennstoffe. Bestimmung des Gesamtgehaltes an Kohlenstoff, Wasserstoff und Stickstoff. Instrumentelle Methoden; 2007, Aug.
- [72] DIN Deutsches Institut für Normung. DIN 51777:2020-04. Mineralölerzeugnisse. Bestimmung des Wassergehaltes durch Titration nach Karl Fischer; 2020, Apr.
- [73] DIN Deutsches Institut für Normung. DIN 51900-1:2000-04. Prüfung fester und flüssiger Brennstoffe. Bestimmung des Brennwertes mit dem Bomben-Kalorimeter und Berechnung des Heizwertes. Teil 1: Allgemeine Angaben, Grundgeräte, Grundverfahren; 2000, Apr.
- [74] ASTM International, ASTM D86-20a. Standard test method for distillation of petroleum products and liquid fuels at atmospheric pressure; 2020. <https://doi.org/10.1520/D0086-20A>.
- [75] Bruno TJ. Improvements in the measurement of distillation curves. 1. A composition-explicit approach. *Ind Eng Chem Res* 2006;45(12):4371–80. <https://doi.org/10.1021/ie051393j>.
- [76] Ferris AM, Rothamer DA. Methodology for the experimental measurement of vapor-liquid equilibrium distillation curves using a modified ASTM D86 setup. *Fuel* 2016;182:467–79. <https://doi.org/10.1016/j.fuel.2016.05.099>.
- [77] Cai J, Wu W, Liu R. An overview of distributed activation energy model and its application in the pyrolysis of lignocellulosic biomass. *Renew Sustain Energy Rev* 2014;36:236–46. <https://doi.org/10.1016/j.rser.2014.04.052>.
- [78] Virtanen P, Gommers R, Oliphant TE, Haberland M, Reddy T, Cournapeau D, et al. SciPy 1.0: fundamental algorithms for scientific computing in Python. *Nat Methods* 2020;17:261–72. <https://doi.org/10.1038/s41592-019-0686-2>.
- [79] SciPy Developers. Release 1.5.1; 2021. <https://pypi.org/project/scipy/>.
- [80] Hindmarsh AC. ODEPACK, a systematized collection of ODE solvers. *IMACS Transactions Of Scientific Computing* 1 1983;55–64.
- [81] Petzold L. Automatic selection of methods for solving stiff and nonstiff systems of ordinary differential equations. *SIAM Journal On Scientific And Statistical Computing* 1983;4(1):136–48. <https://doi.org/10.1137/0904010>.
- [82] MathWorks. MATLAB. Release 2019b; 2019.
- [83] Poling BE, Prausnitz JM, O'Connell JP. *The properties of gases and liquids*. 5th ed. New York, NY, USA: McGraw-Hill; 2001.
- [84] DIN Deutsches Institut für Normung. DIN EN ISO 1183-1:2019-09. Kunststoffe. Verfahren zur Bestimmung der Dichte von nicht verschäumten Kunststoffen. Teil 1: Eintauchverfahren, Verfahren mit Flüssigkeitspyknometer und Titrationsverfahren (ISO 1183-1:2019, korrigierte Fassung 2019-05); 2019, Sep.
- [85] ASTM International, ASTM D7896-19. Standard test method for thermal conductivity, thermal diffusivity, and volumetric heat capacity of engine coolants and related fluids by transient hot wire liquid thermal conductivity method; 2019. <https://doi.org/10.1520/D7896-19>.
- [86] ASTM International, ASTM D2766-95. Standard test method for specific heat of liquids and solids. 2017. <https://doi.org/10.1520/D2766-95>.
- [87] ASTM International, ASTM D4052-18a. Standard test method for density, relative density, and API gravity of liquids by digital density meter; 2018. <https://doi.org/10.1520/D4052-18A>.
- [88] DIN Deutsches Institut für Normung, DIN EN ISO 3219:1994-10. Kunststoffe/Polymere/Harze in flüssigem, emulgiertem oder dispergiertem Zustand. Bestimmung der Viskosität mit einem Rotationsviskosimeter bei definiertem Geschwindigkeitsgefälle; 1994, Oct.
- [89] Choi YS, Johnston PA, Brown RC, Shanks BH, Lee K-H. Detailed characterization of red oak-derived pyrolysis oil: integrated use of GC, HPLC, IC, GPC and Karl-Fischer. *J Anal Appl Pyrolysis* 2014;110:147–54. <https://doi.org/10.1016/j.jaap.2014.08.016>.
- [90] Ingram L, Mohan D, Bricka M, Steele P, Strobel D, Crocker D, et al. Pyrolysis of wood and bark in an auger reactor: physical properties and chemical analysis of the produced bio-oils. *Energy Fuels* 2007;22(1):614–25. <https://doi.org/10.1021/ef700335k>.
- [91] Jampolski L, Morgano MT, Seifert H, Kolb T, Willenbacher N. Flow behavior and aging of pyrolysis oils from different feedstocks. *Energy Fuels* 2017;31(5):5165–73. <https://doi.org/10.1021/acs.energyfuels.7b00196>.
- [92] Turgut A, Tavman I, Tavman S. Measurement of thermal conductivity of edible oils using transient hot wire method. *Int J Food Prop* 2009;12(4):741–47. <https://doi.org/10.1080/10942910802023242>.
- [93] Merrick D. Mathematical models of the thermal decomposition of coal. 2. Specific heats and heats of reaction. *Fuel* 1983;62(5):540–46. [https://doi.org/10.1016/0016-2361\(83\)90223-5](https://doi.org/10.1016/0016-2361(83)90223-5).
- [94] Dahmen N, Abeln J, Eberhard M, Kolb T, Leibold H, Sauer J, et al. The bioliq process for producing synthetic transportation fuels. *WIREs Energy Environ* 6(3). <https://doi.org/10.1002/wene.236>.
- [95] Miura K, Maki T. A simple method for estimating f(E) and k0(E) in the distributed activation energy model. *Energy Fuels* 1998;12(5):864–69. <https://doi.org/10.1021/ef970212q>.