LogistEC

Logistics for Energy Crops' Biomass
Deliverable D3.4: Assessment of improved pre-treatment technologies
Seventh Framework Programme

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Logistics for Energy Crops' Biomass

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Deliverable D3.4
Assessment of improved pre-treatment technologies

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Glossary and Definitions

CENER	Fundación CENER-CIEMAT
CRIBE	Centro di Ricerche Interuniversitario Biomasse da Energia
CRL	Coppice Resources Ltd
ECN	Stichting Energieonderzoek Centrum Nederland
FCBA	Institut Technologique FCBA
GC/MS	Gas chromatography / Mass spectrometry
HHV	Higher Heating Value
INRA	Institut National de la Recherche Agronomique
L/S	Liquid / Solid ratio on a weight basis
Multiclave	Setup of 6 small digestion vessels of 125 ml in a heating block, which are magnetically stirred, in order to do initial screening experiments
Risø DTU	Risø National Laboratory for Sustainable Energy DTU
RRes	Rothamsted Research
SGB	SG Bio-Drying Ltd
SRC	Short Rotation Coppice
SSSA	Scuola Superiore Sant'Anna
TGA	ThermoGravimetric Analysis
TORIPO	Torwash Rioolwaterzuivering Pilotontwerp
VRSC	Very Short Rotation Coppice
wt%	Weight percentage; mass fraction expressed as a percentage

Summary

Objectives: **To test the behaviour of the LogistEC feedstocks during TORWASH and Torrefaction, and to evaluate their suitability as raw materials for the production of solid bioenergy carriers.**

Rationale: **Both TORWASH and Torrefaction are pre-treatment technologies that can improve the supply chain of biomass, by increasing the energy content of the fuel, and improving its fuel characteristics. This leads to the production of sustainable solid bioenergy carriers. In addition, TORWASH can reduce the salt content of tenacious herbaceous biomass.**

Teams involved: **ECN (Netherlands) using biomass samples from CENER (Spain), SGB, CRL (UK), FCBA, INRA (France), SSSA (Italy)**

Both TORWASH and torrefaction are technologies that improve the fuel characteristics of biomass, by increasing the energy density, while simultaneously making the material more brittle and easier to mill. In addition to this, TORWASH is able to selectively remove ash components from herbaceous types of biomass. Torrefaction is typically used for woody types of biomass. ECN develops and commercialises both these technologies together with industrial partners. ECN has facilities ranging from lab to pilot scale, and developed an extensive array of characterisation methods.

Miscanthus, Fibre sorghum, Triticale and Arundo donax (giant reed) were subjected to washing and TORWASH conditions in order to identify the differences between these biomass feedstocks. A similar set of conditions were used to identify any differences between Miscanthus samples grown under different conditions. Two selected types of biomass were evaluated at 2-liter scale, after which a series of 20-liter tests were performed to analyse all inputs and outputs, and to produce a liquid TORWASH residue to perform fertilizer tests. The experiments with Miscanthus and Arundo donax demonstrated the highest solid matter recovery. Washing tests remove already a significant amount of salts from the biomass. The 20-liter tests showed that Arundo donax can be converted to a solid bioenergy carrier that complies with the ENplus A1 standard, which is the most stringent standard for biomass pellets. The extent of ash removal was such that the fuel can be used in any thermal conversion process without the need for any further treatment.

Exploratory torrefaction tests using thermogravimetric analysis (TGA) were performed using a total of 10 different samples from various species of biomass: Poplar, Willow, Eucalyptus, Triticale and Fibre sorghum. Significant differences were observed between non-woody biomass (Triticale and Fibre sorghum) and woody biomass, which means that the non-woody biomass must be torrefied at a different temperature than the woody biomass.
Batch tests at kilogram scale were performed using Triticale, Fibre sorghum and Willow. As expected, an increase in torrefaction temperature yielded an increase in energy content of the solid bioenergy carrier produced. The herbaceous biomass samples showed relatively high ash contents in excess of 5 wt%, but also Willow, containing also small branches and bark, showed a relatively high ash content of 2 wt%. Clean wood typically has an ash content below 2 wt%.

1. Torwash

Authors: Jan Pels, Raimo van der Linden, Michiel Carbo

1.1. Introduction

TORWASH is a technology that is under development at ECN for the conversion of herbaceous biomass into an attractive solid bioenergy carrier. The feedstock for TORWASH often combines three undesirable characteristics: 1) high moisture content, 2) high salt content, and 3) being tenacious and bulky. Herbaceous biomass is typically not suitable for direct utilization as fuel for combustion or gasification. An increased moisture content corresponds to a lower net calorific value. The increased salt concentration – in particular potassium and chloride – can cause problems like corrosion, agglomeration, slagging and fouling upon thermal conversion. Furthermore herbaceous biomass can result in issues during milling due to its flexible nature. Finally, the bulky nature and the high moisture content result in relatively expensive logistics. By applying TORWASH, all of these undesirable characteristics (salt, water, tenacity) are drastically improved. The product of TORWASH is a solid bioenergy carrier with characteristics equal to those of torrefied wood.

TORWASH, also known as wet torrefaction, is a hydrothermal treatment step that is performed under pressure, at temperatures between 150 and 250°C. The treatment changes the structure by making the fibres brittle so that the biomass becomes easy to mill. Simultaneously water that permeates the biomass dissolves most chloride and alkali salts. After the heat treatment, the biomass is mechanically dewatered, in order to remove the majority of the water and salts without the use of thermal drying. The combination of washing, thermal treatment and mechanical dewatering typically realizes salt removal rates in excess of 98%. The resulting pressure cake contains less than 35% moisture. The washing, thermal treatment (TORWASH) and mechanical dewatering are shown in the process scheme below in Figure 1, in combination with the densification (pelletization and briquetting) which is also studied within the LogistEC project, and will be reported in D3.5.

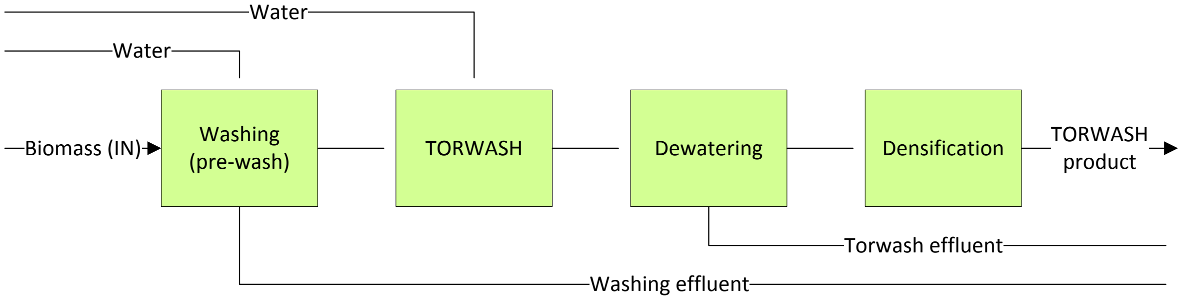

Figure 1 TORWASH process scheme

The TORWASH technology can be applied to nearly all forms of biomass, but the best results are obtained for fresh feedstocks (grass, straw, reeds, leafs, bamboo) and sludges (digestate, sewage sludge).

This chapter describes TORWASH tests that have been conducted with several biomass feedstocks which were selected within the EU LogistEC Project. The tests were performed in the framework of the LogistEC project in June/July and November/December of 2013.

The experiments were conducted to obtain information on the extent of upgrading that can be accomplished, by applying TORWASH to the feedstocks used in the LogistEC project. The first experiments aimed at identifying differences between feedstocks through:

1. A set of multiclave experiments aimed to provide an initial indication of four different feedstocks.
2. A set of multiclave experiments aimed at identifying differences between the same feedstocks grown under different conditions.

Secondly, after limiting the number of feedstocks, the goal was to obtain an indication of the optimal TORWASH conditions. These were obtained by means of:

3. Experiments in a 2L autoclave with a limited number of feedstocks, in order to obtain the optimum conditions for further TORWASH tests in the large autoclave (20 L).

Thirdly, the impact of TORWASH was established by increasing the scale of the experiments:

4. Experiments in a 20L autoclave at optimal conditions, using one feedstock, and analysing all input and output streams.

The experiments in the 20 L autoclave were performed several times at identical conditions in order to have sufficient material for mechanical dewatering tests by Averinox in an industrial press, and to get at least 100 litre of effluent for shipment to CRIBE (partner in the LogistEC project [1]) for further testing. The solid products were preserved for further testing by partners as well.

1.2. Experimental

Multiclave tests with Miscanthus, Fibre sorghum, Triticale and Arundo

The multiclave TORWASH tests were performed with Miscanthus, Fibre sorghum, Triticale and Arundo donax (Giant reed). Samples were provided by LogistEC partners (CENER, INRA, and SSSA). Pre-treatment consisted of size reduction of the different samples below 1 mm. For the multiclave and autoclave experiments demineralized water was added and temperatures were selected in the range between 150 - 250°C. Since tests were done in the multiclave, heating and cooling rates were relatively fast, while stirring was done by magnet. After cooling the treated samples, the contents were first filtered and the filter cake was pressed in a Carver Die at 67 bar static pressure to form wet discs. The discs were dried overnight at 105°C, to determine the eventual solid matter recovery in the disc.

Multiclave tests with Miscanthus and Switchgrass grown under different conditions

An additional set of multiclave TORWASH tests were performed with four Miscanthus samples and two Switchgrass samples, which were grown under different conditions. The samples were provided by INRA. One sample was identical to the sample used in the first multiclave test. The temperature was kept constant, while other test conditions and procedures were identical to those during the first multiclave tests.

Washing tests with Miscanthus, Fibre sorghum, Triticale and Arundo donax

[1] SSSA represents CRIBE

The tests were carried out with the same starting materials as the first multiclave tests described above. Pre-treatment consisted of size reduction of the sample below 10 mm. The washing was done with warm water at ambient pressure in 3 stages, with a total of 10 times the mass in water (L/S = 10). Liquid samples were analysed for chlorine content to determine the efficiency of the washing.

Autoclave (2 L) tests for Miscanthus and Triticale
Based on the results of the multiclave and washing tests, Miscanthus and Triticale were selected for TORWASH tests in the 2L autoclave. Washed materials (L/S = 10, see above) were subjected to TORWASH conditions in a 2L autoclave at a range of conditions that followed from the multiclave tests. The obtained slurry was filtered after each TORWASH test and three samples of about 20 gram were taken from the filter cake to press discs in the Carver Die at 67 bar static pressure. These discs were dried overnight at 105°C, to determine the eventual solid matter recovery in the disc.

Autoclave (20L) tests with Arundo donax
After discussion with project partners, and based on earlier multiclave tests, Arundo donax (giant reed) was selected for the 20L autoclave tests in cooperation with the project partners. During TORWASH, its behaviour is similar to Miscanthus, so that the results of the 2L tests of Miscanthus made it possible to determine the optimal TORWASH conditions for Arundo donax.

A new sample of Arundo donax was provided by CRIBE. Pre-treatment consisted of size reduction of the sample below 10 mm. The experiments started with washing of three batches of 5 kg Arundo donax in an industrial washing machine. The material was put in a mesh bag washed for 15 minutes in warm demineralized water at a ratio of L/S = 5 (based on dry matter). The material was dried by spinning. TORWASH was performed using 7 batches of washed Arundo donax in a 20 L autoclave. Demineralized water was added at a ratio of L/S = 7.5 (dry base). After cooling, the contents were filtered. The wet filter cakes were collected and shipped to Averinox for trials at an industrial scale press. Small samples of the filter cake were pressed in a Carver Die at 67 bar static pressure to form wet discs. The discs were dried overnight at 105°C, to determine the eventual solid matter recovery in the disc.

Analyses conducted after 20L autoclave tests
Various analyses were done on samples of the washing runs and selected TORWASH runs. The three solid samples were analysed with respect to proximate, ultimate, ICP, chlorine content and calorific value:

- Input Arundo donax, cut to < 1 cm (single sample)
- Washed Arundo donax (mixed sample from 3 runs)
- Discs pressed from TORWASHed Arundo donax

The two liquid effluent streams were analysed with respect to ICP, total carbon content, chlorine content, sugars and sugar decomposition products through (GC/MS):

- Effluent from washing of Arundo donax (mixed sample from 3 runs)
- Effluent from filtration of TORWASHed Arundo donax (mixed sample of 7 TORWASH runs)

1.3. Results

1.3.1. Multiclave tests with Miscanthus, Fibre sorghum, Triticale and Arundo

The TORWASH multiclave tests were successful. The solid matter recovery generally lies between 55% and 80% of the weight of the dry feedstock. The recovery at lower temperatures is about 10% higher than at higher temperatures. All feedstocks display the same trend, which can be seen in Figure 2.

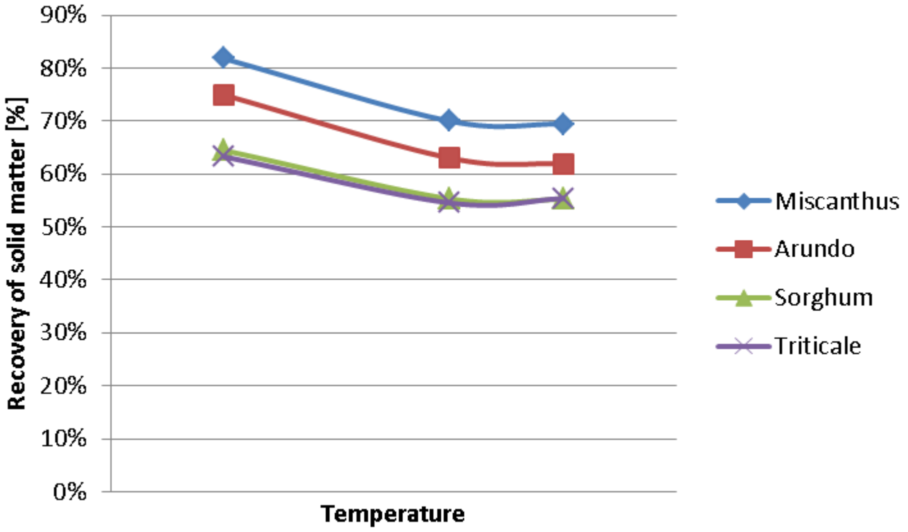

Figure 2 Recovery of solid matter from TORWASH tests in multiclave tests

The dry matter content of the various feedstocks after pressing the discs generally displays a slightly increasing trend as function of increasing temperatures, with dry matter content ranging for the different feedstocks ranging between 62 and 69%.

Fibre sorghum and Triticale display a similar behaviour, both in trends and in absolute values. Miscanthus and Arundo donax also display similar trends, although Miscanthus has a slightly higher dry matter content and a higher solid matter recovery. This appears to be unattributable to increased contents of sand or other inert ash-forming materials; in fact Miscanthus has the lowest ash content of all four untreated feedstocks.

The effluent streams that were obtained during all press tests were clear with one exception concerning Fibre sorghum that was TORWASHed at high temperatures. The pressing of the wet samples occurred faster for samples that were subjected to higher TORWASH temperatures. At relatively low TORWASH temperatures larger fibres were observed in the discs, while the presence of larger fibres decreased upon increasing temperature. The Miscanthus discs displayed an increased amount of larger fibres in comparison with the other three materials. The presence of larger fibres could not be attributed to the use of a magnetic stirrer in the multiclave setup (versus a mechanical stirrer in the autoclave setup), since these were not observed during the subsequent experiments with Switchgrass.

Figure 3 Pressed discs of (from left to right) Miscanthus, Fibre sorghum, Triticale and Arundo donax, with the lowest temperature at the top and highest temperature at the bottom

Miscanthus and Triticale were selected for use during the 2L autoclave experiments; Miscanthus and Arundo donax displayed similar behaviour, while Fibre sorghum and Triticale are nearly identical. These autoclave experiments will be conducted at relatively higher temperatures.

1.3.2. Multiclave tests with Miscanthus and Switchgrass grown under different conditions

In order to investigate the influence of different growing conditions, a set of multiclave tests was conducted using four Miscanthus samples and two Switchgrass samples that were cultivated under different conditions. The samples originate from different plots which were established in different years (2009 and 2010). The multiclave tests were performed at identical conditions for each sample; the most important results are provided in Table 1.

Table 1 Characteristics of various kinds of TORWASHed Miscanthus and Switchgrass

	Solid matter recovery	Dry matter content of disc	Density of dried disc [kg/m^3]
Miscanthus M13B11	69%	70%	952
Miscanthus M13B12	67%	68%	830
Miscanthus M13E11	66%	68%	958
Miscanthus M13E12	67%	68%	1014
Switchgrass V14	60%	68%	1086
Switchgrass V03	60%	68%	934
Reference Miscanthus	69%	69%	942

The solid matter recovery for the different types of Miscanthus lies between 66-69%, compared to 69% for the Miscanthus during the previous multiclave experiments, while the recoveries for the two Switchgrass samples are identical. The dry matter content of the discs that are pressed from TORWASHed Miscanthus ranges between 68%-70%, while the dry matter content of the two Switchgrass discs amounted 68%.

Despite the small differences in solid matter recovery and dry matter content of the discs, the differences in density of the discs pressed from Miscanthus varies somewhat. It should be noted that only one single disc has been pressed from each sample, with a thickness of 1.5-2.0 mm. There appears to be a correlation with the visible length of the fibres: the density of the disc is higher when shorter fibres are observed, i.e. for Miscanthus M13E12 and Switchgrass V14.

The conclusion of these multiclave results is that there are no significant differences between various Miscanthus samples in terms of TORWASH behaviour, and the same applies to the two Switchgrass samples. The densification ability appears to improve for two samples, being Miscanthus M13E12 and Switchgrass V14, while Miscanthus M13B12 displayed slightly lower densification ability than average.

1.3.3. Washing tests with Miscanthus, Fibre sorghum, Triticale and Arundo

The liquid effluent samples obtained during washing were analysed with respect to the chlorine content. The cumulative degree of chlorine removal is calculated by adding up the amounts of chlorine that were removed in the three liquid samples, divided by the total amount of chlorine in the feedstock. The resulting cumulative degree of chlorine removal for four different feedstocks is displayed in Figure 4.

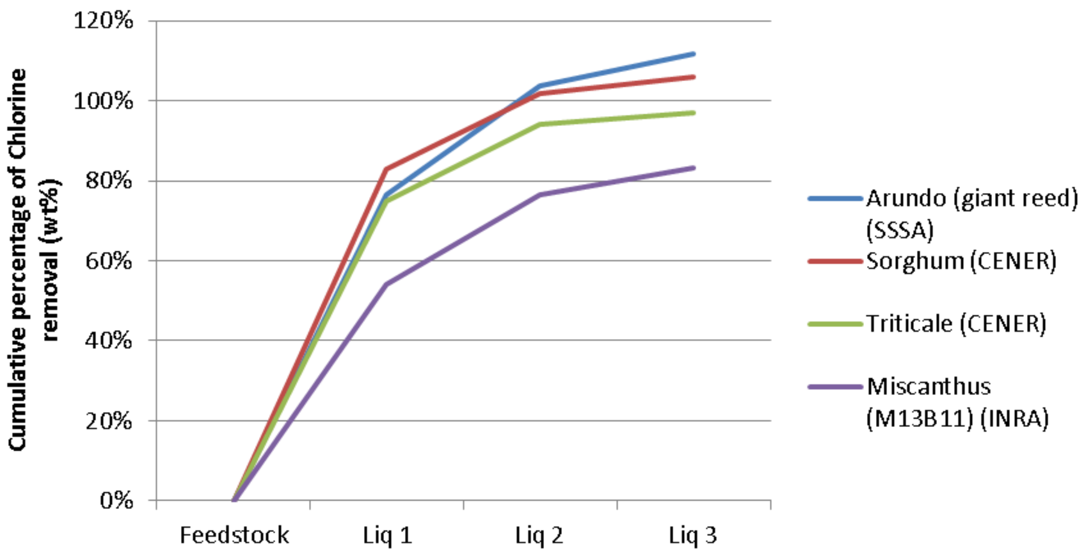

Figure 4 Cumulative removal of chlorine from four materials after repeated washing

The figure above demonstrates that the different samples all display similar trends for the chlorine removal rate upon subsequent washing steps; consecutive washing steps can each remove a significant part of the remaining chlorine content from the feedstock. In two occasions the cumulative chlorine removal rate exceeds 100%, this is probably attributable to small variations in chlorine content in the different samples. The Miscanthus sample appeared to be the most difficult sample to wash, even though the absolute chlorine level is relatively low. The conclusion from the washing experiments is that the four samples display no significant differences in behaviour and all feedstocks could be equally suitable. It should be noted that –in spite of the promising chlorine removal rates– a subsequent TORWASH step is still required to remove any traces of chlorine and other ash forming components, but also to obtain a more brittle material that is suitable for densification.

1.3.4. Autoclave (2 L) tests with Miscanthus and Triticale

Miscanthus and Triticale were selected for further testing under TORWASH conditions in the 2L autoclave. The tests were conducted at three temperature-settings. The slurry was filtered and samples were pressed into discs. Besides visual observations, solid recovery rates and dry matter content of the discs were measured. The results of the experiments are provided in Table 2.

Table 2 Characteristics of TORWASHed Triticale and Miscanthus in the 2L autoclave

Material	TORWASH conditions	Solid matter recovery based on total mass	Dry matter content of disc	Density of dried disc [kg/m^3]
Triticale	Low-T	63%	68%	730
Triticale	Medium-T	62%	69%	755
Triticale	High-T	62%	70%	792
Miscanthus	Low-T	71%	69%	848
Miscanthus	Medium-T	68%	69%	921
Miscanthus	High-T	66%	68%	946

The solid matter recovery for Miscanthus decreases upon increasing temperature. Similar trends have been observed in the past for various feedstocks. The solid matter recovery for Triticale in the 2L autoclave is 5% higher than during the multiclave experiments, while the recoveries are not significantly decreasing upon increasing temperatures.

The dry matter content in the discs pressed from TORWASHed material all range between 68% and 70%, both for Miscanthus and Triticale. These numbers are consistent with results that were obtained for various feedstocks in the past. The values lie within the same range as the multiclave experiments. The differences between TORWASHing Miscanthus and Triticale at various temperatures are small in terms of recovery and dry matter content of the pressed disc.

However, the visual differences are significant; at the lower temperatures the material is noticeable lighter in colour and more fibres are observed. The presence of fibres is also observed when a dried disc is ground in a mortar. The Miscanthus that is TORWASHed at high temperature can be pulverised and breaks into fine particles. Miscanthus that is treated at medium temperature is difficult to pulverise and fibres can be clearly observed in the powder. The density of the discs after drying increases upon increasing TORWASH temperatures. This implies that more energy can be stored in the same volume, but also that densification could be easier. The filtration was straightforward for all slurries; while TORWASHed Miscanthus is somewhat easier to dewater.

1.3.5. Autoclave tests (20L) with Arundo donax

A new batch of Arundo donax (Giant reed) was used as a feedstock for a series of identical washing tests and autoclave tests (20L). Miscanthus was initially selected for these tests, because of its high recovery and abundant availability worldwide. However, Arundo donax was selected after careful considerations together with project partners. SSSA will test the fertilizer properties of the TORWASH residues by growing Arundo donax. Therefore, the use of Arundo donax to produce the residue would mean that this test is now a recycle of the nutrients from Arundo donax into the next crop of Arundo donax. SSSA have chosen Arundo donax as it has a high uptake of nutrients and because it is able to retain these nutrients also in winter, which reduces the chance of minerals leaching, groundwater contamination and eutrophication of surface water.

The differences in trends and optimal conditions are relatively small for Miscanthus and Arundo donax, therefore both would have been a suitable candidate for the 20L autoclave experiments.

Preliminary test in 0.5 L autoclave
To be sure that Arundo donax was indeed behaving like Miscanthus, a single 0.5 L autoclave test was performed in a similar fashion as for Miscanthus in the 2L autoclave. The solid matter recovery was lower at 61%. Although dewatering was straightforward and yielded discs with 69% dry matter, it was found that it behaved the same as the previous batch of Arundo donax that was tested in the multiclave.

Three washing tests
About 14 kg (dry matter) of Arundo donax has been washed with a total of about 72 litres water. This yielded three batches of wet, washed Arundo donax at a total weight of 25.4 kg on wet basis which corresponds to 12.5 kg on dry basis. The moisture content has increased to almost 50%. The washing was done by tumbling a bag of chipped feedstock in demineralized water in a washing machine. The overall liquid / solid ratio of this operation was L/S = 5.2.

Comparing the dry matter before and after washing, it was calculated that 90% of the dry matter has been recovered. The analyses of the components which are dissolved are provided later in this paragraph. In addition, some material losses occur by slips through the mesh of the washing machine and additional handling steps.

The recovery of total mass, energy, ash and individual elements of Arundo donax in pre-washed material and in the TORWASH product are presented in Figure 5, where the red bars represent the Arundo donax after washing (and green bars represent the TORWASH product, which is discussed later in this chapter).

The higher heating value (HHV) on dry basis did not change significantly, roughly 90% of the energy content of the feedstock was kept in the solid phase. The same applies to the carbon, hydrogen and oxygen content, which also display 90% recovery. It indicates that essentially the organic matrix has not been altered.

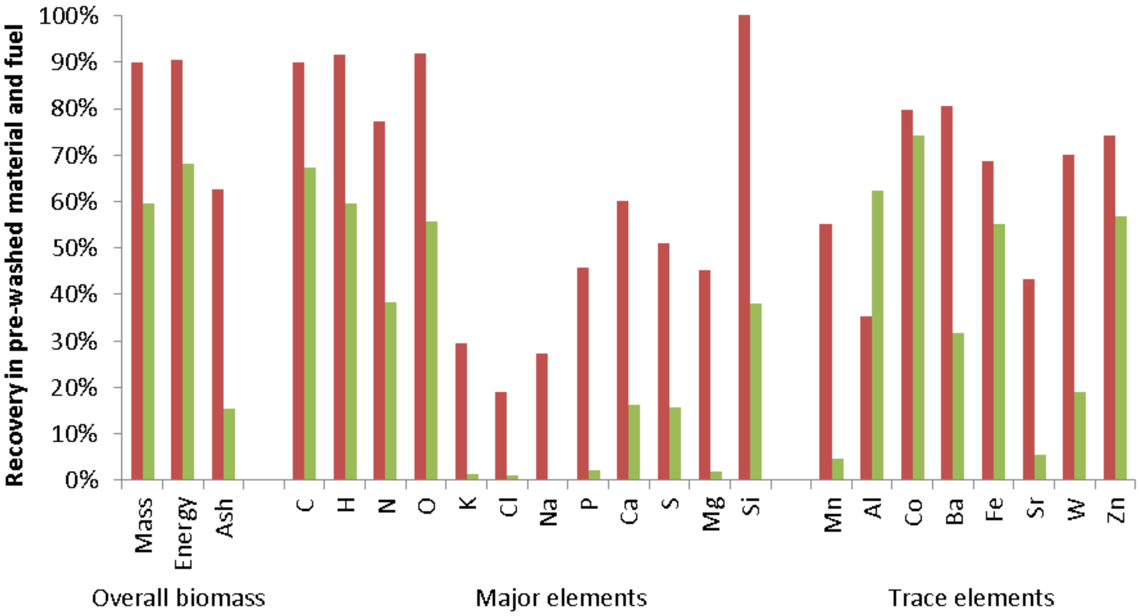

Figure 5 Recovery of mass, energy, ash and elements in pre-washed material (red bars) and TORWASHed product (green bars) as a percentage of the amount present in the feedstock

The ash-forming elements have been leached to a much larger extent than the organics. Only silicon appears unaffected by the pre-washing: 100% of it has remained. All other analysed elements display recoveries below 90%. The lowest recoveries were obtained for potassium and sodium at about 30%, while chlorine displayed a recovery of a mere 20%. Overall the total ash content decreased from 2.3 wt% to 1.6 wt%, which implies 37% extraction as opposed to total mass loss of only 10%.

A total of 60 kg effluent was recovered during the washing. It contains mostly sugars (some monomers, mostly glucose, but mostly complex sugars). The concentration of dissolved material is 0.020 kg per kg of effluent. In addition fines are suspended in the effluent, about 0.19 kg in total or 0.005 kg fines per kg of effluent. The fines settle to the bottom of the storage container and could be recovered during commercial-scale operation.

Seven 20L autoclave tests – TORWASH

A total amount of 12.4 kg washed Arundo donax (dry basis) was TORWASHed in seven batches. The resulting slurry was filtered and approximately 30 kg of filter cake was recovered, which contained 8.3 kg solid matter thus resulting in a solid matter content of 27.4%. A total of 73 kg filtrate (liquid effluent) was collected with an estimated concentration of dissolved components amounting 5.5 wt%.

Calculations show that 67% of the solid matter that went into the TORWASH step was recovered as solid matter. The remaining 33% has been largely dissolved (salts, sugars and derivatives). An earlier project called TORIPO [2] revealed that about 5% of input solids are converted to CO_2 and H_2O. A few percent (~ 2%) is lost as a result of handling, while 26% of the input solid material has been dissolved in TORWASH.

Lab-scale pressing of TORWASH slurry

Samples that were obtained from the filter cake of the second TORWASH run were subjected to a press test in the Carver Die. The test yielded discs with 69% dry matter, which is an excellent result, and identical to the number found in the preliminary test in the 0.5 L autoclave. It implies that TORWASH has accomplished its goal: the production of solid matter that is both weak enough to collapse under pressure, and strong enough to keep some channels open where liquid can leave the material.

Furthermore, calculations show that during pressing 1.6% of the solid matter in the cake is expelled. This is material that went into solution during TORWASH and is dissolved in the liquid that is still present in the filter cake. Even in pressed discs there is still some of this liquid left. The amounts are very small, but calculations show that this residual liquid is where the last very small traces of potassium, sodium and chlorine are present.

Figure 6 Raw Arundo donax (left) and Arundo donax after TORWASH (right)

Product composition

The discs pressed from the filter cake that have a solid matter content of about 70% (i.e. 30% moisture) are regarded as the end-product of these TORWASH tests. When the recovery of washing, TORWASH and pressing are combined, an overall yield of 60% of solid matter is found in the TORWASHed product, which is represented by the green bars in Figure 5. Approximately 10% of the solid matter in the feedstock is removed by washing, 25% of the solid matter of the feedstock is dissolved in TORWASH and 5% has reacted to gas and water in TORWASH.

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[2] Dutch national project “Torwash Rioolwaterzuivering Pilotontwerp (TORIPO)”, EOSLT10018

In the 60% mass that is recovered in the TORWASHed product, 68% of the energy that was originally present in the feedstock is recovered. These numbers are in good agreement with results that were obtained in an earlier project (TORIPO) where hay and reed were used as feedstock.

In Figure 5, the effects of TORWASH are presented as green bars for mass, energy, ash and elements in the product (compared to the original amounts in the feedstock). The ash content of the TORWASHed product (the discs) has dropped to 0.6 wt%. It corresponds to a substantial removal of ash-forming components. The organic matrix has been enriched in carbon relative to hydrogen and oxygen. This is reflected also in an increase in higher HHV. Potassium and chlorine have been removed by 99%. The sodium content has decreased below the detection limit, which indicates at least 97% removal but probably more. Further elaboration on these results is presented in the discussion.

Dissolved matter
A large number of different components are dissolved in the washing effluent and the TORWASH effluent. These effluent streams were analysed for organic components, such as sugars (mono-saccharides), and several other biomass degradation products as well as for the overall chloride and carbon content.

Sugars and sugar derivatives
In the washing effluent a mixture is present with fructose as dominant mono-saccharide. In the TORWASH liquid, glucose is dominant. However, the concentrations are very low and these only represent a small fraction of the dissolved material. The identified simple sugars account for 1% and 2% respectively of the total of dissolved matter.

Table 3 Concentrations of simple sugars (mono-saccharides) in effluents

Sugars	**Washing effluent**	**TORWASH effluent**	
Arabinose	37	<5	mg/kg
Fructose	110	89	mg/kg
Galactose	19	23	mg/kg
Glucose	13	913	mg/kg
Mannose	<10	38	mg/kg
Rhamnose	<5	<5	mg/kg
Xylose	31	90	mg/kg
Total	**210**	**1153**	**mg/kg simple sugars**
	1%	2%	of dissolved matter

The washing and TORWASH effluents have also been analysed for various other organic components. In the washing effluent only acetic acid was above the detection limit at 0.1%, which is only a small fraction (5%) of the dissolved matter. In the case of TORWASH effluent, more components were found. A total of 17210 mg/kg effluent, which accounts for 37% of the total amount of dissolved material. The rest are below the detection limits or unknowns.

Table 4 Concentrations of identified organic substances in effluents

Compound	**Washing effluent**	**TORWASH effluent**	
Methanol	<250	311	mg/kg
Hydroxyacetone	<100	500	mg/kg
Acetic acid	951	6501	mg/kg
2-furaldehyde	<100	7153	mg/kg
Formic acid	<250	586	mg/kg
5-(Hydroxymethyl)-2-furaldehyde	<100	2258	mg/kg
Total		**17210**	**mg/kg**
		37%	of dissolved matter

In the washing and TORWASH liquids, ash-forming components are dissolved as well. A brief calculation, based on the changes in ash content of feedstock, washed Arundo donax and product, shows that these ash-forming components should be present at about 2000 mg/kg effluent in the washing liquid. These are mainly dissolved ions, notably potassium and chlorine, but also calcium, magnesium and sulphur-containing ions. In the TORWASH effluent, there is also about 2000 mg/kg dissolved matter originating from ash-forming components in the feedstock. The same elements are contributing with one exception: silicon displays the highest concentration, while in the washing effluent its concentration was nearly zero.

The distribution of dissolved materials is provided in Table 5, and shows a large quantity of unknown components. Probably these unknowns are complex sugars (oligosaccharides) and a large variety of other larger organic fragments that originate from decomposed hemi-cellulose, and to a lesser extent cellulose and lignin.

Table 5 Classification of materials dissolved in washing and TORWASH effluents

	Washing liquid	TORWASH effluent
Simple sugars	1%	2%
Other identified organic compounds	5%	37%
Dissolved ash-forming compounds; K, Cl, Si and others	10%	4%
Unknown	> 80%	> 55%

Carbon and chloride balances

The liquids were analysed for organic components, as well as total carbon and chlorine content. These two elements show a reasonable closure of the element balances. Of the carbon, present in the feedstock, 67% was found in the solids (discs), 6% was dissolved in the washing liquid and slightly less than 2% was present in fines floating in the washing liquid. 15% was dissolved in the liquid after TORWASH. From previous experience, it is known that about 5% of the carbon is converted into CO_2. This adds up to 97% closure of the carbon balance.

In case of chlorine (most likely 100% of it as chloride), 80% of the chloride originally present in the feedstock was dissolved in the washing liquid; 15% was dissolved in the TORWASH liquid and 1% remained in the compressed solids. This results in 96% closure of the chlorine balance.

Table 6 Percentage of carbon and chlorine recovered in output streams

Output	**C**	**Cl**
Dissolved in washing effluent	6%	80%
Fines suspended in washing effluent	2% (estimated)	0% (estimated)
TORWASH effluent	15%	15%
Evaporated as gas during TORWASH	5% (estimated)	0% (estimated)
Compressed solids	67%	1%
Total	**97%**	**96%**

Notes on pressing at industrial scale (Averinox)
After taking samples for lab-scale press testing, the remaining filter cake was sent to Averinox for pressing in an industrial press. At Averinox about 10 kg (dry matter) of this material was pressed into large discs. The dry matter content of the discs amounted 60-75%, depending on pressure and press velocity. This agrees with press tests done on TORWASHed hay and reeds in the TORIPO project. The material dries in ambient air to an equilibrium moisture content of approximately 7-8%.

Materials for partners
The washing effluent and the TORWASH liquids from filtration and pressing were shipped to CRIBE in Italy, for testing as fertilizer. The recovered solids were dried and sent to Risø DTU and CENER for pelletization, storage and leaching tests.

1.4. Discussion

The overall recovery and other characteristics of the TORWASHed Arundo donax product are in agreement with the mass recovery of TORWASHed hay and reed as found in the TORIPO project. The recovery of 68% of the ingoing energy (based on HHV of dry material) is in accordance with expectations, and is 5-10% higher than the mass recovery. The calorific value of the TORWASHed Arundo donax is nearly identical to the calorific value of TORWASHed hay.

Table 7 Comparison of recovery and calorific value of Arundo donax with data from the TORIPO project

Material	Arundo donax	Hay	Reed
Mass recovery [%]	60%	52%	65%
Energy recovery [%]	68%	61%	N/A
Calorific value of feedstock, HHV (d.b.) [MJ/kg]	19.2	18.2	N/A
Calorific value of produced fuel, HHV (d.b.) [MJ/kg]	21.9	21.6	N/A

Distribution of elements
The combination of washing and TORWASH operations demonstrate a very effective means to separate combustible matter from ashes. Especially, the undesired potassium and chlorine have been removed effectively, which is clearly demonstrated in Figure 5.

Washing has resulted in a mass loss of 10%, while equal losses are observed for carbon, hydrogen and oxygen contents, being the main constituents. Nitrogen displays a slightly higher loss. The total ash removal is 37% during washing, which is substantially higher than the total mass loss, hence it can be stated that ash-forming elements have been selectively removed. All ash-forming elements that are present above the detection limit are selectively removed, except for silicon, which is not removed at all. The highest removal rate is observed for chlorine, being 80%. The alkali elements potassium and sodium are removed with 70%. These numbers are consistent with other washing experiments (single washes) done at ECN and with literature data on washing of biomass, as well as experiences with leaving biomass outside in the rain after harvesting.

The cumulative weight loss of the washing and TORWASH (including pressing) is 40%. The carbon content is reduced by 33%, while the oxygen content is reduced by 44%. Both are expected results and agree with earlier TORWASH experiments. The net effect is a solid bioenergy carrier that is more mature and has a higher calorific value than the feedstock. Potassium and chlorine have been removed by 99%. As intended these elements have gone in dissolution completely and there is only 1% remaining as a result of effluent that is not expelled from the solids. Sodium in the product is below the detection limit, which means that at least 97% has been removed. The absolute potassium and chlorine concentration are to 116 mg/kg and 46 mg/kg respectively, which is well below the limits of a very clean solid bioenergy carrier. The ENplus A1 limit for clean wood pellets prescribes a chlorine content below 100 mg/kg. For potassium there is no criterion, but a concentration below 500 mg/kg is considered good, and below 200 mg/kg is excellent for use during thermal conversion.

The removal rates of nitrogen, sulphur, iron, zinc and calcium are in the range that is normally observed during TORWASH. The removal rates of phosphorous and magnesium are surprisingly high: 98%. This implies that the expelled liquid effluent may be suitable as a fertilizer. Furthermore the removal rate of silicon is surprisingly high at 62%. Typically 10-20% removal is observed during TORWASH experiments. The high removal rate could be attributable to increased acidity or more dispersed presence of silicon in the feedstock.

The overall result is that the ash forming components are removed with 84%, which is a very high number. The resulting ash content of 0.6 wt% is a very promising result and it means that this material is an attractive fuel.

Comparison to ENplus standard

With respect to the composition, the produced solid bioenergy carrier complies with the ENplus A1 standard, which is the highest standard for biomass pellets. This compliance makes both future trading of this material, as well as thermal conversion quite straightforward.

Dissolved matter

The dissolved matter in the washing liquid and the TORWASH liquid are dissolved sugars and dissolved ashes, but a substantial part of the mass dissolved in both liquids is unknown. Probably these unknowns are complex sugars (oligosaccharides) and a large variety of other larger organic fragments originating from decomposed hemi-cellulose and to a lesser extent cellulose and lignin.

1.5. Conclusion

The behaviour of four types of biomass at washing and TORWASH conditions were successfully studied in a multiclave. Small differences in behaviour during the washing and TORWASH process were observed for the different feedstocks. All four types of biomass yielded a product with improved fuel properties compared to the feedstock. Miscanthus gives the highest recovery of solid matter during TORWASH. Trends from earlier projects were confirmed. There were no measureable differences between different batches of the same Miscanthus feedstock.

Arundo donax can be successfully subjected to TORWASH conditions in 20 L batches. The results of the 20 L autoclave tests match tests in 0.5 L and 2 L autoclaves, taking into account that these have different heating and cooling rates. Simple washing and spinning (centrifuge) already removes significant amounts of salts (70-80% of potassium and chlorine). TORWASH and subsequent mechanical dewatering can remove a total 99% of certain salts. Silicon is least dissolved of the ash-forming components. Mass recovery is 60%, energy recovery is 68% in the solids. This agrees with previous tests on hay and reeds. With respect to the composition, the produced solid bioenergy carrier complies with to the ENplus A1 standard, which is the highest standard for biomass pellets.

The liquids expelled as effluents after washing and TORWASH contain the expected constituents: dissolved sugars and its reaction products, like acetic acid and furfural, as well as dissolved salts. The distribution of elements is similar to earlier TORWASH results, with the exception of nearly complete dissolution of phosphorus.

2. Torrefaction

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2.1. Introduction

Torrefaction is a thermochemical process that finds its roots in the roasting of coffee beans and gives coffee its characteristic flavour. For biomass, it is used as a pre-treatment process in the typical range between 250-300°C in order to upgrade the biomass and convert it into a high-value solid bioenergy carrier.

The chemistry behind torrefaction involves mainly the removal of oxygen from the biomass structure after exposure to a hot, inert atmosphere. This causes the biomass to transform into a hydrophobic, homogeneous and dense solid energy carrier, that typically contains about 70% of the mass and 90% of the energy initially present in the biomass. Torrefaction side-products are vapours and gases which can be combusted to generate process heat, creating a self-sustaining overall process. The torrefied product can be further processed into densified pellets or briquettes obtaining a high-quality product adjusted to logistics and end-use requirements.

Torrefaction testing facilities at ECN vary from milligram-scale batches up to a continuous throughput of 50-100 kilograms per hour covering a vast range of torrefaction research possibilities. Small scale torrefaction tests can be realized under well-defined conditions which are translated into larger scale applications and solutions. ECN has completed the first steps into commercialization of its torrefaction concept as a result of a co-operation with Andritz Pulp & Paper, which has led to a fully operational 1 ton/h torrefaction demonstration plant in Sønder Stenderup, Denmark. Recently, 200 tons of pellets from torrefied spruce produced at the demonstration plant were successfully co-fired in a DONG Energy power plant in Studstrup, Denmark. Torrefied spruce pellets were fed to a dedicated roller mill, resulting in co-firing share of approximately 33%.

The EU LogistEC project aims to test pre-treatment and densification technologies, at pilot-scale, using several types of biomass. During the first year of the project, the available biomass within the project was listed and arranged by quantity (small, medium or large amounts available) and by expected harvest time. The types of biomass, and the technologies used were arranged in supply chains such that the producer always produces sufficient material for the consumer within the project. The available biomass samples are first tested at a smaller scale, which is reported in this Chapter.

2.2. Experimental

At ECN the first exploratory torrefaction tests were performed using 10 different feedstocks:

- Poplar from CENER, INRA, SSSA, FCBA (Short Rotation Coppice (SRC) and Very Short Rotation Coppice (VSRC))
- Willow from SGB
- Eucalyptus from FCBA (SRC and VSRC)
- Triticale from CENER
- Fibre sorghum from CENER

The first tests performed were Thermogravimetric analyses (TGA) using milligram-scale samples that were subjected to selected thermal treatments in an inert gas environment. The torrefaction behaviour of the different types of biomass were investigated and three materials were selected for lab-scale torrefaction tests. The selection criteria were:

- Torrefaction behaviour
- Sufficient material for pilot-scale trials within the project available
- Delivery time

The lab-scale tests using samples of a few kilograms were performed in the batch torrefaction reactor and based on these tests two materials were selected for larger scale tests in the ECN torrefaction pilot plant.

2.3. Results

The exploratory torrefaction tests performed at ECN, i.e. TGA measurements, were temperature treatments in a small nitrogen gas flow to pre-determined torrefaction temperatures. The samples used were 10-20 mg of finely ground biomass and the weight loss of the samples was recorded accurately. The thermal degradation behaviour of the biomass was therewith determined. Each biomass sample was tested at four different torrefaction conditions (temperatures of 240, 260, 280, and 300°C at a residence time of 45 minutes) and the weight loss was determined from the recorded data. The mass yields (mass of the torrefied sample divided by dry initial mass of the sample) were subsequently calculated.

From the ten different feedstocks that were tested, three materials were selected for batch-scale torrefaction experiments. ECN can rely on elaborate experience with Poplar and Eucalyptus, therefore the non-woody feedstocks Triticale and Fibre sorghum, as well as the short rotation coppice Willow, were selected as feedstocks for batch experiments. The latter comprised of small branches and a relatively large amount of bark. The mass yields of the selected feedstocks were plotted against the torrefaction temperature and are shown in Figure 7.

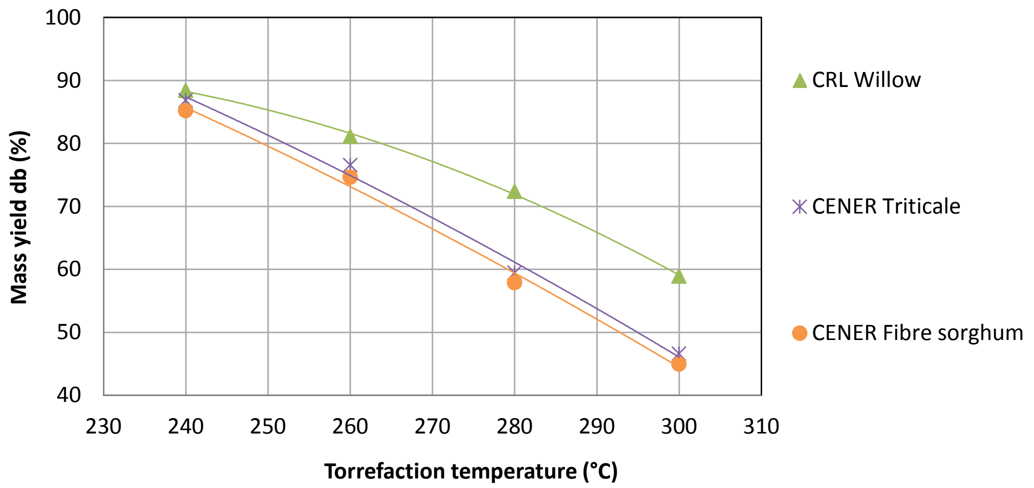

Figure 7 Mass yields from the TGA measurements versus temperature for feedstocks selected for batch reactor tests

From this graph it was clear that Triticale and Fibre sorghum, being the only non-woody feedstocks, showed a totally different torrefaction behaviour compared to the woody feedstock like Willow.

The batch-scale torrefaction tests were performed in a 20 liter metal vessel using a heated nitrogen gas flow. The three selected feedstocks, being Triticale and Fibre sorghum from CENER and Willow from SGB, were sieved to remove the fines and the reactor was filled with fibres or chips for torrefaction tests at 240, 260, and 280°C for 45 minutes. Pictures of the used feedstocks are shown in Figure 8.

CENER Triticale CENER Fibre sorghum SGB Willow

Figure 8 Pictures of the raw feedstocks for batch reactor testing

Mass yields have been determined by comparing the starting (dry) mass and the mass of the samples after torrefaction. In Figure 9 the mass yields from all the batch torrefaction tests are displayed.

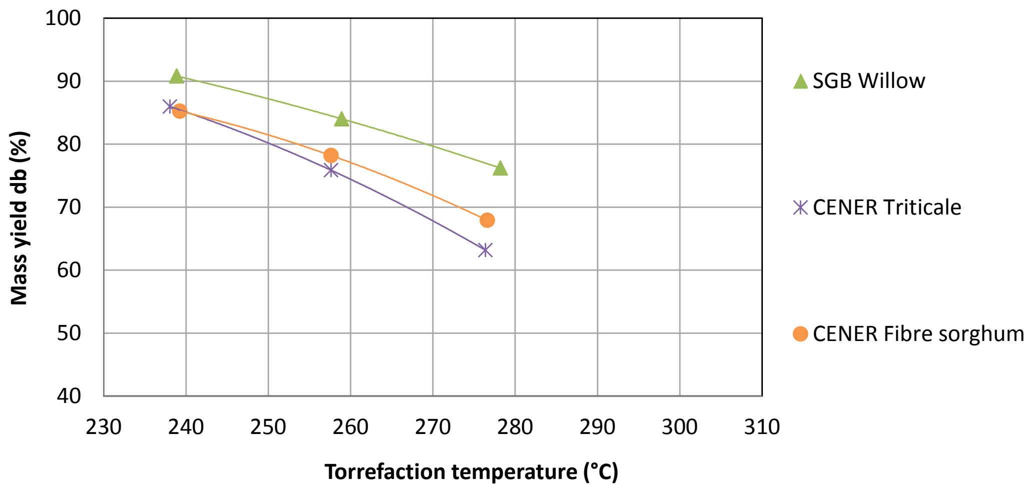

Figure 9 Mass yields from the batch reactor tests versus actual torrefaction temperature

Temperatures shown in the graph are not the torrefaction set-points but the actual recorded temperatures in between the material during the tests. Accurate temperature control is more difficult to establish in the batch reactor compared to the TGA, because of the relatively large reactor volume, the larger particle sizes (chips) of the feedstocks (enabling the gas to create preferential gas channels in the bed) and the exothermal behaviour of material during torrefaction.

Figure 10 **Pictures of the raw and torrefied materials from all the batch reactor tests**

Pictures of all the raw and torrefied materials are shown in Figure 10. Small samples have been taken from these materials for chemical analyses. The results are shown in Table 8. In the first column the mass yields from the batch torrefaction tests are shown. The next columns show the calorific value of the materials, the calculated energy yields, the ash content determined at 550°C and the content of the 7 most prominent elements.

Table 8 Chemical analyses results of all raw and torrefied materials

chemical analyses	mass yield	HHV	energy yield	ash (550°C)	K	Si	Ca	Cl	P	Mg	Na
	(%) db	(MJ/kg) db	(%) db	(%) db	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
Triticale raw		18.2		4.2	10913	5075	3978	2992	2057	1528	2497
Triticale 240	86.0	19.5	92.8	4.7	12867	5585	4516	2789	2617	1831	2944
Triticale 260	75.9	20.3	85.7	5.3	14065	6812	4989	2781	2588	1943	3207
Triticale 280	63.2	22.0	78.0	6.6	17222	7974	6083	2600	3371	2397	3787
Fibre sorghum raw		18.1		5.4	13262	9365	2774	7004	1324	2665	234
Fibre sorghum 240	85.2	18.9	89.6	5.9	17163	12182	3705	6585	1687	3508	272
Fibre sorghum 260	78.2	19.3	84.2	6.7	17171	12127	3705	6286	1696	3506	265
Fibre sorghum 280	67.9	20.1	76.4	7.8	19990	13999	4202	5669	1952	3945	313
Willow raw		19.3		2.0	3679	472	3934	259	1034	708	94
Willow 240	90.8	20.1	95.1	1.9	3905	199	4294	171	1088	742	89
Willow 260	84.0	20.7	90.9	1.9	4015	199	4297	123	1111	753	90
Willow 280	76.2	21.6	86.3	2.5	5084	398	5576	128	1408	970	112

The most interesting results from these analyses are the increasing calorific values with increasing torrefaction temperature, caused by the relative increase in carbon and hydrogen concentration and relative decreasing oxygen content. Unlike TORWASH, torrefaction typically results in a slight increase of the ash content due to the decrease in organic content. Ash-forming elements are generally retained in the solid phase. The ash content of the Willow is relatively high due to increased bark content of the feedstock.

These batch-scale torrefaction tests have been performed to select two feedstocks for the pilot-scale torrefaction tests. All tests have shown good results and because of the fact that Triticale is a residue stream and has a higher density compared to Fibre sorghum, and Willow is the only woody feedstock of these three feedstocks, Triticale and Willow have been selected for pilot-scale testing.

2.4. Conclusions

Triticale is an interesting new feedstock for the torrefaction process. Willow has been used as a feedstock for torrefaction before, but always as clean stem wood chips. This feedstock (mixture of small branches, bark and small clean stem wood chips) is also a new feedstock for the pilot torrefaction reactor. The chemical analyses performed on samples from all the batch reactor tests showed high energy yields for Triticale and Willow, but also a relatively high ash content in excess of 5% for Triticale and approximately 2% for the Willow bark and branches, while values below 0.5% are typically observed in clean stem wood.