Results of the IEA Bioenergy Round Robin on the Analysis of Heteroatoms in Biomass Liquefaction Oils

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ABSTRACT A round robin study evaluating the analysis of biomass liquefaction oils (BLOs) from fast pyrolysis and hydrothermal liquefaction (HTL) was performed, receiving data from fourteen laboratories in seven countries in order to assess the current status of analytical techniques for the determination of nitrogen, sulfur, and chlorine content in BLOs and evaluate potential differences in origin (i.e. fast pyrolysis vs HTL). The BLOs were produced from a range of feedstocks including pine, mixed softwoods, forest residues, micro-algae, miscanthus, and wheat straw to cover a variety in nitrogen, sulfur, and chlorine content and speciation. Nine samples were distributed, comprised of eight separate BLOs and one blind duplicate produced by five producers. The samples were analyzed for water, carbon, hydrogen, nitrogen, sulfur, and chlorine content. No analytical test method was mandated; laboratories were encouraged to utilize whichever method they determined would be most applicable, relying on the existing body of BLO literature as a guide. The results of this round robin study are presented in this paper. The results of the carbon, hydrogen, and water measurements as reference analyses had relative standard deviations (2.9%, 3.5, and 5.6%, respectively) that were comparable to those found in past round robin studies on fast pyrolysis bio-oil. The analysis of nitrogen, sulfur, and chlorine showed higher levels of variability. Laboratories mostly chose the same method for water, carbon, hydrogen and nitrogen determination whereas there were a variety of methods chosen for sulfur and chlorine determination. The results suggest that specific analytical methods for the determination of nitrogen, sulfur, and chlorine should be further refined to ensure reproducible and accurate results for BLO analysis due to their importance on emissions, material selection, and catalyst activity.

1. INTRODUCTION

Solid biomass can be liquefied using a range of technologies including fast pyrolysis, hydrothermal liquefaction (HTL), and solvothermal liquefaction.[1–3] In pyrolysis, biomass is thermally decomposed in environments containing no or very limited amounts of O_2 and can yield a pyrolysis oil or bio-oil. In typical fast pyrolysis, dry biomass (> 90 wt.% solids content) is heated to about 400 – 600 °C and vapour residence times are limited to the order of seconds or less. The biomass thermal decomposition products are quenched, forming a liquid referred to as fast pyrolysis bio-oil (FPBO).[4,5] In hydrothermal liquefaction, wet biomass (< 40 wt.% solids content) is processed in hot compressed water at temperatures around 250 – 374 °C and pressures of 100-220 bar, creating a liquid referred to as HTL bio-crude (often bio-crude for short).[6] In this study, all of the above-mentioned liquids will be referred to collectively as biomass liquefaction oils (BLOs).

Ultimately, inter-laboratory studies of test methods (i.e. round robin testing) is one component of a process that allows for the standardization of these unique renewable liquid fuels to occur. Pyrolysis oil standardization has occurred to some degree. ASTM International has published the standard ASTM D7544 *Standard specification for pyrolysis liquid biofuel* that specifies a set of properties for pyrolysis liquid derived from biomass to be used as fuel in boilers. Although the ASTM standard does not prescribe that the pyrolysis liquid biofuel must come from fast pyrolysis, the specifications do represent properties that are achievable in a fast pyrolysis process. Likewise, CEN has standards and technical reports on the use of FPBO in boilers, engines and turbines (EN 16900 and CEN/TR 17103:2017). In order to meet these standard specifications, these properties must be quantified by standard analytical methods (e.g. ASTM E203 Standard test method for water using volumetric Karl Fischer titration). Previous international collaborations and round robins, such as those detailed later in this article, have been critical for establishing appropriate test methods for the standardization of pyrolysis oils from biomass.

Thermally liquefied biomass from hydrothermal liquefaction (i.e. bio-crudes), have not seen the same level of standardization. Furthermore, to the authors' knowledge, there are no previously published international inter-laboratory studies on the analysis of hydrothermal bio-crudes. These liquids share some but not all of the characteristics of FPBO. Just as there has been and there continues to be a need for systematic testing of bio-oils for the further development of standards, there is a need to begin developing the data that will help enable the standardization of bio-crudes. As an example, among the differences between bio-oils and bio-crudes, nitrogen content can be elevated in bio-crudes derived from some feedstocks such as algae (see Table 1).

For the purposes of this study, the term heteroatom has been used to refer to nitrogen, sulfur or chlorine. While oxygen is commonly considered a heteroatom, in the context of BLOs, it is inherent to the chemical structure of these liquids. Further, it is typically determined 'by difference', instead of directly measured. In contrast, heteroatoms such as nitrogen, sulfur, and chlorine are typically seen as undesirable "extras" and are determined by direct analysis. These components can cause complications for utilization of the liquid or require additional downstream steps to deal with them. As examples, an elevated nitrogen content will have additional catalytic burden during heteroatom removal used to remove oxygen in upgrading bio-oils and bio-crudes,[7,8] and NO_x emissions are strongly related to fuel nitrogen content.[9] Chlorine and sulfur are also well known catalyst poisons; accurate analytical methods are required to be able to quantify load in oils and prepare for catalyst treatment.[10] Trace chlorine analysis is also needed for determining the potential for chloride stress corrosion and materials compatibility in equipment, particularly considering the prevalence of austenitic stainless steel in bio-oil and bio-crude handling, upgrading reactors, and potential biomass insertion points into refineries.[11–13] For direct combustion applications of BLOs, such as use as a renewable heating fuel, heteroatoms also play important roles. Excessive chlorine has caused combustion issues with other biofuels including emissions[14] and heat transfer surface corrosion.[15,16] Sulfur in the fuel is the source for SO_2 emissions.[9] Under some regulatory frameworks, due to the importance of these heteroatoms for emissions potential, the heteroatom content in the fuel can be regulated. As an example, the International Maritime Organization (via MARPOL Annex VI) has reduced the allowed sulfur content in fuels from 3.5% to 0.5% and to 0.1% in Sulfur Emission Control Areas, as of 2020.[17–19]

Since BLOs are often suggested as alternatives or replacements for petroleum-derived liquids and capacity to conduct analysis of petroleum-derived liquids is relatively widespread, several of the analytical methods commonly used to characterize BLOs are based on existing methods used for petroleum-derived liquids. However, BLOs and petroleum are very different in nature (Table 1).[5,20] Therefore, there has been a need to verify if petroleum methods are applicable, and if not, modify them or develop new ones. This will enable the consistent quantification of BLO properties, providing confidence to the end users and accelerating their use as biofuels.

Table 1. Approximate properties of BLOs and petroleum fuel oil, as wet basis.

Property	**Bio-crude (algal)**	**Bio-crude (wood)**	**Bio-oil (wood)**	**Fuel oil (petroleum)**
Carbon (wt. %)	65 – 80	70 – 82	40 – 55	82 – 87
Hydrogen (wt. %)	7 – 11	6 – 8	7 – 8	11 – 15
Oxygen (wt. %)	10 – 20	10 – 25	40 – 55	0 – 1
Water (wt. %)	5 – 15	3 – 10	15 – 30	0 – 1
Nitrogen (wt. %)	1 – 10	0 – 1	0.0 – 0.5	0 – 1
Sulfur (wt. %)	0 – 2	0.0 – 0.5	0.0 – 0.1	0 – 5
Density at 15 °C (kg/L)	0.95 – 1.1	0.95 – 1.1	1.1 – 1.3	0.82 – 1.02

Lower Heating Value (MJ/kg)	30 – 37	30 – 38	13 – 18	38 – 44
Kinematic Viscosity at 40 °C (cSt)	100 – 5000	500 – 1,600,000	15 – 100	1 – 1000

Efficacy of standard hydrocarbon oil analyses have been tested upon bio-oils[21–25] and modifications have been suggested when needed. The first analytical round robin study for pyrolysis oils under the IEA (International Energy Agency) was performed in 1994 by McKinley, Overend and Elliott.[26] This established that EN95 for xylene distillation cannot be used for the determination of water content of FPBO due to over reporting the water content because of its inability to distinguish the volatile, water-soluble fraction from the water itself. The recommendation from this study was that Karl-Fischer titration was a suitable method for water content analysis of FPBO.

In 1997, two round robin studies were commissioned, the first from the EU PyNe (Pyrolysis Network),[27] and a second from IEA PYRA (Pyrolysis Activity).[28] Conclusions from both of these were that for pyrolysis oil, analytical precision for carbon, hydrogen, density, and water (by Karl-Fischer) were good. However, analytical variations were high for the analysis of nitrogen, viscosity, pH, and solids content.

In 2004, an analytical round robin study was performed by the IEA-EU PyNe cooperation, where four different biomass sourced FPBOs were analyzed by twelve laboratories.[29] This demonstrated that most of the physical and elemental analyses had sufficient accuracy, and included carbon, hydrogen, water, solids content, pH, and viscosity, while it was found that nitrogen and physical stability tests were not as accurate.

In 2011, a round robin study was performed on bio-oils analyzing viscosity and stability and an accelerated aging method for evaluation of long-term stability during storage.[30]

In 2015, a round robin study analyzed FPBO for their chemical composition, representing a first attempt to evaluate methods for carbonyl quantification, carboxylic and phenolic acid numbers, aliphatic, phenolic and carboxylic –OH functional group quantification, and quantification of target analytes by GC-MS.[31] That same year a large round robin was performed by Petrolab GmbH for CEN/TC 19, wherein seventeen laboratories completed analysis of a selection of as-marketed FPBO.[32] A total of fourteen tests were performed with prescribed methods and the data from which were used to produce Annex C in EN 16900.

The present article reports the results of the recent round robin study coordinated within the activities of IEA Bioenergy Task 34 – Direct Thermochemical Liquefaction. Several BLOs produced by different technologies and from different feedstocks were distributed for analysis to multiple laboratories. The objective was threefold: 1) assess the best available methods for the determination of heteroatoms in BLOs focusing on nitrogen, sulfur, and chlorine; 2) evaluate bio-crudes from HTL in addition to a range of FPBOs; and 3) identify gaps in current analytical procedures and methods, providing recommendations for further development. Ultimately, the data generated in this and future round robin studies can be used to establish analytical method standards as well as providing input for the BLO specifications.

2. MATERIALS AND METHODS

2.1 DESCRIPTION OF BLO SAMPLES

In this round robin study, eight BLOs were sourced from different countries and were produced via fast pyrolysis or hydrothermal liquefaction using a range of different feedstocks (Table 2). The BLOs from the suppliers were collected in a single location where a sub-sample of each BLO was placed in 20 mL vials. The lot of BLO that was initially sub-sampled to produce sample set F was later sub-sampled in a second sub-sampling campaign to provide a blind duplicate, which was designated as sample set I. Pyrolysis oils were sub-sampled by wide-mouth pipet after coming to room temperature and agitated vigorously. Hydrothermal liquefaction samples were similarly sub-sampled after heating to 65 °C and agitated vigorously. Macroscopic phase separation was reported by some labs for sample D. For samples that could be easily applied to a microscope slide, microscopic images were taken by one participating laboratory in order to support interpretation based on homogeneity considerations. Further homogeneity discussions are contained in the Supporting Information.

Table 2. Sample ID with feedstock and technology used to produce the BLOs.

Identifier	**Feedstock**	**Liquefaction Technology**
A	Forest residue – mix of softwoods	Fast Pyrolysis
B	Micro algae	Hydrothermal liquefaction
C	Pine	Fast Pyrolysis
D	Wheat straw	Fast Pyrolysis
E	Forest residue pine	Hydrothermal liquefaction
F and I [a]	Miscanthus	Fast Pyrolysis
G	Softwood (mostly pine)	Fast Pyrolysis
H	Wood mix (pine, forest residue pine, hybrid poplar)	Fast Pyrolysis

[a] Blind Duplicate

The institutions that kindly contributed with BLOs were:

- BTG Biomass Technology Group, Enschede, The Netherlands
- CanmetENERGY, Ottawa, Canada
- Karlsruhe Institute of Technology, Karlsruhe, Germany

- National Renewable Energy Laboratory, Golden, United States of America
- Pacific Northwest National Laboratory, Richland, United States of America

2.2 PARTICIPATING LABORATORIES

Fifteen laboratories agreed to take part in the round robin study and fourteen of those laboratories returned results. The participating laboratories self-identified as having experience handling and characterizing BLOs. Some laboratories granted permission to acknowledge their name while some chose to remain anonymous. Those that granted permission to acknowledge their name, in alphabetical order (not correlated to Laboratory number), were:

- CanmetENERGY, Devon, Canada
- CanmetENERGY, Ottawa, Canada
- German Biomass Research Center, Leipzig, Germany
- KTH Royal Institute of Technology, Stockholm, Sweden
- National Renewable Energy Laboratory, Golden, United States of America
- Neste Oyj, Kulloo, Finland
- MoRe Research Örnsköldsvik and RISE Processum, Örnsköldsvik, Sweden
- Pacific Northwest National Laboratory, Richland, United States of America
- RISE ETC, Piteå, Sweden
- Scion, Rotorua, New Zealand
- Thünen-Institut für Holzforschung, Barsbüttel-Willinghusen, Germany
- VTT Technical Research Centre of Finland, Espoo, Finland

Not all laboratories provided results for all analytes. Each laboratory was shipped 20 mL of each sample in July of 2018. Laboratories were asked to record date of receipt and condition of samples.

Some of the sample packages were tampered with during shipping; this is suspected to be due to customs control.

2.3 ANALYTICAL METHODS AND INSTRUCTIONS

A document outlining handling and general testing instructions was sent to each laboratory detailing purpose, storage and disposal procedures, analysis considerations, and reporting requirements. Laboratories were instructed to analyze the samples only after adequate agitation to ensure homogeneity, and to (when possible) attempt to use pasture pipettes or large bore syringes to ensure that solid components in the BLO samples were included in analytical aliquots.

The laboratories were requested to analyze water content, carbon, hydrogen, nitrogen, sulfur, and chlorine. Specific analytical test methods were not prescribed to the laboratories. Each was allowed to use the method that they typically use for BLOs, and encouraged to report multiple methods, if available. If more than one method was used by a laboratory, it is reported by adding a letter "B" to the laboratory identifier. For example, laboratory 12 reported results via two methods for sulfur, the additional results are indicated throughout this report as results from Lab 12B.

2.4 DATA REPORTING

After the completion of the analyses, laboratories filled in a supplied reporting template and returned all the data to the study coordinator. Any errors suspected in the data were resolved by contacting the laboratory for confirmation of results. Laboratories were requested to provide a description of the method and, if applicable, a standard test method identifier (e.g. ASTM or EN number). Three months elapsed from the shipment of samples to receiving the last set of results (July-October 2018).

2.5 STATISTICAL ANALYSIS

Statistical analysis was performed using R statistical software. Laboratory results of '0' or reported as less than the Limit of Quantification (LOQ) or Minimum Detection Limit (MDL) were dropped prior to analysis. Outlier results were determined using Rosner test;[33] a maximum of the lesser of 10% or three results were excluded for each sample test result set.

The results from this study are presented as a "beeswarm" box-whisker plot. In a box-whisker plot, the mean of all results is represented by the heavy horizontal line in the grey box. The box itself covers from the 25th to 75th percentile of results. The vertical lines above and below the box terminate at a cross bar, representing the largest and smallest value within 1.5 times the interquartile range, that is, the range that the box covers. As individual results would overlap, they are plotted with some randomly applied horizontal separation to ease visualization.

3. RESULTS AND DISCUSSION

The compiled results of the analysis (with outliers removed) are shown below in Table 3. Anonymized raw data are provided in the Supporting Information. Table 3 shows that despite the differences in feedstock and producer that many FPBOs had roughly similar elemental compositions. Most FPBOs had between 42 and 46% carbon and all had between 7 and 8% hydrogen. Sample A and D deviated most from the other FPBOs, having lower water content, more carbon, more nitrogen, more sulfur and more chlorine compared the other four (C, F, G, and H). The two HTL bio-crudes, although having similar carbon content, were substantially different in composition of other elements, as would be expected owing to the established differences between HTL bio-crude from algae versus that from woody materials.

Table 3. Average results (wt. %, wet basis) and standard deviations for all parameters and samples (outliers removed).

Sample	**Water**		**Carbon**		**Hydrogen**		**Nitrogen**		**Sulfur**		**Chlorine**	
	Mean	**SD**	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**
A	18.2	0.62	50.2	1.3	7.78	0.16	0.62	0.12	0.043	0.0071	0.0831	0.0065
B [a]	8.14	0.41	71.7	1.5	10.3	0.15	4.92	0.33	0.58	0.10	0.013	0.018
C	21.7	0.80	43.1	0.53	7.55	0.16	0.122	0.069	0.0088	0.0033	0.0068	0.0079
D	13.8	0.96	55.8	0.96	7.21	0.19	1.13	0.11	0.077	0.016	0.0259	0.0085
E [a]	5.1	1.4	72.6	0.97	7.40	0.21	0.304	0.066	0.012	0.0053	0.0063	0.0090
F [b]	20.1	1.2	45.7	0.70	7.52	0.23	0.279	0.079	0.025	0.0050	0.0146	0.0060
G	21.3	0.98	45.0	0.80	7.55	0.20	0.131	0.073	0.0076	0.0034	0.0073	0.0086
H	22.7	1.1	42.8	0.67	7.44	0.26	0.19	0.10	0.011	0.0034	0.0066	0.0070
I [b]	21.4	1.4	45.0	0.65	7.56	0.27	0.173	0.088	0.0092	0.0073	0.0081	0.0085

[a] HTL Bio-Crude Samples

[b] Blind Duplicate Sample

3.1 WATER CONTENT

The results of water analysis are shown in Figure 1. Most laboratories reported water content by ASTM E203 (or similar Karl Fischer volumetric methods) which is the method specified for analysis of pyrolysis oils in ASTM D7544, EN16900 and CEN/TR17103. One lab reported results from ASTM D6304 and one lab specified D6304 method C (coulometric Karl Fischer methods). No significant deviation was noted between laboratories that followed ASTM E203 method for water analysis versus those who followed the other standard Karl Fischer test methods. Laboratories reported difficulty in analyzing sample E due to its viscosity. Despite instructions to heat the HTL samples to 65 °C, some laboratories sampled the BLO by metal spatula, others diluted in dry methanol and reported the corrected results. Water content in FPBO has been previously tested by round robin studies,[26–30] these results are compared to previous studies to determine whether consistent repeatability was met or if there had been any challenging samples. Furthermore, it was important to determine how well the water content of HTL bio-crudes could be assessed.

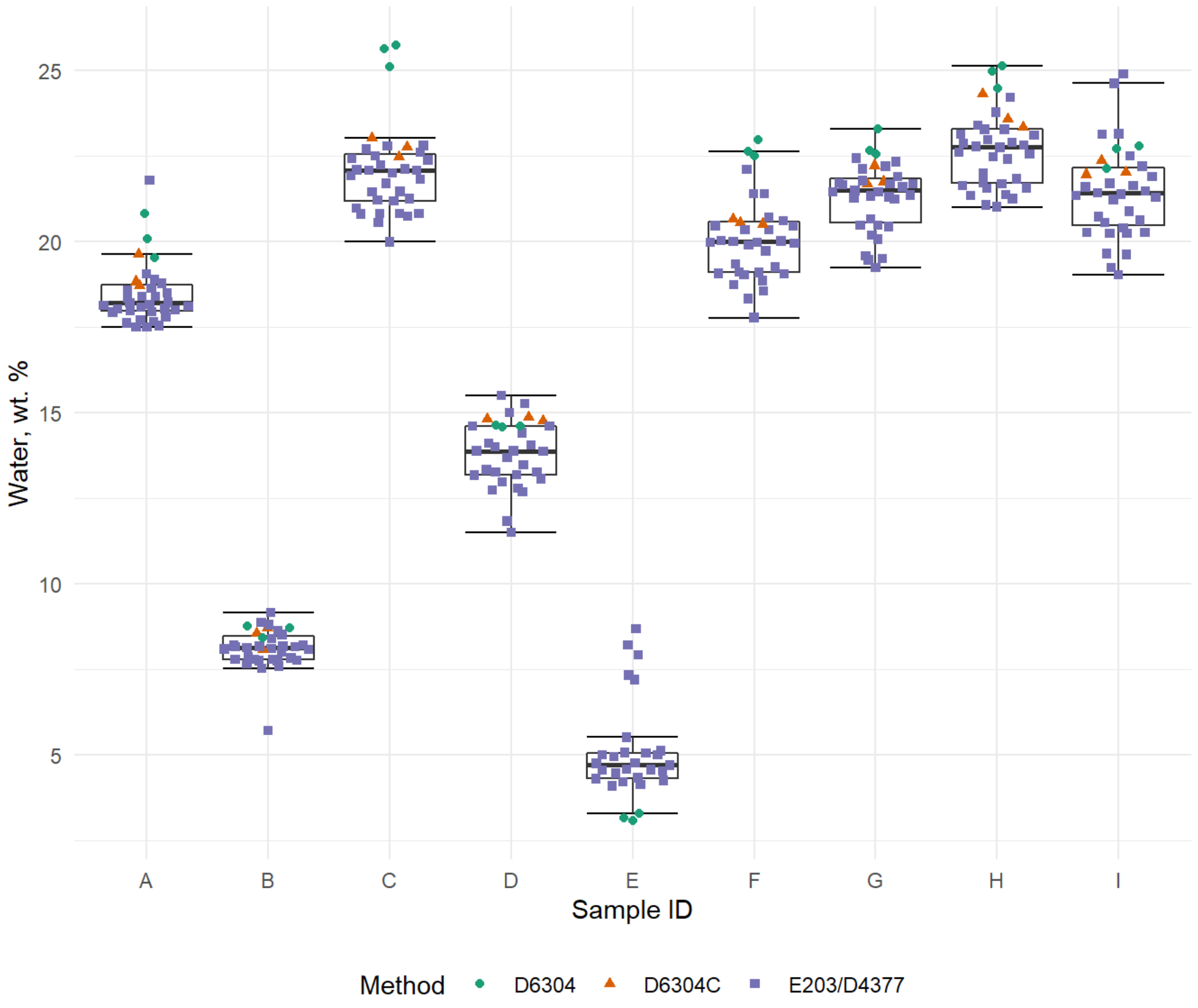

Figure 1. Water content of BLOs as analyzed by 12 laboratories using 3 methods.

Results were, on average, in line with relative standard deviation (%RSD) values similar to those reported in previous round robin studies. The average %RSD for BLO produced by fast pyrolysis was 5.6 %; previous studies report %RSD of 4.9 % for pyrolysis oils.[29] Samples B and E were HTL bio-crude samples. Sample B had 8.1 wt. % and standard deviation of 0.6 (7.2 %RSD). Sample E had an average water value of 5.1 wt. % and standard deviation of 1.4 (28.3 %RSD). This sample shows both increased scatter for water content determination between laboratories, and the relative error between the triplicates within each laboratory. It may be that methods for water content in HTL bio-crudes could be better optimized for the sample type, or that laboratories struggled with the analysis of HTL bio-crudes due to their increased viscosity (see Table 1). Laboratories with experience with FPBOs are likely more familiar with room temperature handling during analysis. However, as HTL bio-crudes are less common in the community, there may be less familiarity with execution of the handling procedures, which indicated that "samples B and E need to be preheated to a flowable state, typically up to 60 °C".

3.2 CARBON AND HYDROGEN

Twelve laboratories reported results for carbon and hydrogen content in BLO. Results were reported as-is, that is, on a wet basis. All laboratories reported ASTM D5291 or ASTM D5373 or similar methods. The results can be seen in Figure 2 for carbon (A) and hydrogen (B). In general, although some individual outliers exist, the results show good agreement between laboratories, surpassing the %RSD results relative to a previous round robin study. These results show %RSD of 2.9 % and 3.5 % for carbon and hydrogen, respectively, while the previous literature results were 3.1 % and 5.0 %.[29]

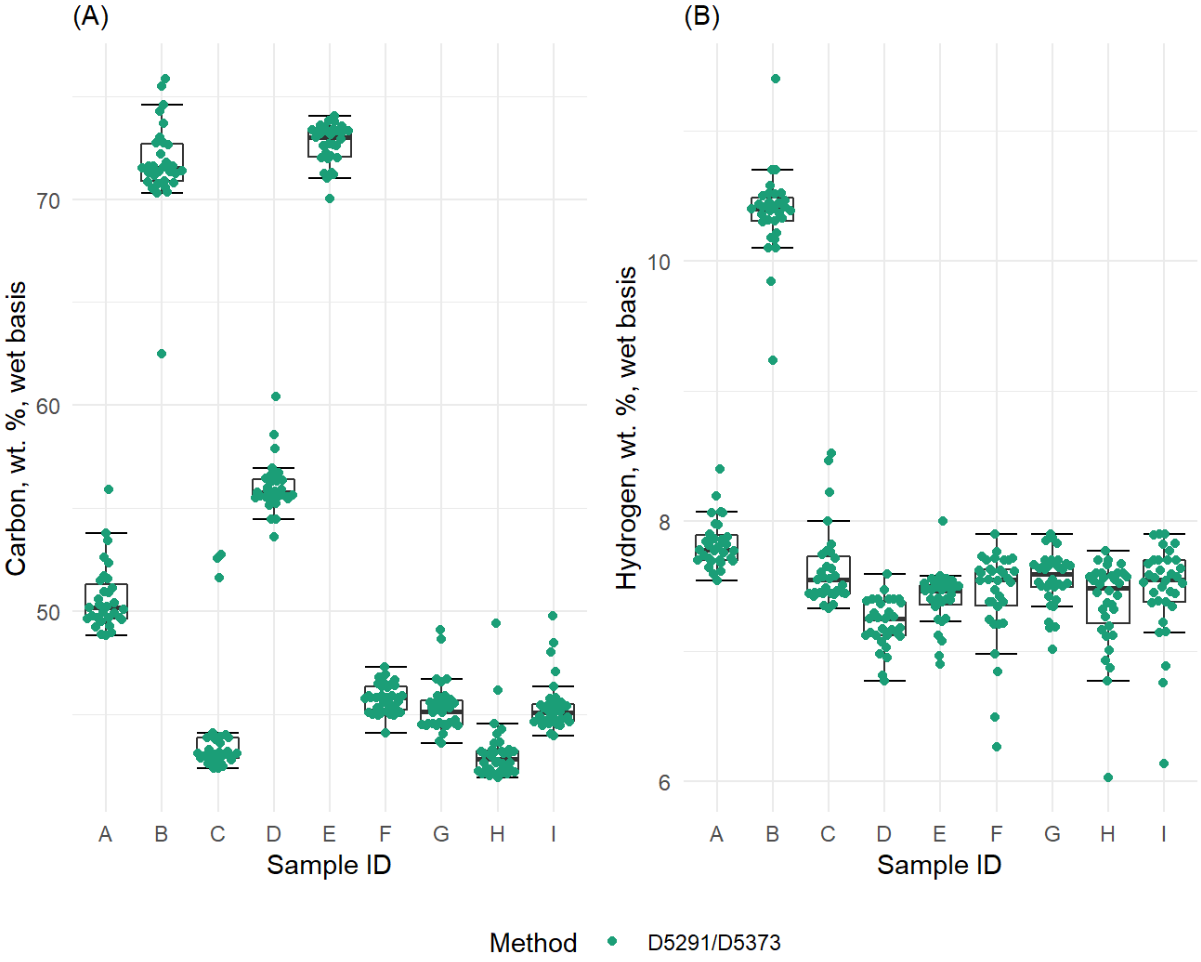

Figure 2. Carbon (A) and hydrogen (B) content of BLOs as analyzed by 12 laboratories. All laboratories used ASTM D5291, D5373 or similar methods.

Results for samples B and E (the HTL bio-crudes) show excellent repeatability for both elements, with %RSD of 2.06 and 1.71 % respectively for carbon, and 1.46 and 2.62 % for hydrogen. This is similar to the reproducibility for ASTM D5291, demonstrating good performance of D5291 and D5373 methods for carbon and hydrogen in HTL bio-crudes.

3.3 NITROGEN

Eleven of the laboratories used a typical CHN elemental analysis method (ASTM D5291, D5373, or a variation) to determine nitrogen content (Table 4). The ASTM D7544 standard has no limit on nitrogen value. Similarly, EN 16900 has no nitrogen limit, but mandates reporting the result by the ASTM D5291 test method.

Table 4. Nitrogen analysis methods used by laboratories.

Method	**Method Detection Technique**	**No of Labs using method**	**Method LOQ (mg/kg)**
ASTM D5291, or similar	TCD	12	1000
(Modified) ASTM D5762	Chemiluminescence	1	40
(Modified) ASTM D4629	Chemiluminescence	1	0.3

Most of the nitrogen results using ASTM D5291 and equivalent methods were grouped together, except for Lab 3, which provided higher values for some samples at low concentrations (Figure 3). More scattering (standard deviation) can be seen for samples at higher concentration, but as expected, they have a lower relative error. For example, sample B has an average value of 4.9 wt. %, a standard deviation of 0.3 wt. %, and a %RSD of 6.3% while sample C has an average value of 0.12 wt. %, a standard deviation of 0.07 wt. %, and a %RSD of 56%. The ASTM D5291 reproducibility statement for nitrogen is a fixed value, and thus a higher %RSD is expected at lower concentrations of nitrogen.

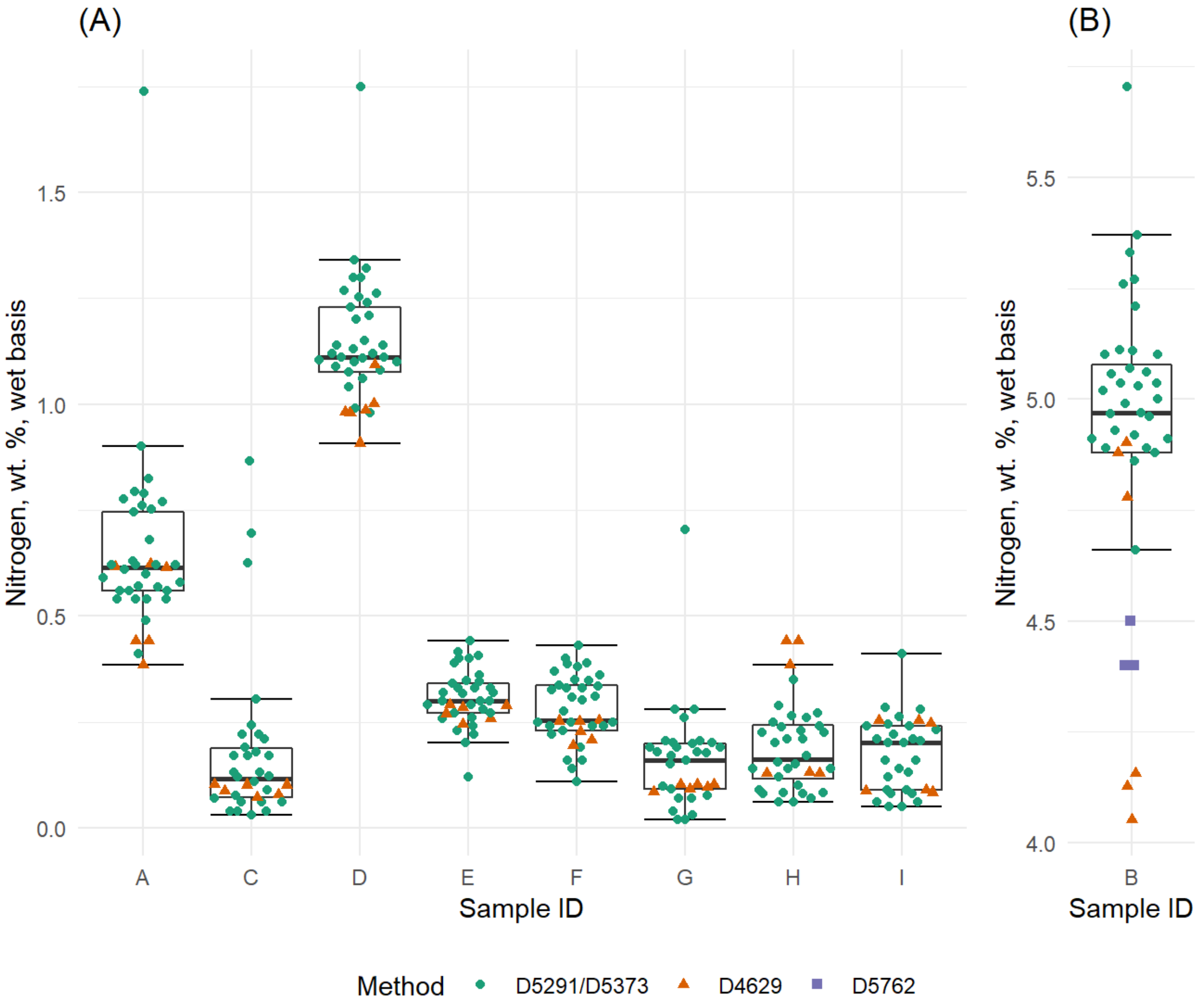

Figure 3. Nitrogen content of BLOs analyzed by 14 laboratories using 3 methods: (A) samples A and C-I, (B) sample B.

Lab 2 used ASTM D5762, a boat-inlet chemiluminescence based method typically used for petroleum liquids, which requires the sample to be diluted in xylene prior to analysis. Xylene is unable to dissolve most BLOs and thus the analysis could not be successfully carried out. Lab 12 also used ASTM D5762, but adapted the method by using methanol as solvent. In this case, the analyses were successful and the results grouped with the other laboratories. This technique is of interest as it can detect nitrogen at lower levels (40 mg/kg) compared to typical elemental analyzers (> 1000 mg/kg).

Lab 6 used ASTM D4629 method based on syringe-inlet oxidative combustion and chemiluminescence detection, diluting the sample in xylene/iso-propanol (1:1 vol.). They indicated that large dilutions needed to be used to not saturate the detector. Unfortunately, they only reported one result and used volumetric based units that could not be compared to the weight-based units of the other laboratories; therefore, their results are not reported in this study. Lab 13 also used ASTM D4629 method, but using toluene/methanol 60:40 (vol.) as solvent. Their results group well with the other laboratories. ASTM D4629 can analyze nitrogen at concentrations as low as 0.3 mg/kg, making this method attractive for samples such as hydrotreated BLOs. However, this method requires syringe addition of the BLO, potentially impacting its ability to deliver representative BLO samples to the analyzer if the BLO contains large solid particles.[29]

As nitrogen content plays a role in NOx emissions from direct combustion of BLOs,[5,9] reliable methods for determining nitrogen content below 1000 mg/kg could be important for jurisdictions with strict NOx emission or fuel nitrogen content limitations. For BLOs containing less than 1000 g/kg, reliable low-level nitrogen measurement could also allow BLO producers to demonstrate low nitrogen content to regulators where monitoring and reporting requirements may differ for low nitrogen content fuels compared to high nitrogen content fuels.

3.4 SULFUR

A total of eleven laboratories reported results for sulfur, using four different method types (Table 5).

It is noted that no laboratories performed ASTM D4294 Test Method for Sulfur in Petroleum and Petroleum Products by Energy Dispersive X-ray Fluorescence Spectrometry despite that method being the preferred method specified in ASTM D7544: Standard specification for pyrolysis liquid biofuel. This method requires matrix matched standards or sample dilution if oxygen content is > 3 wt. %, which is the case for BLO samples. As no certified BLO standards are available, this method cannot be performed as specified. Five laboratories provided data using ultraviolet fluorescence detection (ASTM D5453 or similar). This is similar to the referee method specified in EN 16900 and CEN/TR17103.

Table 5. Sulfur analysis methods as reported by the participating laboratories.

Laboratory	**Method**	**Reported Method LOQ (mg/kg)**
Lab 1	ASTM D5453: Combustion of the sample in oxygen followed by analysis of the gases by UV fluorescence.	1.0
Lab 3	Modified EPA 200.9: Digestion in open vessel followed by ICP-MS.	Not Reported
Lab 4	ASTM D4239: Combustion of the sample in oxygen followed by analysis of the gases by IR detector.	2200 (ASTM Limit)
Lab 7	Schöniger combustion followed by ion chromatography of the collected solutions.	Not Reported
Lab 8	ASTM D5453	1.0
Lab 10	Digestion in CEM MARS5 microwave followed by ICP-OES.	5.0
Lab 11	ASTM D4239/D1552: Combustion of the sample in oxygen followed by analysis of the gases by IR detector.	400
Lab 12	ASTM D5453	1.0
Lab 12B	ASTM D5453 modified: Sample combusted with WO3 promoter in air followed analysis of the gases by UV fluorescence.	Not Reported
Lab 13	ASTM D5453: Using a 60:40 (vol.) toluene/methanol as solvent.	1.0

Lab 15	Samples combusted in bomb calorimeter (DIN EN 14918), followed by ion chromatography of the collected solutions.	Not Reported

The range of methods used include digestion followed by ICP, combustion followed by infrared (ASTM D4239) or ultraviolet fluorescence (ASTM D5453/EN ISO 20846) detection, or combustion followed by ion chromatography of the collected washed solutions, (see Table 5). Results for sulfur analysis are shown in Figure 4. One set of sulfur results are outside the grouping, demonstrating irregular results for both low and high concentration from Lab 3. However, the Digestion/ICP result used by this lab was also used by Lab 10 to generate sulfur results that were consistent with other laboratories. Thus, the outlier sulfur data is less likely due to the ICP method, and more likely stems from systematic sample interaction, such as handling, preprocessing, or calibration. The results of Lab 3 are not considered in the rest of the interpretation of the results. The results of the other laboratories group together with much larger scattering for samples B (HTL of algae) and D (fast pyrolysis of wheat straw).

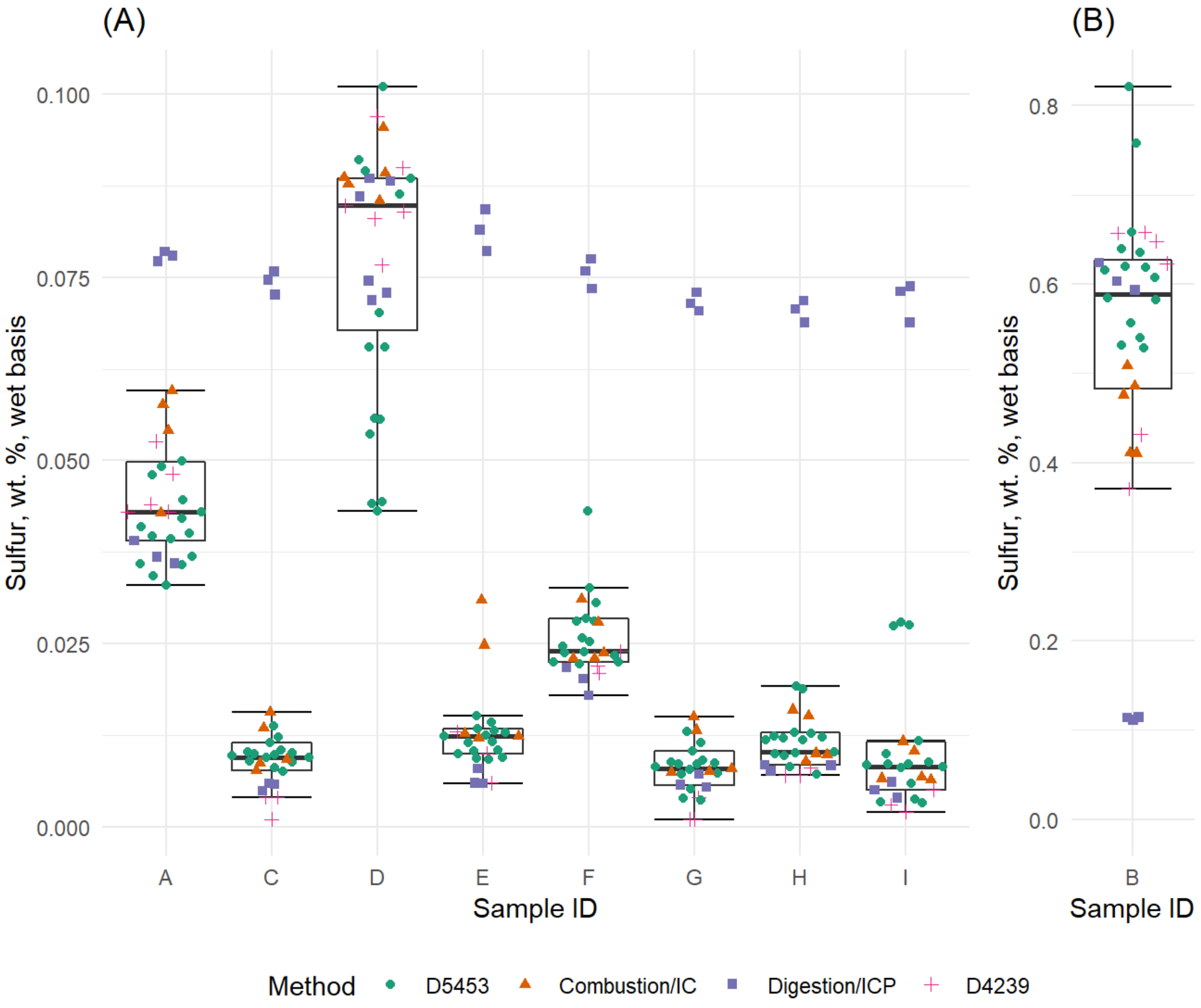

Figure 4. Sulfur content of BLOs analyzed by 11 laboratories using 4 methods: (A) samples A and C-I, (B) sample B.

Of some concern is the fact that samples F and I are supposed to be the same sample (blind duplicate), and thus, should have the same sulfur content. However, the results show very different amounts of sulfur, with sample F averaging 255 mg/kg and sample I, 92 mg/kg. This is discussed further in section 3.6.

It is unfortunate that the results have a wider scatter than what the methods specify, as the accurate determination of sulfur content is required for any use of BLOs as liquid fuels. The ASTM

D7544 requires pyrolysis oils to have a sulfur content under 500 mg/kg to be used in industrial boilers. BLOs as marine fuels will have to meet international sulfur specifications as low as 0.1% or require blending schemes or other routes to meeting the requirements.[17] For some routes to transportation fuels, the sulfur content will poison some low temperature hydrogenation catalysts.[10] All BLOs in this study except for sample B (algae feedstock) and D (wheat straw feedstock) had an inter-lab average sulfur content below 500 mg/kg.

3.5 CHLORINE

Eight laboratories reported results on chlorine content with four main method types employed (see Table 6). No laboratories used any X-ray fluorescence methods, although one (ASTM D4294/EN ISO8754) is mentioned as a possible specification method in the CEN/TR 17103 standard for quality determination of FPBOs. Labs 1 and 2 used a microcoulometry method. They provided almost identical results, showing good consistency between laboratories. This method also has the lowest reported LOQ, between 1 and 5 mg/kg. Microcoulometry detects all halides as chlorine. However, since the results of this method are similar to the ones of the other laboratories, the concentration of the other halides is likely much lower than chlorine in the analyzed samples. Lab 4, 11, 12, and 15 used a bomb calorimeter to combust the samples followed quantification of the ions in the collected washed solutions. Lab 4 quantified chlorine by ion specific electrode analysis, while the other laboratories used ion chromatography. Specific electrode analysis has a higher LOQ of 220 mg/kg. Lab 12 and 15 reported LOQ of 15 and 11 mg/kg, almost as low as microcoulometry method. Lab 11 reported a high LOQ of 100-300 mg/kg even when using ion chromatography quantification. Even though Lab 3 and 7 used ion chromatography, their results were very different from the other laboratories indicating that open-vessel digestion or Schöniger combustion may introduce too much error for the determination of chlorine.

Table 6. Chlorine analysis methods as reported by the participating laboratories.

Laboratory	**Method**	**Reported Method LOQ (mg/kg)**
Lab 1	Combustion of the sample at high temperature and quantifying the halide ions from the combustion gases in a temperature-controlled titration cell (microcoulometry). This method quantifies total halides as chlorine.	5.0
Lab 2	UOP779 (or ASTM D4929-15A or EN 14077-03): Similar to Lab 1.	1.0
Lab 3	Digestion in open vessel followed by ion chromatograph.	Not reported
Lab 4	ASTM D4208: Bomb combustion in calorimeter followed by ion specific electrode analysis of the collected solutions.	220
Lab 7	Schöniger combustion followed by ion chromatography of the collected solutions.	Not reported
Lab 11	EPA Method 5050/9056: Bomb combustion in calorimeter followed ion chromatography of the collected solutions.	100-300 [a]
Lab 12	ISO 18806: Samples combusted in bomb calorimeter, followed by ion chromatography of the collected solutions.	15
Lab 15	Samples combusted in bomb calorimeter (DIN EN 14918), followed by ion chromatography of the collected solutions.	8-11 [a]

[a] Depending on sample size

Based on these results (Figure 5), it appears that both bomb calorimeter followed by ion chromatography and microcoulometry methods provide good results for chlorine determination at levels above 15 mg/kg. Microcoulometry might be preferred as it provides a lower LOQ (1-5 mg/kg) and it is a one-step method, removing possible operator/handling error compared to the two-step bomb calorimeter/ion chromatography method. However, further round robin studies will need to be performed to ensure good repeatability of the methods and to confirm their agreement on chlorine content before any method could be specified in any standard. Accurate chlorine analysis is a particular need for BLO applications such as boilers and hydrotreating, as chlorine is understood to be potentially highly corrosive in end use applications.[12]

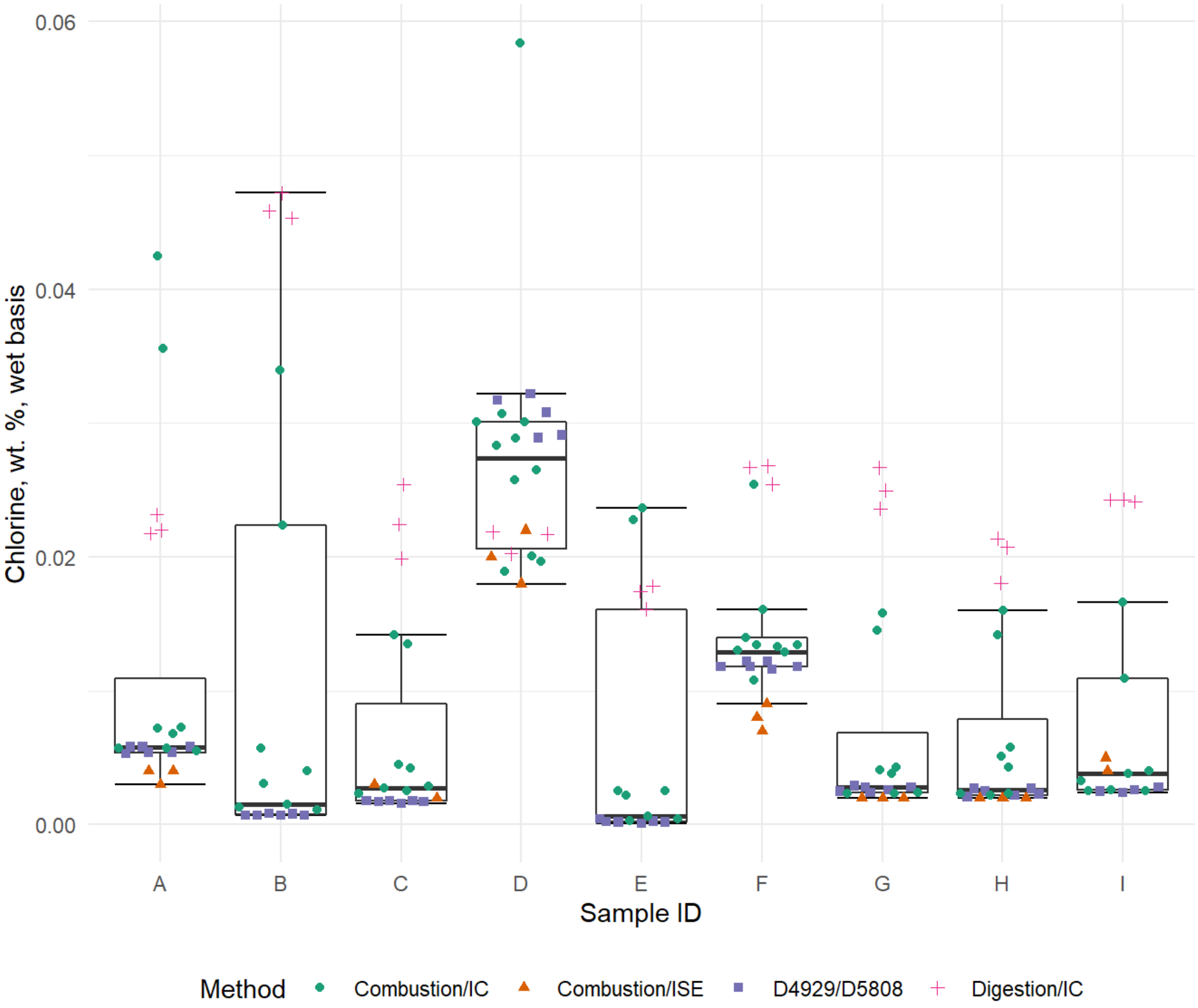

Figure 5. Chlorine content of BLOs analyzed by 8 laboratories using 4 methods.

3.6 BLIND DUPLICATE REPEATABILITY

As previously noted in discussions of sulfur and chlorine, the samples identified as F & I were intended to be blind duplicates. While some analyses appeared to repeat reasonably well (such as carbon and hydrogen), others had obvious variation in the analytical results between these two samples. Statistical evaluation of the result equivalence using the Student's *t* test were performed, the results of which are shown in the Supporting Information. All of the analyses except hydrogen vary by statistically significant amounts (despite large %RSD values for sulfur and chlorine), indicating a strong likelihood of non-equivalent samples analyzed as blind duplicates.

While the exact cause of this variation is unknown, it may result from initial sample preparation technique. Ideally, a large volume of the source miscanthus bio-oil would have been subsampled and each subsample randomly identified as sample F or I. However, because the decision to include a duplicate was made after the sub-samples were made, the subsampling campaign for sample I was performed the week after the campaign to generate samples A through H. Thus, the differences between F and I may be considered a check against sub-sampling technique consistency. As the magnitude of difference was greater for the heteroatoms nitrogen and sulfur, it is possible that inconsistent pre-mixing of the bulk sample between the F and I evolutions resulted in segregation of a minor phase to which sulfur and nitrogen preferentially report in the miscanthus bio-oil sample. If a minor sulfur- and nitrogen-rich phase was more prevalent in sample F as compared to sample I it could lead to the observed results.

4. CONCLUSIONS

This article reports the results of the IEA Bioenergy round robin for the characterization of biomass liquefaction oils (BLOs) focusing on the heteroatoms nitrogen, sulfur, and chlorine. Unlike previous IEA Bioenergy Round Robin studies, this study included biocrude samples prepared by hydrothermal liquefaction in addition to a range of FPBOs in order to consider datasets for analytical method suitability for HTL bio-crudes. Despite the range of different FPBOs tested, the results seemed to show a similar level of variability for each FPBO.

Quantification of carbon, hydrogen, and water content was satisfactory. However, greater relative standard deviation was found for water in HTL samples. The greater relative standard deviation was found in both intra- and inter-lab results. Further refinement of ASTM E203 may be warranted for HTL bio-crudes. Explicit handling procedures that can accommodate this type of samples should be included in analytical procedures to improve the reproducibility.

Three types of nitrogen determination methods were used: organic elemental analysis (ASTM D5291) and two chemiluminescence methods (ASTM D5762 and ASTM D4629). For chemiluminescence-based methods developed for petroleum processes, the use of solvents compatible with BLOs (e.g. toluene/methanol mixtures or methanol alone) was found to be necessary for successful analysis. The typically used ASTM D5291 elemental analysis methods are acceptable when the nitrogen content in the sample is high, (such as the 4.9 wt. % reported for Sample B), but some laboratories indicated difficulties at concentrations below 1 wt.%. The chemiluminescence-based methods can provide more accurate results at low concentrations, with limit of quantification (LOQ) as low as 0.3 mg/kg for petroleum samples. Further development and validation of these methods (including the selection of appropriate solvents) to determine low concentrations of nitrogen in BLOs is recommended.

The participating laboratories used multiple methods to determine sulfur content, with five of them using the ASTM D5453, a UV fluorescence method similar to the EN ISO 20846 method specified by CEN 16900:2017. None of the participating labs chose to use ASTM D4294, the method specified by ASTM D7544-12. The results of all the methods tended to group together, although with relatively large scatter. When analyzing low concentrations of sulfur (<200 mg/kg), the inter-lab relative error was between 30% and 47%, indicating the need to improve analyses at those low concentrations.

Several methods were used to analyze chlorine in BLOs, mostly using a two-stage approach. The results showed the importance of sample handling in between steps. The most promising method was microcoulometry, which provided a low limit of quantification (1-5 mg/kg) and removed possible operator/handling error, as the combustion gases are analyzed immediately without the need of additional sample handling.

With respect to differences in the blind duplicate in samples F and I, it revealed two conclusions. First, reliable, consistent sub-sampling of BLOs can be difficult even under controlled circumstances. Second, that for the blind duplicate to be of value in identifying analytical error, a future blind duplicate set should be prepared by sub-sampling twice the required number of sub-samples of a single BLO, and randomly assigning them to one of two sample identifiers.

Table 7. Summary Findings and Recommendations.

Analyte	**Consensus Method**	**Suitability for FPBO**	**Suitability for HTL Bio-crude**	**Recommended R&D needs**
Water	ASTM E203	Suitable	Suitable (with the recognition that %RSD may be higher due to the lower water content of bio-crudes).	Potential further refinement of ASTM E203 for HTL bio-crudes.
Carbon	ASTM D5291, D5373 or similar	Suitable	Suitable	None
Hydrogen	ASTM D5291, D5373 or similar	Suitable	Suitable	None
Nitrogen	ASTM D5291	LOQ and typical concentrations are often close. Suitability depends on acceptable error level.	Suitable for high N-containing bio-crude. For wood derived bio-crude, similar result as for bio-oil.	The accepted method has a relatively high LOQ for N (1000 mg/kg). Complete an interlaboratory study of methods with LOQs below 1000 mg/kg.

Sulfur	No consensus method. ASTM D5453 (or a modified D5453) was most common.	Cannot conclude	Cannot conclude	Determine which method appears most promising and complete interlaboratory study to assess suitability.
Chlorine	No consensus method. Most common approach was to combust sample followed by ion chromatography.	Cannot conclude	Cannot conclude	Complete interlaboratory study to assess suitability and performance of microcoulometry.

ASSOCIATED CONTENT

Supporting Information.

The following files are available free of charge.

RR2018_All_Data.csv – all reported data

RR2018_Homogeneity_Tables.docx – microscope images of oils and statistical tables

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