

Contents lists available at [ScienceDirect](http://www.sciencedirect.com)

Biomass and Bioenergy

journal homepage: <http://www.elsevier.com/locate/biombioe>

Research paper

Torrefied biomass as feed for fast pyrolysis: An experimental study and chain analysis

A.C. Louwes^{*}, L. Basile, R. Yukananto, J.C. Bhagwandas, E.A. Bramer, G. Brem

Thermal Engineering Group, Faculty of Engineering Technology, University of Twente, P.O. Box 217, 7500AE Enschede, The Netherlands

ARTICLE INFO

Article history:

Received 3 March 2017

Received in revised form

9 June 2017

Accepted 19 June 2017

Keywords:

Fast pyrolysis

Torrefaction

*Fraxinus excelsior**Picea abies*

Mixed waste wood

Chain analysis

ABSTRACT

A torrefaction pre-treatment could enhance the fast pyrolysis process to produce bio-oil by decreasing the required energy for grinding biomass particles and by improving bio-oil characteristics so they resemble more those of fossil fuels. To evaluate this hypothesis, this work compares fast pyrolysis experiments of raw and torrefied woody biomass feedstocks, using a 500 g h^{-1} entrained down flow reactor. The feedstocks used were hardwood (ash wood), softwood (spruce) and mixed waste wood. These feedstocks were torrefied at various temperatures between $250 \text{ }^\circ\text{C}$ and $300 \text{ }^\circ\text{C}$ by means of two torrefaction processes: a directly heated moving bed, and the Torbed[®] process. The effect of pelletizing was also analyzed for the hardwood feedstock, comparing torrefied chips and torrefied pellets. The obtained bio-oils from experiments with torrefied feedstock had overall improved oxygen and heating value properties compared to bio-oils from raw feedstock. Hardwood pellets torrefied at $265 \text{ }^\circ\text{C}$ with a residence time of 45 min produced the oils with the highest quality with respect to oxygen mass fraction (decreased from 45.7% to 37.2%) and higher heating value (increased from 19.1 MJ kg^{-1} to 23.1 MJ kg^{-1}), compared to bio-oil produced from raw hardwood feedstock. However, these properties came at a severe loss of oil yield, decreasing from 44% for raw feedstock to an average of 31% for torrefied feedstock. Nonetheless, a chain analysis shows that a torrefaction pre-treatment could be more attractive on energy basis compared to a conventional fast pyrolysis process with a deoxygenation upgrading step.

© 2017 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Biofuels could play an important role in our future energy system. They are renewable, and as such do not affect the climate. They can be produced locally, diminishing the dependence on fossil fuels from countries with fossil reserves, thereby increasing energy security. And they are carbon based, making them suitable for use in a biorefinery to produce chemicals, as an alternative to fossil oil in oil refineries. Application as fuel in cars, ships, airplanes, or to produce clean heat and power in boilers, engines and turbines are possible, replacing the currently used fossil fuels.

Bio-oil produced from the fast pyrolysis process is an attractive candidate in this regard. The fast pyrolysis process is fast, simple and relatively cheap, and can accommodate many different biomass feedstocks [1]. The liquid form allows for a high energy density, and the inherent separation of minerals from the main product makes it possible to close the mineral cycle. The fast

pyrolysis process typically operates at temperatures of $450 \text{ }^\circ\text{C}$ – $550 \text{ }^\circ\text{C}$ and residence times of a few seconds, under an oxygen-free environment. To acquire a high liquid yield, very high heating rates and short vapor residence times are required [1,2].

The produced bio-oil does not have the same properties as its fossil cousins: notably, its heating value is lower, its acidity and viscosity higher, and it suffers from poor stability during storage. Most of these disadvantages are caused by the abundant oxygenated compounds in bio-oil [2]. To be used in boilers and gas turbines, the bio-oil's quality has to be improved by reducing its oxygen content, which also affects its stability, heating value and acidity [1,3]. Chemical and physical upgrading of bio-oil has been thoroughly investigated. The main routes are hydrodeoxygenation with typical hydrotreating catalysts (sulfided CoMo or NiMo), zeolite upgrading, or forming emulsions with diesel fuel; alternatively, bio-oils can be converted into H_2 or syn-gas by steam-reforming or gasification [4,5]. Pre-treating the biomass has gained more attention in recent years, with a few studies showing some promising results on both leaching (e.g. with surfactants [6] and acids [7]) as well as torrefaction of the feedstock [8–12].

^{*} Corresponding author.

E-mail addresses: a.c.louwes@utwente.nl, a.c.louwes@gmail.com (A.C. Louwes).

Torrefaction is a mild form of pyrolysis where biomass is heated in the absence of oxygen at a temperature of about 200 °C–300 °C for a residence time typically up to 60 min [13]. An overview of state-of-the-art technologies can be found in Koppejan, Sokansanj, Melin and Madrali [14]. The process breaks down fibers in woody biomass and releases some of the oxygen-rich acidic components [15]. The produced torrefied material has the advantages of a lower moisture mass fraction, lower oxygen to carbon (O:C) ratio and a slightly increased heating value [14]. Moreover, it is hydrophobic, making transport and storage more convenient [13]. Breaking down the tough fibers in raw woody biomass has the added advantage of greatly improving grindability, reducing grinding costs up to 85% [16]. This is especially interesting for fast pyrolysis, as very small particles are required for maximum oil yield. This statement is supported by the study of Shen, Wang, Garcia-Perez, Mourant, Rhodes and Li [17], who found bio-oil yields increasing from 47% at particle sizes > 1 mm to 62% at 0.5 mm, as well as Westerhof, Nygård, Van Swaaij, Kersten and Brilman [18], whose bio-oil yields increased from 62.5% at 1.2 mm to 74% at 0.25 mm.

A disadvantage of torrefaction is the mass loss and accompanying energy loss that occur during the torrefaction process, with mass losses varying from 5% (for willow torrefied for 30 min at 230 °C) to 48% (for pine torrefied for 30 min at 300 °C) [19]. This disadvantage leads to some discussion in literature on the viability of a torrefaction pre-treatment. Chen, Zheng, Fu, Zeng, Wang and Lu [9] claim that a torrefaction pre-treatment is promising, based on their experiments with cotton stalk. The fuel properties of their produced bio-oils improved significantly. They do however remark that torrefaction consumes energy, which could be partly offset by the biomass' improved grindability and hydrophobicity. Both Zheng, Zhao, Chang, Huang, Wang, He and Li [8] and Meng, Park, Tilotta and Park [10] conclude that torrefaction is an effective method to increase the quality of bio-oil. However, at an earlier time, Zheng, Zhao, Chang, Huang, He and Li [12] found only a slight improvement in quality and a significant loss in liquid yield, and Boateng and Mullen [11] found that a significant part of the potential energy was converted to the char product. All these data are based on biomass torrefied at lab scale. Data on the fast pyrolysis process of torrefied material produced on a larger scale (pilot or industrial) is however lacking in literature; a similar situation exists for chain analyses to compare a conventional fast pyrolysis chain with the proposed chain which includes a torrefaction pre-treatment. Furthermore, a comparison of fast pyrolysis experiments of both raw and torrefied woody biomass in an entrained down flow reactor has, to the best knowledge of the authors, not yet been published in literature. The current work attempts to shed more light on the viability of a torrefaction pre-treatment for the fast pyrolysis process by filling in these gaps.

2. Experimental

2.1. Materials

Two categories of bio-oils are studied in this work: one from dried wood, and one from torrefied wood. The wood is subclassified into hardwood, softwood and mixed waste wood; mixed waste wood was used to also incorporate a feedstock from current industrial standards in this study, to show the effect of samples acquired from current industrial torrefaction plants. The hardwood was debarked and chipped ash wood of the family *Olacaceae*, genera *Fraxinus excelsior*, obtained from Van den Broek B.V. (The Netherlands). The softwood was debarked and chipped spruce wood of the *Picea* family, genera *Picea abies*, also obtained from Van den Broek B.V. (The Netherlands). Both wood species were delivered by the supplier in chips of dimensions of (length x width x

height) > 2 mm × 2 mm × 2 mm to ≤ 40 mm × 40 mm × 15 mm, and subsequently torrefied by a 50 kg h⁻¹ directly heated moving bed pilot plant by the Energy Research Centre of the Netherlands (ECN) [20]. Mixed waste wood (forest waste, raw and torrefied) was supplied by Topell Netherlands B.V. To torrefy the mixed waste wood, Torbed[®] technology was used, which utilizes a heat carrying medium, blown at high velocities through the bottom of the bed to acquire a high heat transfer [21]. The Torbed[®] technology has the characteristic of a very short residence time of below 5 min. Next to wood chips of these feedstocks, the effect of pelletizing torrefied biomass on bio-oils produced via fast pyrolysis was also investigated. For clarification, a graphical overview of the used feedstocks is shown in Fig. 1, and further specifications are given in Table 1. Before fast pyrolysis, all feedstocks were comminuted and sieved to a particle size of 0 μm–800 μm and dried at a temperature of 105 °C for 24 h. Particle size distributions of the hardwood and mixed waste wood feedstocks can be found in the supplementary material. These particle sizes are below the particles size limit of <2 mm recommended in the literature to avoid heat transfer limitations for entrained flow reactors, where heat transfer is mainly provided by convection [22].

To characterize the materials, proximate and ultimate analyses were carried out, as shown in Table 2. The table reveals as expected that mass fractions of moisture are lower for the torrefied feedstocks, while mass fractions of ash and heating values are higher. A notable exception is mixed waste wood: for mixed waste wood, it was harder to achieve homogeneity in the feedstocks. Furthermore as expected, the mass fraction of carbon increases for the torrefied feedstocks, and the mass fraction of oxygen decreases, due to removal of light volatiles containing oxygenated compounds, as well as removal of water. The results are amplified at higher torrefaction temperatures. The torrefied hardwood pellets seem to be a more condensed version of the torrefied hardwood chips when looking at the results. The softwood chips differ by having a significantly higher mass fraction of moisture after 24 h of drying (as measured), and a lower mass fraction of ash. As the minerals in the ashes can have an autocatalytic effect on the fast pyrolysis process [23,24], the starting mass fraction of ash should be kept in mind, especially the relatively high mass fraction of ash in mixed waste wood.

2.2. Experimental setup and procedure

The fast-pyrolysis experiments were conducted in a lab-scale (≤1 kg h⁻¹) entrained down-flow reactor [1]: the process is based on small biomass particles being fed to a hot down-flow reactor, where heat is transferred from the hot gas to the biomass particles. This type of reactor offers the advantage of having a fixed particle residence time, which in these experiments was calculated to be on average 2 s. The pyrolysis reactor, shown in Fig. 2, was a cylindrical tube (stainless steel type 316) with a length of 420 cm and an internal diameter of 5 cm. The tube was electrically heated to a temperature of 500 °C by heating coils (type HBQ, total electrical power input 8 kW) mounted around the walls. Seven thermocouples (K-type) were installed at various heights (about evenly spaced) inside the reactor (in the middle of the gas flow) to control and register the temperature of the reactor. Another thermo-couple was used to control and register the temperature in the oven where the cyclones are located; the oven was kept at a temperature of 400 °C to prevent condensation in this section.

Biomass was fed from the screw feeder on top of the reactor, the mass flow was adjusted with a screw feeder with a variable rotational speed to a mass flow of 0.3 kg h⁻¹ to 0.6 kg h⁻¹. The biomass entered the reactor together with nitrogen as inert carrier gas (both at room temperature).

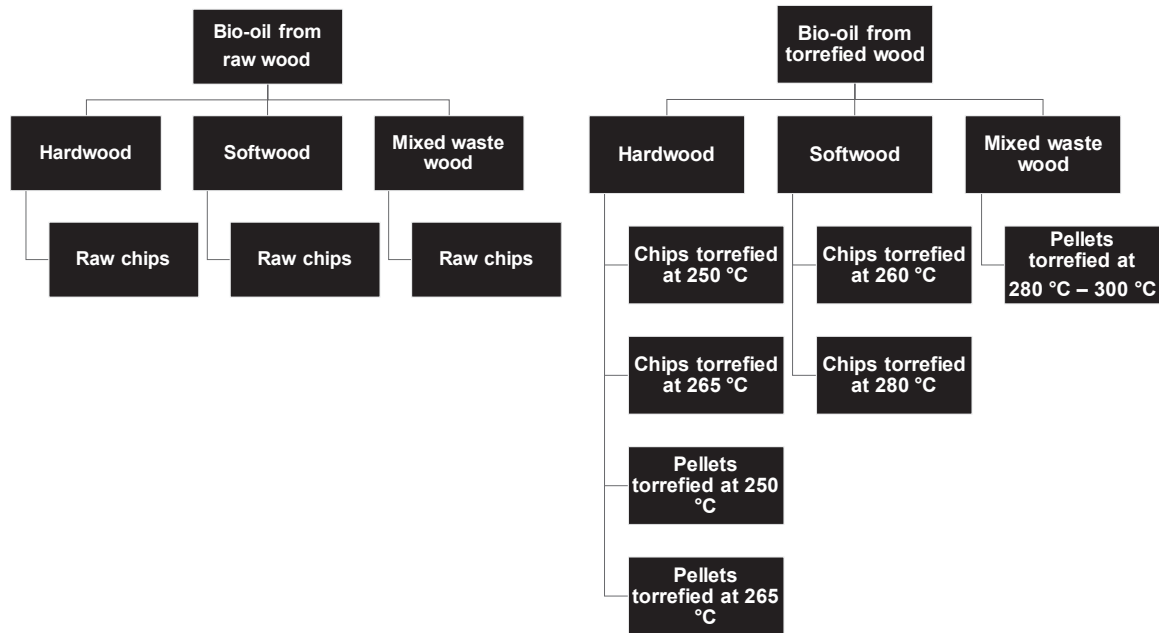


Fig. 1. Graphical overview of the used feedstocks. Left side: bio-oils produced from raw feedstocks. Right side: bio-oils produced from torrefied feedstocks.

Table 1

Overview of the used feedstocks.

Biomass feedstock	Code name	Torref. temperature	Torref. technology	Torref. residence time	Mass loss during torref.
<i>Hardwood</i>					
Raw chips	RC_HW	–	–	–	–
Torrefied chips	TC_HW250	250 °C	DHMB ^a	45 min	23%
Torrefied chips	TC_HW265	265 °C	DHMB	45 min	27%
Torrefied pellets	TP_HW250	250 °C	DHMB	45 min	23%
Torrefied pellets	TP_HW265	265 °C	DHMB	45 min	27%
<i>Softwood</i>					
Raw chips	RC_SW	–	–	–	–
Torrefied chips	TC_SW260	260 °C	DHMB	45 min	21%
Torrefied chips	TC_SW280	280 °C	DHMB	45 min	Not registered
<i>Mixed waste wood</i>					
Raw chips	RC_MWW	–	–	–	–
Torrefied pellets	TP_MWW	(280–300) °C	Torbed [®]	Below 5 min	26% (est.)

^a Directly Heated Moving Bed.

Table 2

Proximate and ultimate analysis of the feedstock (AR).

Feedstock	Moisture	Ash	HHV ^a	C	H	N	O ^b
	Mass fraction of material AR (%)		(MJ kg ⁻¹)	Element mass fraction of material (%)			
RC_HW	4.0	0.9	18.9	46.0	6.0	0.1	47.8
TC_HW250	2.2	1.0	21.4	52.9	5.7	0.1	41.2
TC_HW265	2.1	1.1	21.5	53.3	5.6	0.1	41.0
TP_HW250	2.0	1.2	21.8	53.8	5.7	0.1	40.4
TP_HW265	1.8	1.5	20.4	51.7	5.4	0.1	42.8
RC_SW	9.3	0.6	19.9	46.4	6.0	0.0	47.6
TC_SW260	4.0	0.4	21.7	53.4	5.6	0.0	41.0
TC_SW280	3.6	0.5	22.0	53.5	5.8	0.1	40.7
RC_MWW	3.7	8.0	20.9	48.4	6.2	0.8	44.6
TP_MWW	10.1	4.3	20.3	47.3	5.5	0.4	46.7

^a On dry basis, calculated using the correlation proposed by Channiwala and Parikh.

^b Calculated by difference.

Produced char was separated from the vapors using two cyclones, placed in series in an oven at a temperature of 400 °C in order to prevent condensation of primary fast pyrolysis vapors.

Three char collectors were installed: one under each cyclone, and one under the drop tube itself for heavy particles. The vapors entered a cyclonic cooler (cooling liquid: water at ± 4 °C) where heavy tars condensed to bio-oil. The cyclonic cooler had a cylindrical form and a hole in the bottom plate; gases and vapors entered tangentially and a cyclonic swirling motion was formed. The non-condensed products continued through a cooling tube (cooled with water) to a rotational mist separator [25] where the remaining vapors and aerosols were separated from the non-condensable gas. Oil samples were taken from the cyclonic cooler and the rotational mist separator. The concentrations of CO, CO₂, H₂ and O₂ in the gasses were continuously monitored: CO and CO₂ by a Siemens ULTRAMAT 23 IR gas analyzer, H₂ by a Servomex K1550 thermal conductivity analyzer and O₂ (to check the inert atmosphere) by a Siemens OXYMAT 61 paramagnetic oxygen analyzer. The run time of an experiment was typically 50 min.

Table 3 presents an overview of the process conditions during the experiments. The biomass feeding flow rate was kept constant over an experiment, but varied per feedstock due to practical limitations of the biomass feeding system. A very slight overpressure (about 500 Pa above atmospheric pressure) was maintained in the

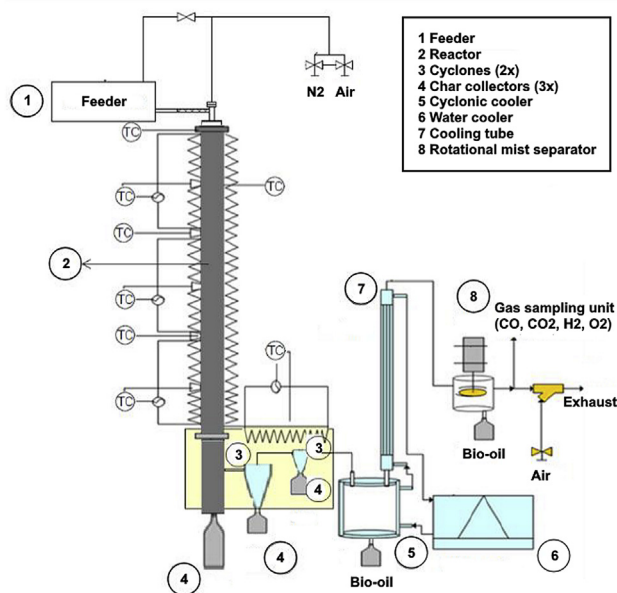


Fig. 2. Schematic overview of the experimental setup.

Table 3
Overview of the fast pyrolysis process conditions.

Parameter	Value
Solid feed flowrate (kg h ⁻¹)	0.3–0.6
Temperature reactor (°C)	500
Temperature cyclone (°C)	400
Pressure (Pa)	101 325
Particle size (µm)	0–800
Inert carrier gas flowrate (L min ⁻¹)	26

system to keep oxygen from entering.

2.3. Analysis and products characterization

Moisture and ash mass fractions were determined using a muffle furnace according to ASTM D4442-16 [26] and D1102-84 (2013) [27], respectively. Elemental analysis was performed according to ASTM D5291-16 [28] with an Inter-science Flash 2000 elemental analyzer; oxygen mass fraction was calculated by difference. The higher heating value was calculated using the empirical equation proposed by Channiwala and Parikh [29] based on the dry elemental composition (in gram per gram feedstock):

$$\text{HHV} = 0.3491 \text{ C} + 1.1783 \text{ H} + 0.1005 \text{ S} - 0.1034 \text{ O} - 0.0151 \text{ N} - 0.0211 \text{ ash}$$

Water mass fraction of bio-oils was determined by Karl-Fischer titration according to ASTM E203-16 [30] using a Metrohm 787 KF Titrino; organics mass fraction was calculated by subtracting the water mass fraction from the total mass. Viscosity was determined according to ASTM D445-15a [31] with a BrookField DV-II + Pro viscometer with a CPE-40 spindle. All characterization analyses were performed at least twice, and the average value is presented.

Storage stability of bio-oil was tested by an accelerated aging procedure: the bio-oils were heated to 80 °C for 24 h under an inert atmosphere of nitrogen, representing 12 months of storage at room temperature [32]. Mass fraction of moisture and viscosity were determined before and after the accelerated aging process.

2.4. Chain analysis calculation

Based on the mass and energy balances of the experiments, a chain analysis was carried out, from feedstock to bio-oil. Two routes were compared:

- (1) a conventional route involving grinding, drying, and fast pyrolysis, followed by a deoxygenation step; and
- (2) a new route including torrefaction, followed by grinding and pyrolysis.

To make the bio-oil of the two different routes comparable, a deoxygenation (DEOX) step was assumed to upgrade the bio-oil (decrease the mass fraction of oxygen) from route (1). In practice, this deoxygenation step could be carried out by e.g. HDO (hydrodeoxygenation) or catalytic pyrolysis. Both routes are depicted in Fig. 3. It is noted that the HDO upgrading step is only added for comparison reasons to get the same oil quality. In practice both routes need full HDO to get a marketable product.

To calculate the energy efficiency of the routes, the following equations were used. In these equations, HHV_{char} , HHV_{oil} , HHV_{gas} and $\text{HHV}_{\text{feedstock}}$ are the higher heating values of the char, bio-oil, product gas and feedstock, respectively, all in MJ kg⁻¹. Furthermore, E_{grinding} , E_{drying} , $E_{\text{torrefaction}}$, $E_{\text{pyrolysis}}$ and E_{DEOX} are the energy input for grinding the feedstock, drying the feedstock, the torrefaction process, the fast pyrolysis process, and the deoxygenation process, respectively, all in MJ kg⁻¹. For the energy efficiency taking into account all products:

$$\eta_{\text{all products}} = \left((\text{HHV}_{\text{char}} + \text{HHV}_{\text{oil}} + \text{HHV}_{\text{gas}}) - E_{\text{grinding}} - E_{\text{drying}} - E_{\text{torrefaction}} - E_{\text{pyrolysis}} - E_{\text{DEOX}} \right) (\text{HHV}_{\text{feedstock}})^{-1}$$

For the energy efficiency to only bio-oil:

$$\eta_{\text{bio-oil}} = \left(\text{HHV}_{\text{oil}} - E_{\text{grinding}} - E_{\text{drying}} - E_{\text{torrefaction}} - E_{\text{pyrolysis}} - E_{\text{DEOX}} \right) (\text{HHV}_{\text{feedstock}})^{-1}$$

The experimental data of this study is used for the heating values; the energy consumption of the other steps and their sources are shown in Table 4.

Drying was calculated to take 0.24 MJ kg⁻¹ per percent point of moisture removal. A decrease in the energy required for grinding of 85% for the torrefied route was assumed [16], from 3.06 MJ kg⁻¹ – 0.46 MJ kg⁻¹ for grinding particles to a size of 500 µm. For torrefaction (including drying), an energy input of 2.1 MJ kg⁻¹ was calculated. For pyrolysis, data from Ref. [33] was taken to arrive at 1.3 MJ kg⁻¹ for the conventional route, and 0.6 MJ kg⁻¹ for the new route as the input for the pyrolysis reactor is already preheated by the torrefaction system. For deoxygenation, the following procedure and assumptions were used: the difference in oxygen mass fraction (between the bio-oils from raw and torrefied feedstock) is

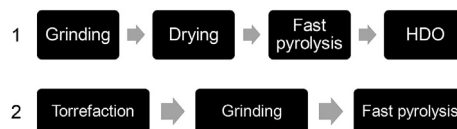


Fig. 3. Two compared routes: (1) A conventional fast pyrolysis route, including grinding and drying, with an additional upgrading step for comparing purposes. (2) A new route comprising torrefaction and grinding, followed by fast pyrolysis.

Table 4
Data sources for chain analysis.

	Route (1) (pyrolysis + HDO)	Route (2) (torrefaction)	Source
Drying	0.24 MJ kg ^{-1a}	–	Calculated
Grinding	3.06 MJ kg ⁻¹	0.46 MJ kg ⁻¹	[16,34]
Torrefaction	–	2.1 MJ kg ⁻¹	Calculated
Pyrolysis	1.29 MJ kg ⁻¹	0.6 MJ kg ⁻¹	[33]
HDO	0.26 MJ kg ⁻¹	–	[35,37]

^a Per % of moisture removal of the original feedstock as received.

expressed as a difference in mass of oxygen (based on 1 kg) and converted to moles. Three moles of hydrogen are assumed to be needed to remove 1 mol of oxygen (using conventional hydro-treating catalysts) [35]. The amount of moles hydrogen is then converted back to mass. It is assumed the energy demand for the production of hydrogen is 0.126 MJ g⁻¹ [36]. Taking into account an assumed total efficiency of 90% for various process equipment, this amounts to 0.26 MJ kg⁻¹ biomass feedstock per percent point of oxygen removal for the deoxygenation step (i.e. if the mass fraction of oxygen of the bio-oil from raw wood was 45% and from torrefied wood was 40%, the difference being 5% points, (5 × 0.26 MJ kg⁻¹) is used as the energy demand for deoxygenation) (based on data from Refs. [35] and [37]).

Three scenarios were analyzed:

- Scenario A takes the mass fraction of moisture as received (i.e. the mass fractions of moisture mentioned in chapter 3), and uses an unspecified external energy source to fuel the various processes.
- Scenario B puts all mass fractions of moisture at 10% for a fairer comparison (taking varying mass fractions of moisture out of the equation), and (similarly to Scenario A) uses an unspecified external energy source to fuel the various processes.
- Scenario C puts all mass fractions of moisture at 10% (similarly to Scenario B), but as opposed to the previous scenarios, in Scenario C the energy of the produced char and gas is used as energy source to fuel the torrefaction and fast pyrolysis processes. This would be more realistic for a commercial process.

The data of the chain analysis can be found in the supplementary materials.

3. Results

3.1. Mass balance

In Table 5, the measured yields of the fast pyrolysis products are given. The total amount of biomass pyrolyzed per experiment was between 250 g and 500 g. The contents of the cyclones that were

captured from the gas stream is referred to here as Solids, containing both char and unconverted biomass. Oil yields for the three raw biomass types are in the same range, on average 42%–45%. The torrefied feedstocks gave lower oil yields than raw biomass, namely 25%–36%, with oil yields decreasing as the torrefaction temperature increases. Solid yields were in the range of 21%–28% for the raw biomass, and a much higher 37%–52% for torrefied biomass. The gas yields varied significantly, with a range of 33%–45% for raw feedstocks and a lower range of 12%–30% for the torrefied variants.

Most experiments, as shown in Table 5, were performed multiple times to check reproducibility. When it became clear that standard deviations for the individual yields of oil, char and gas were below 5%, the reproducibility was deemed satisfactory for the final experiments to take place only once. Mass balance closure averaged at 97.33% for 22 experiments. While the standard deviation of the total balance was high for the RC_SW feedstock, the individual standard deviations of the yields of oil, char and gas were below 5%. For this type of experiment (due to relatively large equipment and relatively small feed rate), these mass balance closures were deemed satisfactory to analyze the results, as the authors were primarily interested in the product analysis. A short discussion on possible limitations with respect to the used fast pyrolysis reactor technology is included in the supplementary material.

3.2. Product characterization

The main products of the pyrolysis process were char, non-condensable gases and condensable vapors that were condensed to bio-oil. In Table 6, an ultimate analysis of the char is presented, and shows a consistent trend of increasing carbon mass fractions and decreasing oxygen mass fractions with respect to torrefaction severity.

The main differences between the bio-oils from raw biomass and torrefied biomass, as shown in Table 7, are the mass fractions of carbon and oxygen. For hardwood bio-oil, the mass fraction of oxygen goes down from 45.7% for bio-oil from untreated hardwood to 41.3% for bio-oil from hardwood chips torrefied at 265 °C, and 37.2% for bio-oil from hardwood pellets torrefied at 265 °C.

Table 5
Mass balances and product yields of the fast pyrolysis experiments.

Feedstock	Mass balance closure	Standard deviation	Number of experiments	Oil yield	Solid yield	Gas yield
	(average)				(average)	
RC_HW	91.1%	7.19%	2	44%	21%	33%
TC_HW250	80.8%	3.82%	2	36%	40%	12%
TC_HW265	90.7%	1.48%	3	27%	37%	12%
TP_HW250	95.4%	–	1	28%	52%	23%
TP_HW265	103.1%	–	1	28%	52%	23%
RC_SW	97.4%	12.37%	2	42%	20%	45%
TC_SW260	103.8%	6.28%	2	35%	36%	30%
TC_SW280	91.2%	5.66%	5	25%	38%	28%
RC_MWW	109.8%	–	1	45%	28%	37%
TP_MWW	100.5%	4.95%	2	27%	45%	27%

Table 6
Ultimate analysis of the captured solids.

Element mass fraction of char (%)	C	H	N	O ^a	HHV (MJ kg ⁻¹)
RC_HW	62.7	4.7	0.2	32.4	24.2
TC_HW250	71.1	4.2	0.3	24.4	27.3
TC_HW265	71.2	4.2	0.3	24.3	27.4
TP_HW250	69.8	4.4	0.2	24.6	27.0
TP_HW265	74.0	4.2	0.2	21.6	28.7
RC_SW	68.4	4.5	0.1	27.0	26.4
TC_SW260	70.5	3.9	0.3	25.3	26.6
TC_SW280	76.2	3.8	0.1	19.9	29.1
RC_MWW	60.7	3.9	0.7	34.7	22.8
TP_MWW	65.2	4.1	0.6	30.1	24.8

^a Calculated by difference.

For mixed waste wood, the mass fraction of oxygen went down from 46.2% to 40.7% for bio-oil from torrefied mixed waste wood. Although the mixed waste wood pellets were torrefied at a higher temperature of 280 °C–300 °C compared to hardwood and softwood, the residence time was much lower (less than 5 min, as opposed to 45 min). Consequently, the overall torrefaction severity of the mixed waste wood pellets could be said to be lower, which translates here in a lower decrease of the mass fraction of oxygen.

A further noticeable difference is the mass fraction of organics shown in Table 7: from 70.5 wt% in bio-oil from untreated hardwood to 77.1 wt% in bio-oil from hardwood pellets torrefied at 265 °C and even 78.7 wt% in bio-oil from torrefied mixed waste wood. Interesting to note is that the mass fraction of organics is higher for all the pellet feedstocks, compared to the chip feedstocks.

In accordance with the increased mass fraction of carbon and decreased mass fraction of oxygen in the bio-oils from torrefied feedstocks, the heating values increase: the HHV of bio-oil from hardwood increased from 17.7 MJ kg⁻¹ for the untreated feedstock, to 21.6 MJ kg⁻¹ for the pellets torrefied at 265 °C. For mixed waste

wood, the HHV of the produced bio-oil increased from 18.3 MJ kg⁻¹ for the untreated feedstock to 21.3 MJ kg⁻¹ for the torrefied variant.

In the pyrolysis gas compositions overview of Table 8, it can be seen that CO and CO₂ were the most abundantly produced gases. Only a very low amount of hydrocarbons was detected (in the 50 cm³ m⁻³ to 100 cm³ m⁻³ range) so these are neglected here. Only a minor amount of H₂ was produced, except in the case of TP_MWW where significantly more CO and H₂ were produced.

Van Krevelen diagrams were created to illustrate the distance between the used feedstocks, their bio-oil counterparts, and fossil fuels. For this reason, references for coal (Northumberland No. 8 – Anth. Coal), lignite (German Braunkohle) and heavy fuel oil were included [29]. An oak-derived bio-oil that underwent an HDO treatment was also added [38]. In Fig. 4, based on the hardwood feedstocks, the area indicating the biomass feedstocks is below the area indicating the produced bio-oils, signaling a small increase in hydrogen to carbon (H:C) ratio when going from biomass to bio-oil; relatively more hydrogen ends up in the bio-oil as opposed to carbon. Furthermore, torrefaction produces a shift towards the origin of the diagram, towards the fossil fuels area of mainly lignite and coal: significantly lower O:C ratios and slightly diminished H:C ratios. The characteristics of the biomass and bio-oil are changing towards the direction of their fossil counterparts.

In Fig. 5, based on the softwood feedstocks, similar trends can be seen here. The decrease in O:C ratio from raw to torrefied biomass is quite pronounced, from about 0.77–0.56. For bio-oil, the difference between raw and torrefied at 260 °C is a slight reduction in O:C ratio. Going to the torrefied chips at 280 °C yields a large reduction in O:C ratio, together with a reduction in H:C ratio.

Also in Fig. 6, based on the mixed waste wood feedstocks, similar trends can be seen: the torrefied variants are moving closer to the fossil fuel references. For mixed waste wood, the bio-oils are significantly higher on the H:C ratio scale, and bio-oil produced from raw chips possess a high O:C ratio.

Table 7
Ultimate analysis (AR) and additional bio-oil characteristics.

	C	H	N	O ^a	HHV	Organics content	Water content	Viscosity (mPa s)		
	Element mass fraction of bio-oil (%)				(MJ kg ⁻¹)	(wt%)	(wt%)	25 °C	40 °C	50 °C
RC_HW	46.9	6.6	0.7	45.7	19.1	70.5	29.5	17.8	9.2	7.6
TC_HW250	48.9	6.5	0.8	43.8	19.9	73.1	26.9	24.7	11.8	8.4
TC_HW265	51.7	6.7	0.7	41.3	21.1	73.8	26.2	24.8	12.1	8.3
TP_HW250	54.0	6.5	0.5	41.1	22.3	76.6	23.4	25.7	12.8	9.0
TP_HW265	55.7	6.5	0.6	37.2	23.1	77.1	22.9	25.9	12.9	9.1
RC_SW	48.7	6.6	0.7	44.1	20.1	74.4	25.6	23.2	10.7	6.5
TC_SW260	49.6	6.7	0.7	43.1	20.8	76.0	24.0	26.5	12.0	7.4
TC_SW280	51.5	6.4	0.7	41.4	21.2	76.0	24.0	29.4	13.1	9.4
RC_MWW	45.4	7.6	0.8	46.2	19.9	77.3	22.7	20.4	8.5	6.6
TP_MWW	50.4	8.2	0.7	40.7	23.1	78.7	21.3	21.2	8.9	6.8

^a Calculated by difference.**Table 8**
Pyrolysis gas compositions.

	Mass fraction of dry gas (%)			HHV
	CO ₂	CO	H ₂	(MJ kg ⁻¹)
RC_HW	50.4	49.0	0.6	5.8
TC_HW250	53.8	45.7	0.5	5.3
TC_HW265	54.0	45.3	0.7	5.6
TP_HW250	54.0	45.4	0.5	5.3
TP_HW265	54.1	45.3	0.5	5.3
RC_SW	50.5	49.1	0.4	5.5
TC_SW260	54.1	45.6	0.3	5.0
TC_SW280	54.2	45.5	0.3	5.0
RC_MWW	52.9	42.1	0.4	4.8
TP_MWW	43.3	53.5	3.2	9.9

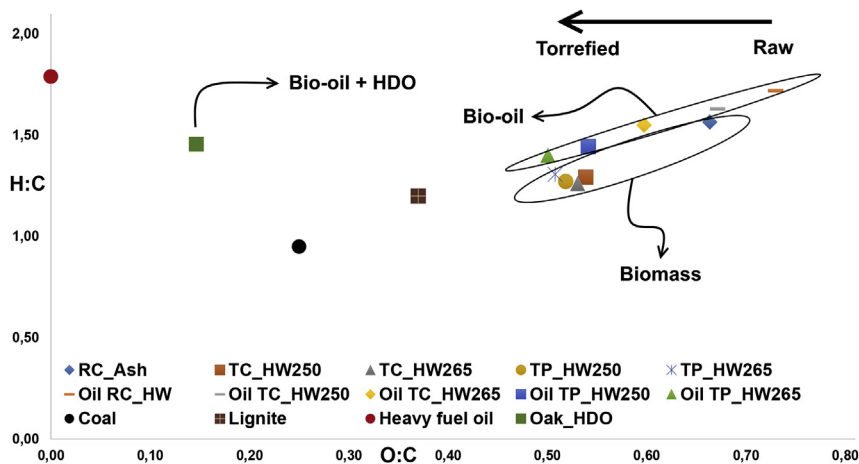


Fig. 4. Van Krevelen diagram of hardwood feedstock and produced bio-oils, showing mole ratios. RC = Raw Chips, TC = Torrefied Chips, TP = Torrefied Pellets, HW = Hardwood.

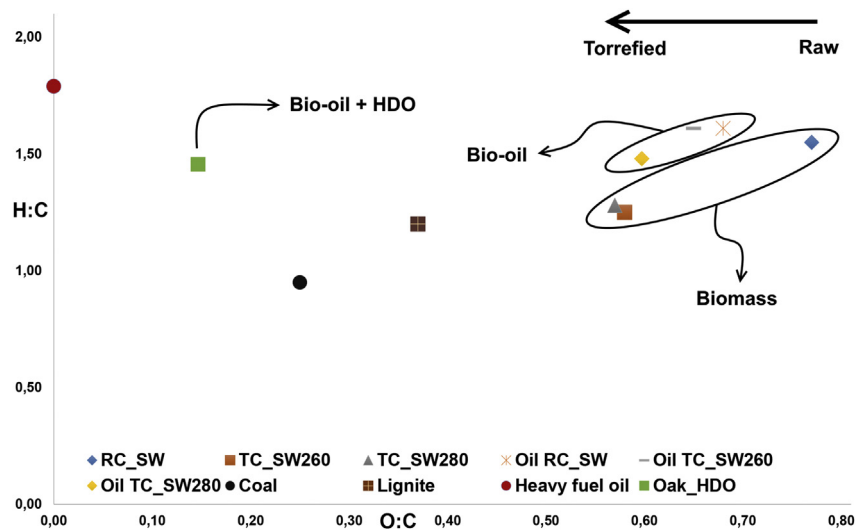


Fig. 5. Van Krevelen diagram of softwood feedstock and produced bio-oils, showing mole ratios. RC = Raw Chips, TC = Torrefied Chips, SW = Softwood.

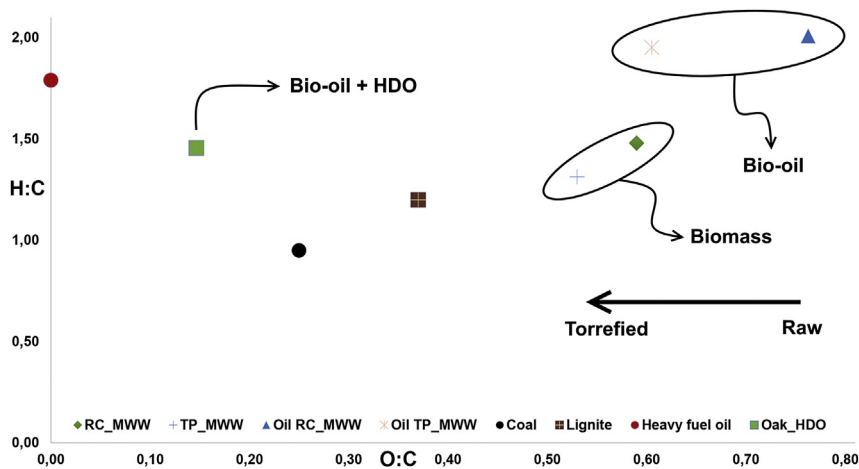


Fig. 6. Van Krevelen diagram of mixed waste wood feedstock and produced bio-oils, showing mole ratios. RC = Raw Chips, TP = Torrefied Pellets, MWW = Mixed Waste Wood.

3.3. Storage stability

To study the influence of torrefaction on storage stability, the three bio-oils from hardwood feedstocks RC_HW, TC_HW250 and

TC_HW265 were subjected to an accelerated aging test and the change in mass fraction of water and viscosity was analyzed. In Fig. 7, the increases for the mass fraction of water can be seen: about 4% for raw hardwood chips, and about 7% for torrefied

hardwood chips. Torrefaction seems to slightly increase the production of water during aging, although the effect is not very significant. Fig. 8 shows that especially at room temperature, the viscosity of the torrefied variants after accelerated aging increased significantly, more than doubling. The results at 40 °C and 50 °C follow a similar trend although with less dramatic results.

3.4. Energy and chain analysis

An energy analysis based on the mass balances and heating values of the feedstock and products is presented here. For the analysis, all mass balances were scaled up to or back to 100%, and Fig. 9 shows the results with the columns representing the energy content per kg of feedstock of the products Oil, Solids and Gas. It can be seen that a larger part of the energy converts into oil for the raw feedstocks as opposed to the torrefied variants. Although the bio-oils from the torrefied feedstocks have increased heating values, these do not offset the decreases in oil yield. A pronounced increase in energy in the solid products (caused by torrefaction) can also be seen in the figure: on average the solids' energy content doubles, even more so for the pelletized feedstocks.

In Fig. 10, the two routes are compared for three different biomass types, with the filled column indicating Scenario A and the striped column Scenario B. The data gives the energy efficiency from feedstock to the sum of all products based on mass and energy balances. For every feedstock, the raw variant and the severest torrefied variant was included. An estimated error (based on the various data used and to the authors' best estimate) was included of 5%. The figure shows a significant improvement of the process energy efficiency from the conventional route to the new route; an increase of about 15% for hardwood, about 25% for softwood, and a doubling of the energy efficiency for mixed waste wood, from 35% to 72% for Scenario B.

In Fig. 11, again the two routes are compared for three different biomass types, with the filled column indicating Scenario A, the striped column Scenario B, and the blocked column Scenario C. Overall, the new route with torrefaction consistently achieves a higher energy efficiency, although the total efficiencies are rather low due to the low yields from the experiments. For softwood, the efficiencies to bio-oil dip beneath the 5% for Scenarios A and B because of the higher mass fractions of moisture and lower calorific values of its products. The energy efficiency of hardwood almost halves when going from Scenario A to Scenario B, and while the energy efficiency of softwood is only slightly reduced, it is still significantly lower. For mixed waste wood, Scenario B even dips

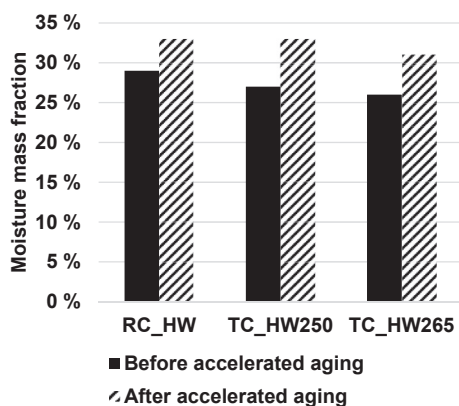


Fig. 7. Results of accelerated aging tests of hardwood feedstocks for mass fraction of moisture; the measurement error for all moisture mass fraction measurements was <1%. RC = Raw Chips, TC = Torrefied Chips, HW = Hardwood.

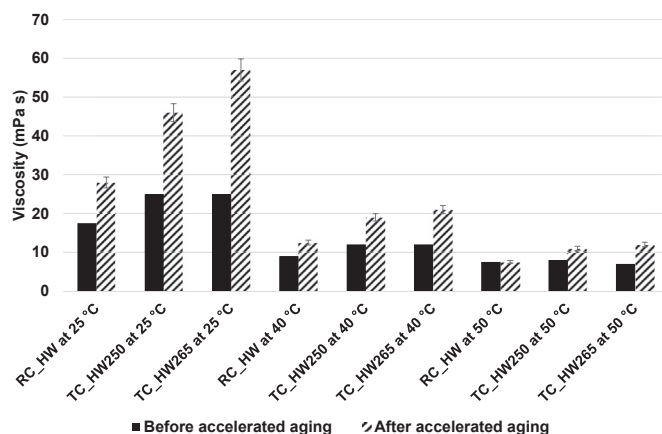


Fig. 8. Results of accelerated aging tests of hardwood feedstocks for viscosity. RC = Raw Chips, TC = Torrefied Chips, HW = Hardwood.

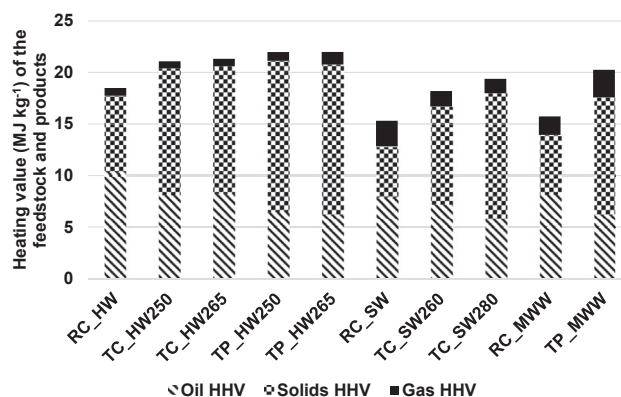


Fig. 9. Energy content of products per kg feedstock, based on scaled mass balance. The heating values were calculated using the empirical equation given in section 2.3, based on the elemental composition; the measurement errors of the elemental analysis were all <1%. RC = Raw Chips, TC = Torrefied Chips, TP = Torrefied Pellets, HW = Hardwood, SW = Softwood, MWW = Mixed Waste Wood.

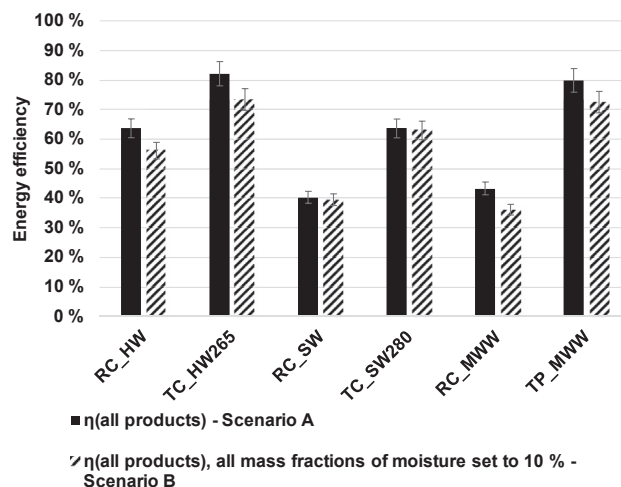


Fig. 10. Energy efficiency of route (1) and (2) of the products (oil, solids and gas) from the products of three biomass feedstocks. RC = Raw Chips, TC = Torrefied Chips, TP = Torrefied Pellets, HW = Hardwood, SW = Softwood, MWW = Mixed Waste Wood.

below 0%, having to put more energy into the process than it yields. With Scenario C the best efficiencies are accomplished, albeit still

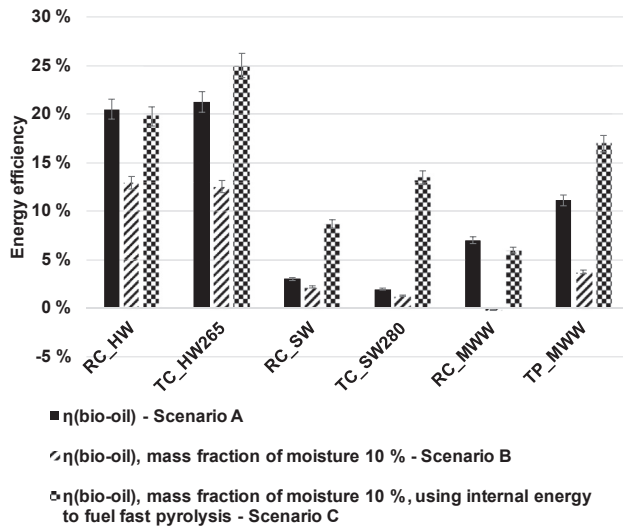


Fig. 11. Energy efficiency of route (1) and (2) of bio-oil from three biomass feedstocks. RC = Raw Chips, TC = Torrefied Chips, TP = Torrefied Pellets, HW = Hardwood, SW = Softwood, MWW = Mixed Waste Wood.

rather low with a maximum energy efficiency of 25% for the torrefied hardwood variant.

It should be noted that in the situations where the process involving torrefaction achieves a higher energy efficiency, this is usually because the oil yield is only marginally lower, the heating value is significantly higher, and the oxygen content is significantly reduced. Coupled with the lower amount of energy required for grinding, in Scenarios A and B the chain with torrefaction performs better than the conventional chain in half of the cases. The chain with torrefaction performs significantly better in Scenario C, where the low oil yields are less important, as the higher char yields are now used inside the process to provide energy for torrefaction and fast pyrolysis.

4. Discussion

4.1. Experimental results

The bio-oil yields for hardwood and softwood were similar, although the bio-oil produced from softwood had a higher heating value and generally a lower mass fraction of oxygen, for both the raw and torrefied feedstocks. As the heating value of the softwood feedstock was higher than that of the hardwood feedstock, and the mass fraction of oxygen lower, these results were expected. The bio-oil produced from pellets had a slightly (about 10%) higher heating value and slightly (about 15%) lower mass fraction of moisture than the bio-oil produced from chips, so pellets produced a slightly better quality bio-oil than chips. Mixed waste wood gave inconsistent results: the bio-oil from raw mixed waste wood contained the highest mass fraction of oxygen, and the bio-oil from torrefied mixed waste wood gave average results.

The decrease in oxygen when going from bio-oil derived from raw biomass to torrefied biomass, shown in Table 7, is favorable for bio-oil. Because the oxygenated compounds in bio-oil decrease its heating value and storage stability and increase its acidity, a lower mass fraction of oxygen should improve these characteristics. Table 7 confirms the increased heating values, in line with other literature [8,9,12]. It must be noted that Table 7 shows as received values for the bio-oil, so a part of the mass fraction of oxygen is in the water. It is however a relatively small influence, as the mass fraction of water only slightly decreases when going from raw to

torrefied feedstock. The effect on the mass fraction of water is in line with what is reported in Ref. [12], but the difference is much larger in Ref. [9] who went from 62.3% in bio-oil from raw cotton stalk to 37.5% in bio-oil from cotton stalk torrefied at 280 °C. As the torrefaction process seems to have a larger effect on the mass fraction of water in bio-oil in species such as cotton stalk that produce bio-oils with relatively high mass fractions of water, the torrefaction pre-treatment could be more interesting for these biomass species if mass fraction of water is of greater concern. When looking at combustion applications such as gas turbines, the main influences of the mass fraction of water are on heating value and viscosity. Decreasing the mass fraction of water in bio-oil will increase its heating value, but also increase its viscosity, the latter negatively impacting atomization of the fuel and possibly requiring pre-heating. Optimization should then take place to make sure the amount of energy going into pre-heating does not undo the extra energy acquired by increasing the heating value.

The viscosity of the various bio-oils, also shown in Table 7, behaves inversely proportional to the mass fraction of water as expected, with bio-oil produced from torrefied variants having higher viscosities and lower mass fractions of water than bio-oil from untreated feedstocks. The shown viscosities are about an order of magnitude larger at room temperature than conventional combustion fuels like diesel, biodiesel and ethanol [39]. The effect of accelerated aging on the viscosity of the bio-oils were in line with results from Ref. [40].

It was expected that CO₂ yields, as shown in Table 8, would decrease for torrefied variants due to removal of hemicellulose [41], and conversely CO yields would increase due to relatively higher mass fraction of cellulose, but this was not the case. Interestingly, only for TP_MWW more CO than CO₂ was produced, and the amount of hydrogen was exceptionally high at 3.2%. The high amount of hydrogen could be caused by the high water content of TP_MWW. Although TP_MWW was torrefied with a much lower residence time than the other torrefied feedstocks, the torrefaction temperature was significantly higher at 280 °C–300 °C, which could have led to a more complete removal of hemicellulose in the feedstock and the obtained gas yields. Furthermore, the results with mixed waste wood showcase the variability caused by using samples obtained from current industrial plants.

4.2. Energy and chain analysis

The energy analysis shows that although the total heating value of the products stays virtually the same as the feedstock and is not influenced by torrefaction, the torrefaction pre-treatment does cause a large decrease of energy in the bio-oil and a large increase of energy in the solid products. Even at the low to moderate torrefaction temperatures employed in this research (with the lowest one being 250 °C), the significantly lower energy conversion of torrefied feedstock to bio-oil was observed, giving rise to an important disadvantage of a torrefaction pre-treatment. This disadvantage tends to increase with increasing torrefaction temperatures.

However, in the chain analysis the lower energy conversion does not translate to lower energy efficiencies. When all products are taken into account, a route including torrefaction pre-treatment increases the energy efficiency significantly compared to a conventional route with an upgrading step for fair comparison. When only oil as a product is taken into account, the argument still holds true, especially if the other products are (partly) used to fuel the torrefaction and pyrolysis processes.

It would be possible that the incomplete conversion affects the oil quality, as the part of the biomass that did not convert has the lowest volatility, and may have a different elemental composition

than the rest of the biomass. The oil yields suffered as a consequence of the incomplete conversion, which influences the chain analysis that used the experimental data. The chain analysis showed a maximum total process energy efficiency from feedstock to bio-oil of 25% with the new chain that includes a torrefaction pre-treatment step, when using the torrefied hardwood feedstock (torrefied at 265 °C). This was obtained with oil, solids and gas yields of 32%, 37% and 13%, respectively. If we assume that another 20% of the solids yield can be converted to bio-oil, that would lead to oil, solids and gas yields of 52%, 17% and 13%, respectively. With these yields, the total process energy efficiency from feedstock to bio-oil would increase to 48.9%, almost a doubling. The combined heating value of the solids and gasses in that case, amounting to 6.4 MJ kg⁻¹, would still be enough to fuel the torrefaction and fast pyrolysis processes.

4.3. Future research

This study shows that a torrefaction pre-treatment can have a positive influence on the fast pyrolysis process under certain circumstances and optimization is needed, and this gives opportunities for future research. A comprehensive study into the effect of various torrefaction severities on the grindability of number of biomass feedstocks could offer insight into both the required degree of torrefaction, as well as the possible gains in energy. An optimum for torrefaction severity should also be found between increased heating value and decreased bio-oil yield.

Furthermore, fast pyrolysis using smaller particles and a pre-heated nitrogen carrier gas flow should allow for full conversion to take place in an entrained down flow reactor such as used in this study. As [18] found increasing bio-oil yields when decreasing particle size up to 0.25 mm, it would be interesting to further explore this range of small particles. Westerhof, Nygård, Van Swaaij, Kersten and Brilman [18] give as explanation for this increasing yield that these small particles only consist of cell wall material, instead of the natural channels in larger lignocellulosic particles. Vapors can leave these small particles much faster, thereby decreasing their residence time and their contact time with char inside a particle. This leads to less secondary cracking reactions, which will increase the bio-oil yield.

Finally, experiments on the application side of bio-oil produced with torrefied feedstock (e.g. with gas turbines) can shed light on the effect of torrefaction on the performance in these applications. As the heating value is increased, the torrefaction pre-treatment could positively impact application if the higher viscosity can be accounted for.

5. Conclusions

This study focused on the differences between fast pyrolysis of raw and torrefied biomass. The successful experiments in the entrained down flow reactor show significant drops in oil yield for the torrefied feedstocks as opposed to their raw counterparts. Solids analysis revealed a drawback to the reactor technology used: the low heating rates were insufficient to fully convert the biomass. However, the obtained oil did have interesting characteristics: an increase in the mass fraction of carbon and a decrease in the mass fractions of oxygen and moisture caused an increase in heating value. The Van Krevelen diagrams show that the O:C and H:C ratios are much nearer to fossil equivalents than the original biomass and bio-oil, giving rise to qualities more similar to their fossil counterparts.

For the softwood feedstock, a torrefaction pre-treatment of 45 min at 280 °C delivered the highest quality oil. The hardwood feedstock gave the highest oil quality with a torrefaction pre-

treatment of 45 min at 265 °C, with hardwood pellets outperforming both hardwood and softwood chips.

A torrefaction pre-treatment before fast pyrolysis could be beneficial from an energy perspective, although the much lower oil yields should be taken into account. A purpose for the higher yields of char and gas should also be found; activating the char to sell it might make this route more attractive.

Acknowledgements

This research was funded in the framework of the Dutch TKI-BBE Invent-Pretreatment programme, for which the authors are very grateful.

The authors would also like to extend thanks to all project partners for the fruitful cooperation and providing samples of the various biomass types.

The authors would also like to acknowledge our students Rendra Firmansyah and Dani Windiarito and our lab technician Henk-Jan Moed for their experimental efforts incorporated in this work.

Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.biombioe.2017.06.009>.

References

- [1] A.V. Bridgwater, Review of fast pyrolysis of biomass and product upgrading, *Biomass Bioenergy* 38 (2012) 68–94.
- [2] D. Mohan, J. Charles, U. Pittman, P.H. Steele, Pyrolysis of wood/biomass for bio-oil: a critical review, *Energy Fuels* 20 (2006) 848–889.
- [3] R.H. Venderbosch, A.R. Ardiyanti, J. Wildschut, A. Oasmaa, H.J. Heeres, Stabilization of biomass-derived pyrolysis oils, *J. Chem. Technol. Biotechnol.* 85 (5) (2010) 674–686.
- [4] A.V. Bridgwater, Renewable fuels and chemicals by thermal processing of biomass, *Chem. Eng. J.* 91 (2–3) (2003) 87–102.
- [5] G.W. Huber, S. Iborra, A. Corma, Synthesis of transportation fuels from Biomass: chemistry, catalysts, and engineering, *Chem. Rev.* 106 (9) (2006) 4044–4098.
- [6] S.W. Banks, D.J. Nowakowski, A.V. Bridgwater, Fast pyrolysis processing of surfactant washed Miscanthus, *Fuel Process. Technol.* 128 (2014) 94–103.
- [7] S.R.G. Oudenhoven, C. Lievens, R.J.M. Westerhof, S.R.A. Kersten, Effect of temperature on the fast pyrolysis of organic-acid leached pinewood; the potential of low temperature pyrolysis, *Biomass Bioenergy* 89 (2016) 78–90.
- [8] A. Zheng, Z. Zhao, S. Chang, Z. Huang, X. Wang, F. He, H. Li, Effect of torrefaction on structure and fast pyrolysis behavior of corncobs, *Bioresour. Technol.* 128 (2013) 370–377.
- [9] D. Chen, Z. Zheng, K. Fu, Z. Zeng, J. Wang, M. Lu, Torrefaction of biomass stalk and its effect on the yield and quality of pyrolysis products, *Fuel* 159 (2015) 27–32.
- [10] J. Meng, J. Park, D. Tilotta, S. Park, The effect of torrefaction on the chemistry of fast-pyrolysis bio-oil, *Bioresour. Technol.* 111 (2012) 439–446.
- [11] A.A. Boateng, C.A. Mullen, Fast pyrolysis of biomass thermally pretreated by torrefaction, *J. Anal. Appl. Pyrolysis* 100 (2013) 95–102.
- [12] A. Zheng, Z. Zhao, S. Chang, Z. Huang, F. He, H. Li, Effect of torrefaction temperature on product distribution from two-staged pyrolysis of biomass, *Energy Fuels* 26 (5) (2012) 2968–2974.
- [13] M.J.C. Van der Stelt, H. Gerhauser, J.H.A. Kiel, K.J. Ptasiński, Biomass upgrading by torrefaction for the production of biofuels: a review, *Biomass Bioenergy* 35 (2011) 3748–3762.
- [14] J. Koppejan, S. Sokansanj, S. Melin, S. Madrali, Status overview of torrefaction technologies, *IEA Bioenergy Task 32* (2012).
- [15] M.J. Prins, K.J. Ptasiński, F.J.J.G. Janssen, Torrefaction of wood Part 2. Analysis of products, *J. Anal. Appl. Pyrolysis* 77 (2006) 35–40.
- [16] V. Repellin, A. Govin, M. Rolland, R. Guyonnet, Energy requirement for fine grinding of torrefied wood, *Biomass Bioenergy* 34 (2010) 923–930.
- [17] J. Shen, X.-S. Wang, M. Garcia-Perez, D. Mourant, M.J. Rhodes, C.-Z. Li, Effects of particle size on the fast pyrolysis of oil mallee woody biomass, *Fuel* 88 (10) (2009) 1810–1817.
- [18] R.J.M. Westerhof, H.S. Nygård, W.P.M. van Swaaij, S.R.A. Kersten, D.W.F. Brilman, Effect of particle geometry and microstructure on fast pyrolysis of beech wood, *Energy Fuels* 26 (4) (2012) 2274–2280.
- [19] J.J. Chew, V. Doshi, Recent advances in biomass pretreatment - torrefaction fundamentals and technology, *Renew. Sustain. Energy Rev.* 15 (2011) 4212–4222.

- [20] P. Nanou, M.C. Carbo, J.H.A. Kiel, Detailed mapping of the mass and energy balance of a continuous biomass torrefaction plant, *Biomass Bioenergy* 89 (2016) 67–77.
- [21] IEA Bioenergy Task 32, Status Overview of Torrefaction Technologies, Enschede, The Netherlands, 2012.
- [22] A.V. Bridgwater, D. Meier, D. Radlein, An overview of fast pyrolysis of biomass, *Org. Geochem.* 30 (12) (1999) 1479–1493.
- [23] T. Wigley, A.C.K. Yip, S. Pang, The use of demineralisation and torrefaction to improve the properties of biomass intended as a feedstock for fast pyrolysis, *J. Anal. Appl. Pyrolysis* 113 (2015) 296–306.
- [24] G. Yildiz, F. Ronsse, R. Venderbosch, R.v. Duren, S.R.A. Kersten, W. Prins, Effect of biomass ash in catalytic fast pyrolysis of pine wood, *Appl. Catal. B Environ.* 168–169 (2015) 203–211.
- [25] B. Brouwers, Rotational particle separator: a new method for separating fine particles and mists from gases, *Chem. Eng. Technol.* 19 (1) (1996) 1–10.
- [26] ASTM International, ASTM D4442–16, Standard Test Methods for Direct Moisture Content Measurement of Wood and Wood-Based Materials, 2016. West Conshohocken, PA.
- [27] ASTM International, ASTM D1102–D1184(2013), Standard Test Method for Ash in Wood, 2013. West Conshohocken, PA.
- [28] ASTM International, ASTM D5291–16, Standard Test Methods for Instrumental Determination of Carbon, Hydrogen, and Nitrogen in Petroleum Products and Lubricants, 2016. West Conshohocken, PA.
- [29] S. Channiwala, P. Parikh, A unified correlation for estimating HHV of solid, liquid and gaseous fuels, *Fuel* 81 (8) (2002) 1051–1063.
- [30] ASTM International, ASTM E203–16, Standard Test Method for Water Using Volumetric Karl Fischer Titration, 2016. West Conshohocken, PA.
- [31] ASTM International, ASTM D445–15a, Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and Calculation of Dynamic Viscosity), 2015. West Conshohocken, PA.
- [32] A. Oasmaa, D. Meier, Norms and standards for fast pyrolysis liquids: 1. Round robin test, *J. Anal. Appl. Pyrolysis* 73 (2) (2005) 323–334.
- [33] J. Rath, M.G. Wolfinger, G. Steiner, G. Krammer, F. Barontini, V. Cozzani, Heat of wood pyrolysis, *Fuel* 82 (1) (2003) 81–91.
- [34] Z. Miao, T.E. Grift, A.C. Hansen, K.C. Ting, Energy requirement for comminution of biomass in relation to particle physical properties, *Ind. Crops Prod.* 33 (2011) 504–513.
- [35] M. Zabeti, Renewable Fuels via Catalytic Pyrolysis of Lignocellulose, Catalytic Processes and Materials, University of Twente, Enschede, 2014.
- [36] T.S. Nguyen, M. Zabeti, L. Lefferts, G. Brem, K. Seshan, Catalytic upgrading of biomass pyrolysis vapours using faujasite zeolite catalysts, *Biomass Bioenergy* 48 (2013) 100–110.
- [37] T.S. Nguyen, Development of an Efficient Catalyst for the Pyrolytic Conversion of Biomass into Transport Fuel, Catalytic Processes and Materials, University of Twente, Enschede, 2014.
- [38] D.C. Elliott, T.R. Hart, G.G. Neuenschwander, L.J. Rotness, A.H. Zacher, Catalytic hydroprocessing of biomass fast pyrolysis bio-oil to produce hydrocarbon products, *Environ. Prog. Sustain. Energy* 28 (3) (2009) 441–449.
- [39] A. Pozarlik, A. Bijl, N.v. Alst, E. Bramer, G. Brem, in: Pyrolysis Oil Utilization in 50KWe Gas Turbine, 18th IFRF Members' Conference, Freising, Germany, 2015.
- [40] J. Meng, A. Moore, D.C. Tilotta, S.S. Kelley, S. Adhikari, S. Park, Thermal and storage stability of bio-oil from pyrolysis of torrefied wood, *Energy Fuels* 29 (8) (2015) 5117–5126.
- [41] H. Yang, R. Yan, H. Chen, D.H. Lee, C. Zheng, Characteristics of hemicellulose, cellulose and lignin pyrolysis, *Fuel* 86 (12–13) (2007) 1781–1788.