KBBPPS - Overview of current relevant sampling and biogenic carbon standards on global level

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KBBPPS
Knowledge Based Bio-based Products' Pre-Standardization

Work package 3

Bio-based carbon content

Deliverable N° 3.3:

Verification of the method for total carbon determination (ruggedness test) Intermediate report

Public

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1 Publishable summary

Given document is an intermediate report that presents the current results of the verification test (so called ruggedness test) on the method to determine total carbon and eventually bio-based carbon content in various products that were collected from different suppliers.

Determination of the biogenic carbon of a finished product includes three steps such as a representative sample preparation, its pretreatment and the C14 analysis of the sample. Our review on sampling standards was given in the Deliverable 3.1. The method to determine total carbon and biobased carbon content was reviewed in Deliverable 3.2 that is converted into the technical specifications *CEN/TS 16640 "Bio-based products — Determination of the bio based carbon content of products using the radiocarbon method.* Since the C14 determination techniques are very accurate and extensively tested, we will verify only the total carbon determination method which is based on a complete combustion of a material. The results of the ruggedness test that are given in this report concern only the repeatability of the method.

Several challenging products (volatile paints, volatile liquids, paint components, sun lotion and all its constituents were tested at the current stage of the ruggedness test). Obtained results on the total carbon fractions in each of analysed materials are in a good agreement with theoretical data (if known) and with data provided by products suppliers (when available). The results of our measurements indicate a very good repeatability.

Current ruggedness test will continue further in order to validate the method on the next set of “difficult” products including biocomposites, biotextile, particle boards, ceramic and gaseous materials.

After the ruggedness test will be completed, we initiate an interlaboratory test for further verification of the method.

2 Introduction. General information on a ruggedness test

Generally, ruggedness test examines the potential sources of variability in one or a number of responses of the method. Another aim of a ruggedness test may be to predict reproducibility. In literature there is a distinction between repeatability and reproducibility. Normally repeatability addresses variability between independent test results gathered from within a single laboratory (**intra**laboratory testing). Reproducibility addresses variability among single test results gathered from different laboratories (**inter**laboratory testing).

Typically, the factors to be investigated in a robustness test are related to the analytical procedure (operational factors) and to the environmental conditions (environmental factors). The operational factors are selected from the description of the analytical method and operating procedure, whereas the environmental factors are not necessarily specified explicitly in the analytical method. The selected factors should represent those that are most likely to be changed when a method is transferred between laboratories, analysts or instruments and that potentially could influence the response(s) of the method.

On a general level, in a ruggedness test several steps can be identified. They are schematically presented in the diagram below.

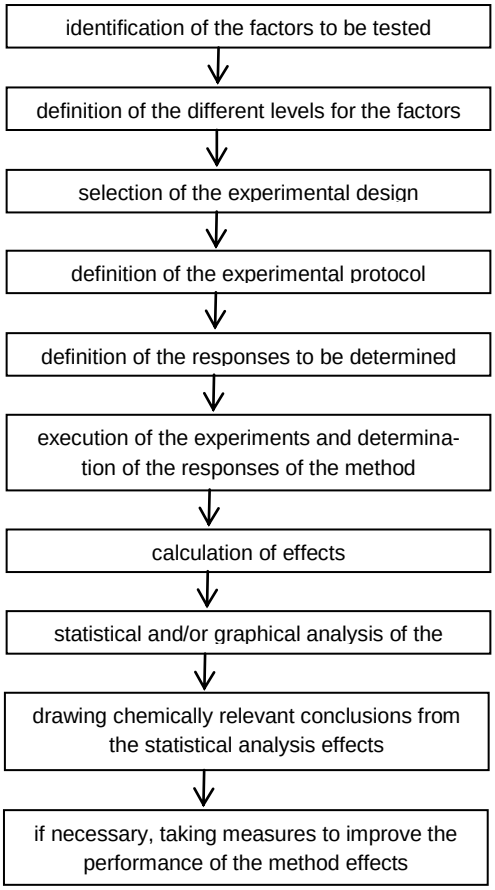

Figure 1 Schematic representation of different steps in a robustness test

3 Ruggedness test and its relation to KBBPPS

The knowledge bio-based products pre-standardization (KBBPPS) project has a goal to develop a horizontal standard and certification systems for bio-based products. The bio-based product market covers a wide range of products such as bio-based plastics, bio-lubricants, composite materials for construction and automotive industries, products for chemical and pharmaceutical industries. Most relevant biobased materials will be covered within the KBBPPS project. In this contest, analysis of impact of the different test methodologies and different labelling is also one of the scopes of the KBBPPS and this in turn demands the performance of a ruggedness test.

As it was already reported in the previous report, for the determination of the bio-based content of materials or products next three methods are recognised: 1 - selective dissolution method (SDM), 2 - manual sorting method (MS), 3 - biogenic carbon (C14) determination method. In turn, within the C14 determination method, three techniques are distinguished: AMS - accelerator mass spectrometry, LSC - liquid scintillation counting, BI - beta-ionization technique. These three techniques are considered to be equivalent, but each of them requires different amount of the CO_2: for AMS measurements the minimum amount of CO_2 is 4 ml, for BI measurements 2l – 10l CO_2 is required, and for LSC measurements the required amount of CO_2 depends on the way the sample is prepared for measurement, but at least a few gram will be required.

When preparing a test sample, usually a bigger sample must be reduced to one or more test portions that are smaller than the original sample. The main principle that has to be hold for sample reduction is that the composition of the sample as taken on site shall not be changed during each stage of the sample preparation: each sub sample shall be representative of the original sample. Solid materials in most cases introduce no practical difficulties in obtaining a representative sample. Usually combustion method and CO_2 trapping is used to sample CO_2 and to determine the C content subsequently. Liquids should be either single phase or relatively homogeneous. The homogeneity in many cases can be achieved by stirring or sample centrifuging. Another approach is to separate the clear liquid and the sediment by centrifuging and then to examine them separately. In case of viscous liquids or materials with volatile components the transfer problems exaggerate weighing problems. Effort should be made to obtain the sample weight in the combustion tube, rather than transferring a previously weighed sample to the oxidation tube.

Practical difficulties can occur when sampling materials that are partially combustion resistant and therefore cannot be combusted completely (ceramics for example), or materials containing volatile components. Such materials are quite peculiar due to their inhomogeneity which cannot be removed by simple mechanical effects (crushing, shaking, centrifuging, mixing, etc.). Determination of their CO_2 content and then the C content demands a different

approach which sometimes is not given in the Standards. If this is the case, then a method of sampling and testing has to be developed first on a laboratory scale.

In general, to make all carbon free, material needs to be completely combusted, irrespectively of solid, liquid, or gaseous state of material. Some materials, as paints for instance, can be difficult to analyse due to the presence of volatile compounds which can cause weighting problems and omitting some carbon which should be included. Ignition problem can also arise when combusting some materials. After combustion procedure, all available carbon is gathered as CO_2 in some absorber: the CO_2 present in a representative stack gas sample is absorbed in an alkaline medium or transferred to a gas bag or lecture bottle. After sampling, the collected CO_2 is prepared for C14 analysis.

Following the KBBPPS project plan, deliverable 3.1 prepared by ECN gives an overview of relevant standards on a global level with respect to the biogenic carbon content determination. This include not only solid, liquid and gaseous materials, but also mixtures of these which introduces practical differences especially at the pre-treatment stage for the bio-carbon analysis. For a reliable biogenic carbon determination it is of importance that both stages - material sampling and material treatment - are performed properly. Deliverable 3.2 describes the method for total carbon and subsequently the biogenic carbon determination and is converted into the technical specification *CEN/TS 16640 - Bio-based products — Determination of the bio based carbon content of products using the radiocarbon method*.

Next step is to perform a ruggedness (sometimes also referred to as a robustness) test in order to validate the carbon content determination method.

As mentioned above, we recognise three stages when determining the C14 content: sampling, treatment and the C14 determination itself. For the determination of the C14 content, the carbon that is present in the sample has to be converted to CO_2. The conversion is done by combustion in oxygen. If necessary, a combustion aid can be used to ensure complete oxydation of the C to CO_2. In given report, our focus is exclusively on the ruggedness test that aims to check the method which is used to retrieve all available carbon from different materials. Since the C14 measurement techniques are already standardized, the ruggedness test we perform concerns only the treatment part and aims to check if we are able to extract all available carbon (via conversion to CO_2) for different types of materials or products. This is the intermediate report that only describes approximately half of the process. In the end of the process an interlaboratory test will be performed on one of the most “difficult“ materials.

4 General list of materials to analyse

The table below represents a general list of materials and samples that have already been (A-D) or will be analysed (E-I). Among these materials there are both product constituents and finished products in different states (solid or liquid or gaseous or powder) and they include sun lotion and its constituents, paints and their constituents, ceramic powder, chipboards particle, composites, textiles, biogas.

Table 1 List of materials for the ruggedness test

Supplier	Materials	Remark
A	Sun lotion and its constituents, 9 different samples in total	analysis is performed
B	water-based matt paint, 5 cans of the same paint	analysis is performed
C	2 different types of samples: bionaphta and biodiesel; 25 samples in total	analysis is performed
D	3 types of samples: resins used to make paint; water based alkyd emulsion; water soluble linseed oil; 6 samples intotal	analysis is performed
E	pressed construction panels	analysis will be performed
F	biocomposites	analysis will be performed
G	biotextiles	analysis will be performed
H	biogas	analysis will be performed
I	ceramic	analysis will be performed

5 Analysed materials and their characteristics

This intermediate report focuses on the materials that have been analysed. List of materials and their brief description is given below. The results are presented and discussed in Paragraph 7 of this document. Due to the confidentiality agreement with sample suppliers, in given report we do not mention names of products and thier supplier.

5.1 Supplier A

Material A1
Glycerin EP/BP, 200g

Materials A2
Yellow liquid, 1 glass bottle of 200g, isopropyl isostearate

Material A3
Yellow liquid, 1 glass bottle of 200g, Sorbitan Isostearate (and) Polyglyceryl-3Polyricinoleate

Material A4
Glass bottle of 200g, yellowish liquid, 200g, sorbitan sesquioleate

Material A5
1/3 of 200ml bottle, white emulsion

Material A6
100mL plastic box, white emulsion

Material A7
4 sample 50g each in small metallic container, ethyl oleate

Material A8
4 sample 50g each in small metallic container; Persea Gratissima

Material A9
Transparent liquid in glass bottle, 200g, raw material, Squalane

Material A10
500ml plastic bottle, white emulsion

5.2 Supplier B

Material B : the paint that is received is a water based matt paint.

5 cans of 500ml each , 3.9kg total weight;
The total percentage of binder is 4.03%
2.9% of acrylic binder
1.13% of renewable binder
The volatile part in the paint is 34.6%.

5.3 Supplier C

25 samples all together that are divided in 5 groups.

Group 1(5samples) – referred to as C1 in Table 2 in this report.
Correspondingly the first sample of this group of 5 samples is marked C1-1.

Group 2 (5 samples), Group 3(5 samples), Group 4 (5 samples) and Group 5 (5 samples). These materials are referred to as materials C2 – C5 in Table 2 in given report.

Group 1 contains C_5-C_{10} isoparaffins and n-paraffins (bionaphta).

Group 2-Group 5 contain C_{10}-C_{20} isoparaffins and n-paraffins (biodiesel).

All the samples are used as fuels or components in fuels and as solvents.

There is no detailed information about those specific samples for their carbon content. The supplier has analysed the carbon contents of similar samples. For similar sample as from Group 1 the carbon content was 83.9wt% and for similar sample as from Groups 2-5 the carbon content was 84.6wt%.

5.4 Supplier D

The samples are resins and emulsions that are used to make paint.

3 types of samples; 6 samples in total - labelled DA1, DA2, DB1, DB2, DC1, DC2; 0.5kg each.

Samples DA en DB are water based alkyd emulsion with a solids content around 45%.
Sample DC is a water soluble linseed oil with a solids content of 100 % in the state as supplied.

All binders are for both interior and exterior application. The total carbon content is unknown.

6 Methodology

In general, for the determination of total carbon and eventually the C14 content, the carbon that is present in the sample has to be converted to CO_2. The conversion is done by combustion in oxygen. If necessary, a combustion aid can be used to ensure complete oxydation of the C to CO_2. As it was already described in Deliverable 3.2 (technical specification *CEN/TS 16640*), depending on the method that will be used for the C14 determination, different preparations are required. When LSC (liquid scintilation counting) method is to be used, then the CO_2 shall be collected in a cooled mixture of carbamate solution and a suitable scintilation liquid. When BI (beta ionisation) or AMS (accelerated mass spectrometry) methos will be used, then the CO_2 shall be collected in 4M NaOH solution or on a suitable solid absorber. More details on the requirements are given in earlier mentioned technical specification.

We use two different approaches to define the total carbon content in the products that we test.

1. Determination of total C fraction in the elemental analyser.
2. Combustion in the calorimeter with subsequent CO_2 gathering in NaOH and titration.

1. Elemental CHNSO analyser determines the percentages of carbon (the analyser also determines how much hydrogen, nitrogen, sulphur and oxygen is present). The key components of CHNSO analyser are auto- sampler, combustion reactors, chromatographic column, and thermal conductivity detector (TCD). The working principle is based on complete combustion of a sample in tin capsule. A sample is burned in a small excess of oxygen at approximately 1700°C. At this temperature the sample will be converted to oxides, salts and metal - the combustion products are separated by a chromatographic column which converts the compound in the form of NO_2,CO_2, SO_2,H_2O that are detected by the thermal conductivity detector. The latter gives an output signal proportional to the concentration of the individual components of the mixture. The instrument is calibrated with the analysis of standard compounds. This method finds greatest utility in finding out percentages of C, H, N, S, O in compounds which are generally combustible at 1700°C.
   When using the CHNO analyser, the following rules must be kept:
   - ✓ Sample must be pure and all contaminants must be removed.
   - ✓ Sample weight should be in between 1-2mg.
   - ✓ Liquid samples should have constant weight.

2. For combustion in the calorimeter at least 0.5g of material is needed. Combustion is done with the subsequent CO_2 gathering in NaOH and titration. For combustion of the sample in a calorimetric bomb, any test method such as ISO 1716, ISO 1928 or EN 15400 can be used. After the complete combustion, the combustion gas is collected in 200mL wash bottle. 1Mol NaOH is used and the titration is done in 0.1Mol of HCl. Carbon recovery per-

centage is determined as a ratio between the carbon fraction obtained by these two approaches: from titration and from CHNO analyser.

For each analysed sample we perform at least 3 measurements (see Annex A and Annex B) to determine its carbon (also hydrogen, nitrogen and oxygen) content. Measurements results that are presented in the next paragraph for each material are the averaged numbers from all numbers of measurements.

Based on the number of measurements, a relative standard deviation due to a random error is calculated for each analysed material. Besides a random error we determine also a systematic uncertainty (in literature sometimes referred to also as percent error) as a relative difference between measured and theoretically accepted value. If theoretically accepted value for some compound is unknown, then the systematic uncertainty remains un-estimated.

Relative standard deviation RSD is calculated as:

$$RSD = \frac{SD}{\overline{X}} 100\%$$

where $\overline{X}$ is averaged experimentally measured quantity, $SD = \sqrt{\frac{\sum_{i=1}^{N}(X_i - \overline{X})^2}{N-1}}$ - standard deviation, *N* – number of measurements.

7 Results of the C content analysis

Up to now, materials A, B, C and D from Table 1 are analysed. The summarizing results obtained by two methods described above are given in Table 2. More details are available in Appendix A for the results obtained by using the CHNO analyser and in Appendix B for CO_2 conversion and titration results.

Table 2 Carbon content as estimated by a supplier, measured and theoretical values

Material	Carbon content from supplier*	Biobased content from supplier	Carbon content measured average (CHNO)	SD	Systematic error (CNHO)	Carbon content theoretical	Carbon content measured average (titration)	SD	Systematic error (titration)	Carbon recovery percentage
A1	39%	100%	38.85%	0.20%	-0.72%	39.13%	37.06%	1.37%	-5.29%	95%
A2	85%	65%	77.20%	0.71%	-0.13%	77.30%	74.46%	1.12%	-3.68%	96%
A3	65%	100%	73.06%	0.31%			74.49%	2.17%		100%
A4	75%	100%	71.57%	0.21%	6.03%	67.50%	69.03%	1.00%	2.27%	96%
A5	45%	87%	42.59%	0.24%			39.86%	1.33%		94%
A6	24%		24.80%	0.22%						
A7	78%	90%	76.93%	0.44%	-0.63%	77.42%	73.88%	1.26%	-4.57%	96%
A8	76%	100%	77.22%	0.41%		-	75.16%	1.89%		97%
A9	85%	100%	85.84%	0.46%	0.62%	85.31%	82.67%	1.64%	-3.09%	97%
A10	45%	100%	42.42%	0.11%			39.75%	0.82%		94%
B			10.47%	0.13%						
C1-1	~ 83.9%		83.81%	0.69%			74.19%	0.29		89%
C2-1	~ 84.6%		84.18%	0.69%			79.44%	0.67		94%
C3-1	~ 84.6%		84.01%	0.5%			80.30%	0.93		96%
C4-1	~ 84.6%		84.73%	0.24%			81.17%	1.24		96%
C5-1	~ 84.6%		84.35%	0.22%			83.42%	0.15		99%
DA1			44.71%	0.34%						
DA2			44.01%	0.44%						
DB1			40.16%	0.35%						
DB2			40.35%	0.15%						
DC1			70.54%	0.16%						
DC2			70.63%	0.27%						

*Total carbon content as estimated by a supplier (± 5% for A1-A9 samples; approximate values for C1-C5 samples).
SD – standard deviation

8 Summary

All performed measurements indicate a very good repeatability and a good agreement with data provided by sample suppliers (when available).

For materials with known theoretical values for their carbon content, there is a reasonable agreement with measured and theoretical values.

Materials from supplier A (A1-A10) are the constituents of sun lotion.

Material B, matt paint: due to high volatile fraction of 34.6% this particular material was more challenging compared to the rest of materials that have been analysed. The difficulty with such types of materials is to combust the paint without losing the carbon fraction that can originate from the volatile part of the paint. Another difficulty that can rise while analyzing paints can be their difficult ignition and possibly a need of igniting enhancer.

Materials C1-C5 are volatile liquids that also demanded a special attention.

Materials D are resins and emulsions that are used in paint production. At the moment of preparation of this report, there were yet no results on carbon content from combustion and titration for materials DA1-DC2.

Note that for most materials that have been analysed there is no information on their theoretical carbon fraction. For such materials the systematic error remains un-estimated. Systematic error with a “-” sign in Table 2 indicates that measured average value is smaller than theoretically accepted value for a given compound.

For materials with known theoretical value, the systematic error of CHNO analyzer is smaller (in absolute values) than the systematic error for carbon content obtained by titration after combustion of these materials. This suggests that the carbon content obtained by CHNO analyzer is more exact than carbon content determined by combustion and titration, but the difference between these two methods for all nalyzed materials is negligible: for materails that have been tested, the CO_2 coversion results indicate a very high carbon recovery rate (see Table 2) and thus prove the reliability of combustion and titration method.

The tests will continue with the rest of materials (see Table 1) in order to make a final conclusion and to give recommendations if/when a special treatment is needed.

9 Next steps

- **Analyzing the rest of samples**
  - ceramic materials
  - particle chip boards or similar
  - bio composites
  - bio textiles
  - bio gas

  Ceramic material that we have is SiC powder. This material can demand a special treatment in order to ensure its complete combustion. Ceramic material will be treated accordingly to NEN-EN-ISO 21068 standard (*Chemical analysis of silicon-carbide containing raw materials and refractory products. Part 1: General information and sample preparation. Part 2: Determination of loss on ignition, total carbon, free carbon and silicon carbide, total and free silica and total and free silicon*).

  With particle chipboards product a special attention should be paid to obtain a representative sample for analysis.

  For help, the deliverable report 3.1 with overview of available standards on a global level can be referred to.

- **Preparation of a final report on the ruggedness test**
  The final report will include information on all collected and analysed materials.

- **Preparation of an interlaboratory test**
  Currently the availability of materials is being checked and contacts with several laboratories that will participate in the test are being established. In total, 8 laboratories are expected to participate in the test.

Annex A Results from CNHO analyser

Material A1

$C_3H_8O_3$					
Measurement	%N	%C	%H	%O	Sum
1	0.10	39.10	8.88	54.46	
2	0.11	39.07	9.06	52.35	
3	0.14	38.79	9.05	52.49	
4	0.11	38.82	8.93	52.99	
5	0.09	38.61	8.97	53.79	
6	0.10	38.68	9.02	53.01	
Measured average	0.11	38.85	8.99	53.18	101.02
Standard deviation	0.02	0.20	0.07	0.80	
%RSD	14.81	0.51	0.79	1.51	
No of measurements	6	6	6	6	
Theoretical value	-	39.13	8.70	52.17	100.00

Material A2

$C_{21}H_{42}O_2$					
Measurement	%N	%C	%H	%O	Sum
1	1.35	77.63	12.89	10.16	
2	1.47	76.61	12.75	9.83	
3	1.68	77.28	12.84	9.64	
4	1.60	76.45	12.75	9.69	
5	1.77	78.34	12.95	9.78	
6	1.20	76.87	12.53	9.65	
Measured average	1.51	77.20	12.79	9.79	99.78
Standard deviation	0.21	0.71	0.15	0.20	
%RSD	14.17	0.92	1.17	2.01	
No of measurements	6	6	6	6	
Theoretical value	-	77.3	12.9	9.8	100.00

Material A3

Measurement	%N	%C	%H	%O	Sum
1	0.11	73.39	11.38	16.51	
2	0.10	73.22	11.44	16.11	
3	0.08	72.58	11.47	16.11	
4	0.08	73.11	11.32	16.13	
5	0.09	73.25	11.33	16.28	
6	0.08	72.81	11.31	16.26	
Measured average	0.09	73.06	11.38	16.23	100.76
Standard deviation	0.01	0.31	0.07	0.16	
%RSD	12.36	0.42	0.59	0.96	
No of measurements	6	6	6	6	
Theoretical value	-	-	-	-	

Material A4

$C_{66}H_{126}O_{16}$					
Measurement	%N	%C	%H	%O	Sum
1	0.09	71.78	10.96	18.23	
2	0.07	71.21	10.93	17.72	
3	0.08	71.65	11.01	18.03	
4	0.11	71.70	10.94	18.35	
5	0.09	71.45	10.95	17.84	
6	0.09	71.64	10.97	18.41	
Measured average	0.09	71.57	10.96	18.10	100.63
Standard deviation	0.01	0.21	0.03	0.28	
%RSD	14.89	0.29	0.26	1.54	
No of measurements	6	6	6	6	
Theoretical value	-	67.5	10.7	21.8	100.00

Material A5

Measurement	%N	%C	%H	%O	Sum
1	0.10	42.64	6.97	13.99	
2	0.08	42.19	6.93	13.55	
3	0.08	42.44	6.99	13.22	
4	0.08	42.87	7.04	13.03	
5	0.08	42.73	7.01	13.63	
6	0.07	42.69	7.08	13.15	
Measured average	0.08	42.59	7.00	13.43	63.10
Standard deviation	0.01	0.24	0.05	0.36	
%RSD	11.83	0.57	0.74	2.69	
No of measurements	6	6	6	6	
Theoretical value	-	-	-	-	

Material A6**Fout! Ongeldige koppeling.**

Material A7

$C_{20}H_{38}O_2$					
Measurement	%N	%C	%H	%O	Sum
1	0.08	76.98	12.30	10.11	
2	1.18	76.99	12.39	9.49	
3	0.12	77.61	12.44	9.66	
4	0.61	76.49	12.22	9.98	
5	0.98	76.60	12.36	9.81	
Measured average	0.59	76.93	12.34	9.81	99.09
Standard deviation	0.50	0.44	0.08	0.25	
%RSD	83.59	0.57	0.69	2.51	
No of measurements	5	5	5	5	
Theoretical value	-	77.4	12.26	10.32	100.00

Material A8

Measurement	%N	%C	%H	%O	Sum
1	0.10	77.28	11.84	10.47	
2	0.10	77.53	11.96	10.40	
3	0.11	76.51	11.65		
4	0.09	77.01		10.70	
5	0.10	77.36	11.91	10.71	
6	0.13	77.64	11.94	10.63	
Measured average	0.10	77.22	11.86	10.58	99.77
Standard deviation	0.02	0.41	0.12	0.14	
%RSD	14.87	0.53	1.05	1.33	
No of measurements	6	6	5	5	
Theoretical value	-	-	-	-	

Material A9

$C_{30}H_{62}$					
Measurement	%N	%C	%H	%O	Sum
1	0.12	85.50	14.83	0.26	
2	0.11	85.92	14.92	0.46	
3	0.16	85.26	14.73	0.23	
4	0.09	86.42		0.34	
5	0.07	86.10	15.00	0.44	
6				0.34	
Measured average	0.11	85.84	14.87	0.35	101.05
Standard deviation	0.03	0.46	0.12	0.09	
%RSD	30.83	0.54	0.79	26.82	
No of measurements	5	5	4	6	
Theoretical value	-	85.3	14.7	-	100.00

Material A10

Measurement	%N	%C	%H	Sum
1	0.03	42.21	6.95	
2	0.04	42.55	6.73	
3	0.03	42.42	6.92	
4	0.04	42.39	7.00	
5	0.04	42.50	6.95	
6	0.04	42.41	6.93	
7	0.03	42.50	7.02	
Measured average	0.04	42.42	6.93	49.39
Standard deviation	0.01	0.11	0.09	
%RSD	14.07	0.26	1.36	
No of measurements	7	7	7	

Material B

Matt Paint					
Measurement	%N	%C	%H	%O	Sum
1	1.16	10.52	4.36	42.12	
2	0.79	10.54	4.25	40.84	
3	0.29	10.30	4.32	42.00	
4	1.70	10.30	4.31	41.23	
5	1.24	10.42	4.28	41.77	
6	1.22	10.55	4.28	40.92	
7	1.42	10.63	4.13		
Measured average	1.12	10.47	4.28	41.48	57.34
Standard deviation	0.46	0.13	0.07	0.56	
%RSD	40.92	1.22	1.68	1.34	
No of measurements	7	7	7	6	

Material C1-1

bio solvent					
Measurement	%N	%C	%H	%O	Sum
1	0.32	84.53	16.26	<0.1	
2	0.39	83.60	16.02	<0.1	
3	0.53	84.43	16.24	<0.1	
4	0.22	82.84	16.14	<0.1	
5	0.21	83.62	16.28	<0.1	
Measured average	0.34	83.81	16.19		100.33
Standard deviation	0.13	0.69	0.11		
%RSD	40.19	0.83	0.67		
No of measurements	5	5	5		

Material C2-1

bio solvent					
Measurement	%N	%C	%H	%O	Sum
1	1.20	84.51	14.99	<0.1	
2	1.03	83.15	15.01	<0.1	
3	1.12	84.17	15.31	<0.1	
4	1.11	85.03	15.41	<0.1	
5	1.39	84.06	15.09	<0.1	
Measured average	1.17	84.18	15.16		100.52
Standard deviation	0.14	0.69	0.19		
%RSD	11.89	0.82	1.24		
No of measurements	5	5	5		

Material C3-1

bio solvent					
Measurement	%N	%C	%H	%O	Sum
1	1.18	83.37	14.94	<0.1	
2	1.21	83.66	15.07	<0.1	
3	1.14	84.56	15.32	<0.1	
4	1.39	84.04	15.23	<0.1	
5	0.83	84.43	15.04	<0.1	
Measured average	1.15	84.01	15.12		100.28
Standard deviation	0.20	0.50	0.15		
%RSD	17.60	0.60	1.00		
No of measurements	5	5	5		

Material C4-1

bio solvent					
Measurement	%N	%C	%H	%O	Sum
1	1.44	84.95	15.16	<0.1	
2	1.31	84.53	15.24	<0.1	
3	1.22	85.03	15.27	<0.1	
4	1.53	84.62	15.13	<0.1	
5	0.90	84.54	15.09	<0.1	
Measured average	1.28	84.73	15.18		101.19
Standard deviation	0.25	0.24	0.08		
%RSD	19.17	0.28	0.50		
No of measurements	5	5	5		

Material C5-1

bio solvent					
Measurement	%N	%C	%H	%O	Sum
1	1.28	84.09	15.28	<0.1	
2	1.75	84.35	15.25	<0.1	
3	1.64	84.37	15.27	<0.1	
4	1.09	84.68	15.31	<0.1	
5	1.75	84.27	15.23	<0.1	
Measured average	1.50	84.35	15.27		101.12
Standard deviation	0.30	0.22	0.03		
%RSD	19.99	0.26	0.19		
No of measurements	5	5	5		

Material DA1

sample biobased DA1				
Measurement	%N	%C	%H	Sum
1	2.29	45.05	10.48	
2	1.73	45.03	10.58	
3	0.91	44.97	10.62	
4	0.67	44.70	10.50	
5	1.82	44.71	10.53	
6	1.84	44.29	10.64	
7	1.03	44.22	10.62	
Measured average	1.47	44.71	10.57	56.75
Standard deviation	0.60	0.34	0.06	
%RSD	40.69	0.77	0.61	
No of measurements	7	7	7	

Material DA2

sample biobased DA2				
Measurement	%N	%C	%H	Sum
1	3.10	44.18	10.53	
2	1.86	43.60	10.51	
3	1.29	43.68	10.56	
4	0.99	43.75	10.71	
5	0.99	44.06	10.61	
6	0.98	44.77	10.50	
Measured average	1.53	44.01	10.57	56.11
Standard deviation	0.84	0.44	0.08	
%RSD	54.67	1.00	0.78	
No of measurements	6	6	6	

Material DB1

sample biobased DB1				
Measurement	%N	%C	%H	Sum
1	1.72	40.61	10.86	
2	2.78	40.53	10.85	
3	2.30	40.08	10.99	
4	1.54	39.67	11.05	
5	3.00	40.08	10.85	
6	3.60	40.02	10.49	
Measured average	2.49	40.16	10.85	53.50
Standard deviation	0.79	0.35	0.19	
%RSD	31.59	0.87	1.78	
No of measurements	6	6	6	

Material DB2

sample biobased DB2				
Measurement	%N	%C	%H	Sum
1	3.71	40.25	10.68	
2	2.67	40.23	10.76	
3	1.56	40.26	10.76	
4	2.37	40.57	10.63	
5	2.32	40.44	10.61	
Measured average	2.53	40.35	10.69	53.56
Standard deviation	0.78	0.15	0.07	
%RSD	30.75	0.37	0.64	
No of measurements	5	5	5	

Material DC1

sample biobased DC1				
Measurement	%N	%C	%H	Sum
1	0.05	70.53	10.49	
2	0.04	70.78	10.50	
3	0.04	70.56	10.48	
4	0.04	70.61	10.57	
5	0.05	70.30	10.44	
6	0.05	70.49	10.63	
Measured average	0.05	70.54	10.52	81.11
Standard deviation	0.00	0.16	0.07	
%RSD	5.43	0.22	0.67	
No of measurements	6	6	6	

Material DC2

sample biobased DC2				
Measurement	%N	%C	%H	Sum
1	0.08	70.62	10.05	
2	0.05	70.34	10.50	
3	0.09	70.45	10.26	
4	0.07	70.45	10.23	
5	0.07	70.95	10.21	
6	0.06	70.95	10.37	
Measured average	0.07	70.63	10.27	80.96
Standard deviation	0.01	0.27	0.15	
%RSD	19.28	0.38	1.47	
No of measurements	6	6	6	

Annex B Results from conversion to CO_2 and titration

A1	volume ml	volume	s.g.(24°C)	titration weight	1ste e.p.	2de e.p.	Δ	total mg CO_2	total g Co2	weight sample	C	C% from CHN	Recovery respectively to CHN
	1.0	196.45	1.04	1.04	1.23	2.08	0.85	750	0.8	0.53	38.60%	38.850	99%
	1.0	196.45	1.02	1.02	1.66	2.51	0.84	742	0.7		38.19%	38.850	98%
	1.0	196.45	1.03	1.03	0.79	1.62	0.83	734	0.7		37.79%	38.850	97%
	1.0	200.72	1.03	1.03	0.87	2.28	1.41	1271	1.3	1.01	34.31%	38.850	88%
	1.0	200.72	1.04	1.04	0.99	2.54	1.54	1391	1.4		37.57%	38.850	97%
	1.0	200.72	1.04	1.04	1.07	2.56	1.49	1338	1.3		36.13%	38.850	93%
	1.0	200.72	1.04	1.04	1.00	2.51	1.50	1355	1.4		36.59%	38.850	94%
	1.0	200.72	1.03	1.03	1.01	2.54	1.53	1382	1.4		37.31%	38.850	96%
											37.06%		95%
A2													
	1.0	198.62	1.04	1.04	1.33	2.79	1.46	1300	1.3	0.48	73.85%	77.200	96%
	1.0	198.62	1.04	1.04	1.22	2.67	1.45	1293	1.3		73.48%	77.200	95%
	1.0	198.62	1.04	1.04	0.96	2.40	1.44	1287	1.3		73.14%	77.200	95%
	1.0	198.9	1.04	1.04	0.88	2.58	1.71	1523	1.5	0.55	75.50%	77.200	98%
	1.0	198.9	1.04	1.04	0.96	2.68	1.71	1529	1.5		75.82%	77.200	98%
	1.0	198.9	1.04	1.04	0.88	2.58	1.69	1511	1.5		74.95%	77.200	97%
											74.46%		96%
A3													
	1.0	202.95	1.02	1.02	1.03	2.63	1.60	1459	1.5	0.52	76.53%	73.060	105%
	1.0	202.95	1.02	1.02	0.99	2.60	1.61	1466	1.5		76.86%	73.060	105%
	1.0	202.95	1.02	1.02	0.58	2.17	1.59	1449	1.4		75.99%	73.060	104%
	1.0	199.33	1.05	1.05	0.75	2.26	1.51	1348	1.3	0.506	72.65%	73.060	99%
	1.0	199.33	1.05	1.05	0.66	2.16	1.50	1343	1.3		72.41%	73.060	99%
	1.0	199.33	1.05	1.05	1.15	2.65	1.50	1346	1.3		72.53%	73.060	99%
											74.49%		102%
A4													
	1.0	205.23	1.04	1.04	1.26	2.67	1.41	1299	1.3	0.503	70.45%	71.570	98%
	1.0	205.23	1.04	1.04	1.30	2.67	1.37	1260	1.3		68.32%	71.570	95%
	1.0	205.23	1.04	1.04	0.95	2.36	1.41	1294	1.3		70.18%	71.570	98%
	1.0	207.03	1.03	1.03	1.11	2.50	1.39	1291	1.3	0.515	68.39%	71.570	96%
	1.0	207.03	1.04	1.04	1.13	2.53	1.39	1295	1.3		68.59%	71.570	96%
	1.0	207.03	1.04	1.04	0.98	2.37	1.39	1289	1.3		68.25%	71.570	95%
											69.03%		96%
A7													
	1.0	204.84	1.04	1.04	1.04	2.38	1.33	1226	1.2	0.444	75.32%	76.930	98%
	1.0	204.84	1.04	1.04	0.90	2.24	1.33	1224	1.2		75.21%	76.930	98%
	1.0	204.84	1.02	1.02	0.63	1.94	1.32	1209	1.2		74.28%	76.930	97%
	1.0	204.23	1.04	1.04	0.81	2.31	1.50	1379	1.4	0.515	73.04%	76.930	95%
	1.0	204.23	1.04	1.04	1.00	2.51	1.51	1383	1.4		73.23%	76.930	95%
	1.0	204.23	1.04	1.04	1.25	2.74	1.49	1364	1.4		72.22%	76.930	94%
											73.88%		96%
A8													
	1.0	205.19	1.06	1.06	0.68	2.25	1.56	1440	1.4	0.504	77.90%	77.220	101%
	1.0	205.19	1.04	1.04	1.14	2.63	1.49	1370	1.4		74.13%	77.220	96%
	1.0	205.19	1.04	1.04	0.80	2.34	1.54	1418	1.4		76.71%	77.220	99%
	1.0	205.19	1.04	1.04	0.70	2.25	1.55	1427	1.4		77.21%	77.220	100%
	1.0	206.13	1.05	1.05	0.63	2.12	1.49	1377	1.4	0.502	74.82%	77.220	97%
	1.0	206.13	1.04	1.04	0.70	2.15	1.44	1336	1.3		72.56%	77.220	94%
	1.0	206.13	1.04	1.04	0.85	2.32	1.48	1367	1.4		74.27%	77.220	96%
	1.0	206.13	1.04	1.04	0.62	2.09	1.47	1356	1.4		73.70%	77.220	95%
											75.16%		97%
A9													
	1.0	205.88	1.03	1.03	0.78	2.45	1.67	1544	1.5	0.502	83.86%	84.840	99%
	1.0	205.88	1.04	1.04	0.93	2.61	1.67	1546	1.5		83.98%	84.840	99%
	1.0	205.88	1.05	1.05	0.77	2.45	1.68	1554	1.6		84.42%	84.840	100%
	1.0	203.48	1.04	1.04	1.00	2.63	1.63	1488	1.5	0.496	81.82%	84.840	96%
	1.0	203.48	1.04	1.04	0.90	2.49	1.59	1454	1.5		79.97%	84.840	94%
	1.0	203.48	1.05	1.05	0.59	2.25	1.66	1514	1.5		83.25%	84.840	98%
	1.0	203.48	1.04	1.04	1.00	2.62	1.62	1480	1.5		81.40%	84.840	96%
											82.67%		97%

A5	volume ml	volume	M NaOH	s.g.(24°C)	titration weight	1ste e.p.	2de e.p.	Δ	totaal mg CO_2	totaal g CO2	Weight Sample	C	Recovery respectively to CHN
	1.0	184.5	1	1.03	1.03	1.57	3.31	1.74	1380	1.4	0.99	38.00%	89.2%
	1.0	184.5	1	1.05	1.05	2.57	4.35	1.78	1407	1.4		38.76%	91.0%
	1.0	184.5	1	1.05	1.05	1.18	2.93	1.75	1389	1.4		38.27%	89.8%
	1.0	202.39	1	1.03	1.03	0.99	2.61	1.63	1477	1.5	0.99	40.69%	95.5%
	1.0	202.39	1	1.05	1.05	1.01	2.63	1.62	1470	1.5		40.50%	95.1%
	1.0	202.39	1	1.04	1.04	0.98	2.58	1.60	1457	1.5		40.13%	94.2%
	1.0	201.2	1	1.04	1.04	0.89	2.72	1.83	1656	1.7	1.09	41.44%	97.3%
	1.0	201.2	1	1.04	1.04	0.56	2.38	1.82	1642	1.6		41.10%	96.5%
												39.86%	93.6%

A10	volume ml	volume	s.g.(24°C)	titration weight	1ste e.p.	2de e.p.	Δ	totaal mg CO_2	totaal g Co2	weight sample	C	C% from CHN	Recovery with respect to CHN
	1.0	202.34	1.037	1.037	1071.1	2709.2	1.64	1488	1.5	1.004	40%	42.42	95%
	1.0	202.34	1.042	1.042	1075.5	2708.1	1.63	1483	1.5		40%	42.42	95%
	1.0	202.34	1.041	1.041	1258.1	2909.7	1.65	1500	1.5		41%	42.42	96%
	1.0	190.21	1.045	1.045	1047.4	2880.1	1.83	1565	1.6	1.086	39%	42.42	93%
	1.0	190.21	1.041	1.041	1057.8	2868.4	1.81	1546	1.5		39%	42.42	91%
	1.0	190.21	1.042	1.042	1142.9	2961.0	1.82	1552	1.6		39%	42.42	92%
											39.75%		94%

	volume ml	volume	s.g.(24°C)	titration weight	1ste e.p.	2de e.p.	Δ	totaal mg CO_2	totaal g Co2	weight sample	C	C% from CHN	Recovery respectively to CHN
C2-1													
	1.0	204.9	1.04	1.04	505.6	1725.0	1.22	1121	1.1	0.38	79.56%	84.18	95%
	1.0	204.9	1.036	1.036	353.5	1580.3	1.23	1128	1.1		80.04%	84.18	95%
	1.0	204.9	1.031	1.031	428.4	1635.0	1.21	1110	1.1		78.72%	84.18	94%
											79.44%		94%
C3-1													
	1.0	201.38	1.033	1.033	483.0	1716.5	1.23	1115	1.1	0.38	79.26%	84.01	94%
	1.0	201.38	1.034	1.034	866.8	2127.7	1.26	1140	1.1		81.02%	84.01	96%
	1.0	201.38	1.031	1.031	435.9	1690.7	1.25	1134	1.1		80.63%	84.01	96%
											80.30%		96%
C4-1													
	1.0	205.87	1.035	1.035	988.1	2242.7	1.25	1159	1.2	0.39	81.78%	84.73	97%
	1.0	205.87	1.035	1.035	669.9	1927.8	1.26	1162	1.2		82.00%	84.73	97%
	1.0	205.87	1.041	1.041	279.1	1502.5	1.22	1130	1.1		79.74%	84.73	94%
											81.17%		96%
C5-1													
	1.0	201.44	1.052	1.052	1031.8	2313.2	1.28	1158	1.2	0.38	83.58%	84.35	99%
	1.0	201.44	1.042	1.042	1157.2	2434.0	1.28	1154	1.2		83.28%	84.35	99%
	1.0	201.44	1.04	1.04	1139.1	2417.4	1.28	1156	1.2		83.39%	84.35	99%
											83.42%		99%
C1-1													
	1.0	200.66	1.026	1.026	708.9	1706.1	1.00	898	0.9	0.33	74.45%	83.81	89%
	1.0	200.66	1.026	1.026	823.9	1818.4	0.99	896	0.9		74.24%	83.81	89%
	1.0	200.66	1.029	1.029	795.1	1784.6	0.99	891	0.9		73.87%	83.81	88%
											74.19%		89%

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