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## Article

# Demineralization of *Miscanthus* Biocrude Obtained from Catalytic Hydrothermal Liquefaction: Conditioning through Acid Washing

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**Abstract:** In this contribution, we successfully applied demineralization (i.e., solvent-assisted separation and acid washing) for the removal of carbonaceous solids and inorganics from a biocrude obtained from the catalytic hydrothermal liquefaction (HTL) of *Miscanthus*. The experimental results of all six employed acids showed that 0.1 M H<sub>2</sub>SO<sub>4</sub> was the most effective and significantly reduced metallic (Fe by 93.9%, <15 µg/g and Mg by 95.6%, 2.1 µg/g) and ash content (by 92.7% to 337 µg/g) from the already filtered biocrude. The utilized demineralizing agents caused a loss of nitrogen and of organic carbon (1% total organic carbon (TOC) and 0.058% total nitrogen (TN) in 0.1 M H<sub>2</sub>SO<sub>4</sub>). Gas chromatography-mass spectrometry (GC-MS) results clarified the nature of this loss, showing that 54% of ketones and 39% of alcohols were removed when 0.1 M H<sub>2</sub>SO<sub>4</sub> was employed. Furthermore, FT-IR spectra remained the same before and after acid washing without affecting any functional groups. This work therefore proposes demineralization as a viable route for the removal of high inorganic content from lignocellulosic HTL biocrudes.

**Keywords:** hydrothermal liquefaction; *Miscanthus* biocrude; solvent-assisted separation; acid washing; demineralization



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## 1. Introduction

The hydrothermal liquefaction (HTL) of biocrudes from diverse biomass feedstocks is currently being researched as an environmentally friendly alternative to fossil crude oil, as it is sustainable and originates from non-edible sources [1]. During the HTL process, wet biomass can be directly converted into a black viscous product, referred to as biocrude, at temperatures of 250–450 °C and pressures of 10–35 MPa without an energy-intensive pre-drying step [2,3]. However, biocrudes produced by HTL cannot be utilized directly as drop-in alternatives to refined fuels [4,5], as they contain considerable concentrations of inorganic/carbonaceous solids (~0.1–38%) [6–8] and heteroatoms, primarily oxygen (O) and nitrogen (N) [2,7]. Therefore, further upgrading (suitable catalytic hydroprocessing) of HTL biocrudes is indispensable to obtain drop-in biofuels (i.e., diesel, jet fuel, etc.). In this regard, the in situ uptake of inorganics on the hydrometallization catalyst surface is limited because of a physical barrier (the catalyst can retain fewer ppm of inorganics during continuous hydroprocessing, because the heterogeneous catalysts are surface limited). For this reason, high inorganic content in HTL biocrudes should preferably be removed prior to hydroprocessing; otherwise, these inorganics will deposit on the catalyst and poison active catalyst sites [9]. Catalyst deactivation and reactor bed plugging due to metal deposition are quite well known in HTL biocrude hydroprocessing [10]. Thereby, serious efforts are needed to effectively remove the high amount of inorganics present in HTL biocrudes prior to hydroprocessing.

At Pacific Northwest National Laboratory (PNNL), most of the inorganic solids are already removed from biocrude during HTL, by means of in situ filtration at high temperature and high pressure (350 °C and 20.7 MPa) [11]. The inorganic removal efficiency of PNNL's method is not stated, but their most recent publications show that the produced sludge biocrudes have an ash content from 600–4600 µg/g [12,13]. Besides PNNL in-line filtration, Biofuels B.V. [14] reported solvent-assisted separation (polar solvent) as an alternative for the removal of filterable inorganic solids from the given biocrude. Furthermore, Steeper Energy ApS [15,16] dissolved the lignocellulosic HTL biocrude in a suitable polar solvent, and subsequently washed it with an acid solution, successfully reducing the ash and metallic content down to 370 µg/g and 41 µg/g respectively. As the presence of inorganics in HTL biocrudes [10] has adverse effects on long-term hydrotreatment, options such as demineralization should be explored in order to lower the concentration of metals to a more satisfactory level.

In fossil crudes, sulfuric acid has been used to remove metallic content for over one hundred years, while effective results have also been achieved by demineralization with other acids such as maleic acid [17,18]. This knowledge cannot necessarily be directly transferred to biocrudes, however. The oxygenated biocrudes are more polar than fossil crudes, and the polarity difference between the oil and demineralizing agents (acids) will thus be low, which could complicate the subsequent separation, primarily due to coalescence [15]. Nevertheless, demineralization by acid leaching seems to be one of the most promising options.

The present literature shows that some research has been done on the demineralization of biomass feedstocks as a pre-treatment step prior to the HTL process. Microalgae, macroalgae and lignocellulosic feedstocks with varying metal content have been washed with different organic and inorganic acids, reducing up to ~95% of inorganics, although with a significant loss of organics in the biomass [19–26]. This pre-treatment enhanced the biocrude properties to some extent but a considerable amount of ash (i.e., inorganics) content was still documented in produced biocrudes. Alternatively, Steeper Energy ApS [15,16] reported the successful demineralization of lignocellulosic HTL biocrude by utilizing a 0.1 M solution of acetic acid, citric acid and hydrochloric acid in the presence of methyl ethyl ketone (i.e., a polar solvent). Moreover, Steeper Energy ApS documented the reduction of ash and metallic content from 3.7% to 0.03% and 850 µg/g to 41 µg/g, respectively. However, they did not discuss or report the effect of the demineralization of HTL biocrude [15,16].

The aim of this study was to explore the applicability of the solvent-assisted separation of carbonaceous and inorganic solids, and thereafter investigate the practicability of the demineralization (acid-washing) of *Miscanthus* biocrude. The main goal was to study the effect of different solvents and the extent of metal removal by utilizing six different organic and inorganic acids. The results showed that demineralization efficiency was greatly dependent on the type of acid employed. The demineralized biocrude was also characterized by elemental analysis and Fourier-transform infrared (FT-IR) spectroscopy to investigate the influence of acid washing on the properties of *Miscanthus* biocrude.

## 2. Materials and Methods

### 2.1. Materials

*Miscanthus* HTL biocrude was received from Aarhus University, Denmark, and was produced by processing under sub-critical conditions at 22 MPa and 350 °C in a continuous pilot-scale HTL plant with a throughput of up to 100 L/h, in the presence of KOH as a catalyst [7].

For the demineralization procedure, citric acid (CA, 99%) and maleic acid (MA, ≥99%) were bought from Sigma-Aldrich; acetic acid (AA, 32%) was obtained from Borup Kemi, sulfuric acid (SA, 98%) and hydrochloric acid (HA, 37%) were acquired from Honeywell Fluka™ and phosphoric acid (PA, 85%) was purchased from VWR Chemicals (Darmstadt, Germany).

## 2.2. Physical Separation

Due to the high concentration of carbonaceous and inorganic solids, the raw biocrude (as received) underwent solvent-assisted separation. This physical separation of carbonaceous and inorganic solids was done by dissolving the raw biocrude in either acetone (Acet.), 2-butanone (methyl ethyl ketone, MEK) or ethanol (EtOH), after which these solvents were vacuum filtered using 5–13 µm filter papers by VWR (Darmstadt, Germany). The solvent-insoluble fraction was then removed as a filter cake, and the solvents were evaporated at 60 °C and ~11 kPa with a rotary evaporator (Büchi AG, Flawil, Switzerland).

## 2.3. Acid Washing

For acid washing, first the filtered biocrude was dissolved in the solvent (acetone) in a 1:1 (*w/w* ratio). Later, six different washing (acidic) agents were added respectively in a 1:3 (*w/w* ratio) of biocrude to each given acid. The samples were then stirred for 4 h by a magnetic stirrer (800 rpm) at room temperature. The solvent was removed by rotary evaporation at 60 °C and 50 kPa. After solvent evaporation, the biocrude and washing agent formed two clear phases. Eventually, the washing agents were collected by gravimetric separation in a separatory funnel. Moreover, deionized water was used as a reference for demineralization experiments. All the investigated acidic solutions had the same molarity (0.1 M). A detailed experimental list is reported in Table 1.

**Table 1.** Summary of demineralization (acid washing) tests for *Miscanthus* HTL biocrude.

Sample Name	Washing Agent	Concentration (M)
M-Raw	-	-
M-Sep	-	-
M1-W	Water	0.1
M2-CA	Citric acid	0.1
M3-AA	Acetic acid	0.1
M4-MA	Maleic acid	0.1
M5-PA	Phosphoric acid	0.1
M6-HA	Hydrochloric acid	0.1
M7-SA	Sulfuric acid	0.1

## 2.4. Biocrude Characterization

Thermogravimetric analysis (TGA) of raw and filtered biocrudes from *Miscanthus* was conducted on a Discovery SDT 650 Simultaneous Thermal Analyzer (TA Instrument Discovery, New Castle, DE, USA) under a nitrogen atmosphere at 800 °C with ramp of 10 °C/min. For ash analysis [27], an electric muffle furnace by Protherm (Ankara, Turkey) at 775 °C was utilized according to ASTM D482-13. The measurements of different metals and elements were carried out on an Agilent 715 (Agilent, Santa Clara, CA, USA) inductively coupled plasma optical emission spectrometry (ICP-OES). Prior to ICP-OES, digestion was performed on an Anton Paar Multiwave 3000 microwave (Anton Paar GmbH, Graz, Austria) digestion system. Approximately 0.1 g of biocrude and filtered solid samples were digested in 2 mL nitric acid (Sigma-Aldrich), after which they were diluted to 50 mL with Milli-Q water.

The elemental composition of the raw, separated and demineralized biocrudes were measured on a Perkin Elmer 2400 Series II CHNS/O Elemental Analyzer (PerkinElmer, Waltham, MA, USA) [28]. By using a correlation proposed by Channiwala et al., the higher heating value (HHV) was estimated from elemental composition [29]:

$$\text{HHV (MJ/kg)} = 0.3491\text{C} + 1.1783\text{H} - 0.1034\text{O} - 0.0151\text{N} \quad (1)$$

The total organic carbon (TOC) and total nitrogen (TN) in the utilized washing agents were measured in a Hach DR3900 VIS spectrophotometer (Hach, Loveland, CO, USA) using LCK386 and LCK138 kits, respectively. Furthermore, the functional groups of the biocrudes

were identified by Fourier-transform infrared (FT-IR) spectroscopy on a Bruker TENSOR II (Omnic 9 software, 2012) with an A225/Q Platinum ATR unit (Thermo Scientific, Waltham, MA, USA) in the range of 400–4000  $\text{cm}^{-1}$  and a resolution of 2  $\text{cm}^{-1}$ . Moreover, different chemical families in the biocrude samples were observed and evaluated based on relative peak areas [4] by using gas chromatography coupled to mass spectrometry (GC–MS) from Thermo Scientific (Waltham, MA, USA), model Trace 1300 ISQ QD Single Quadrupole.

### 3. Results and Discussion

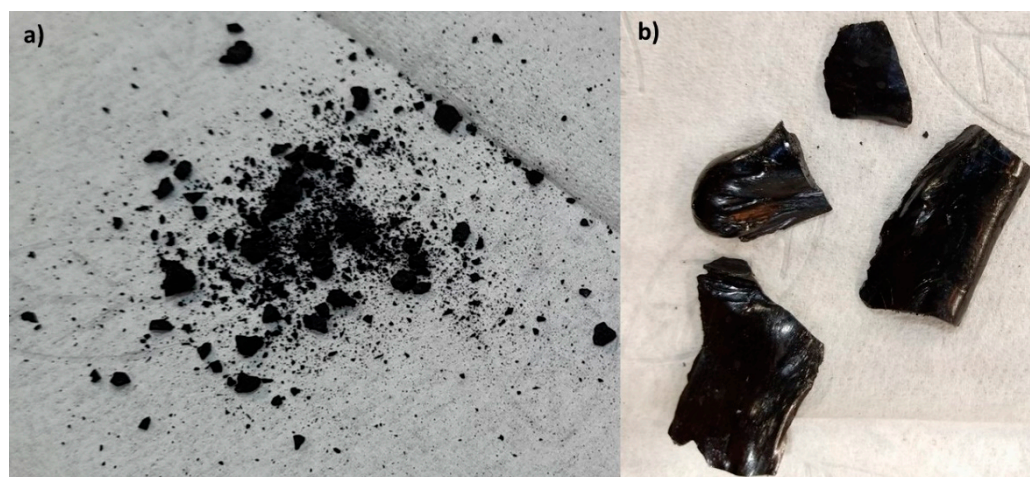
#### 3.1. Biocrude Filtration

Initially, raw *Miscanthus* biocrude was a non-flowable and sticky semi-solid. However, separation of the carbonaceous and inorganic solids by filtration resulted in biocrude flowability even at room temperature, which was then much easier to handle.

By using acetone and MEK, 4.4% and 4.2% of solids were filtered from the raw biocrude, while filtration with EtOH removed 8.5% of solids (Table 2). The solids obtained after filtration with the acetone and MEK had the texture of dry powder (Figure 1a), while filtration with ethanol also formed wax-like semi-solids (Figure 1b). These wax-like semi-solids could possibly have appeared due to the precipitation and removal of organic compounds related to asphaltenes. In the fossil crude literature, a solvent mixture with EtOH has already been reported as an environmental friendly alternative for the removal of asphaltenes [30].

**Table 2.** Solvent-assisted separation (i.e., filtration) for the removal of solids and reduction in ash content.

	Raw	Acetone	MEK	EtOH
Filtered solids (%)	-	4.4	4.2	8.5
Ash content (%)	2.3	0.47	0.39	0.80



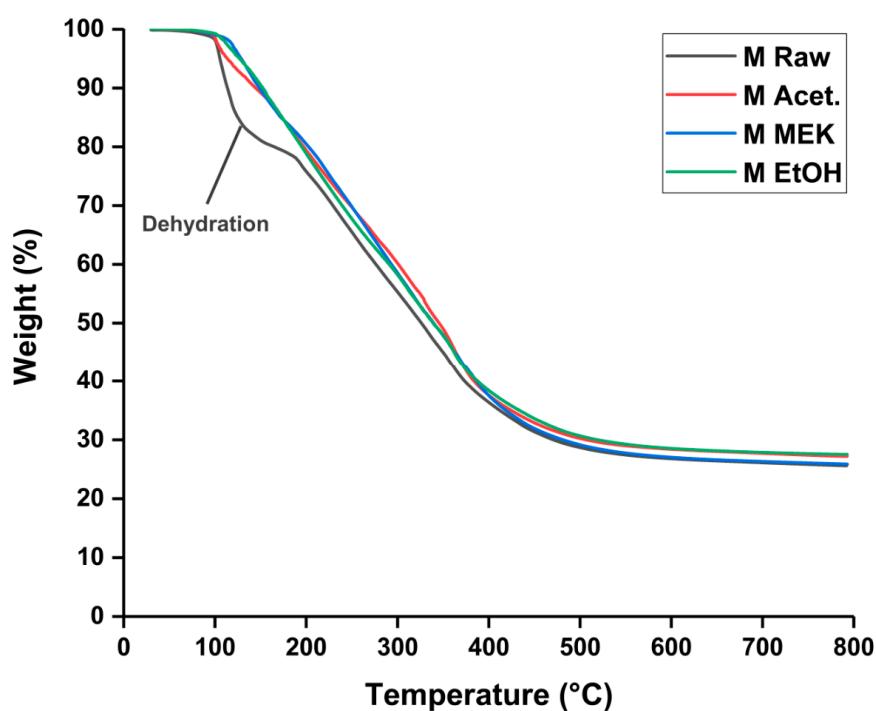
**Figure 1.** Picture of obtained solids after acetone/MEK filtration (a) and EtOH (ethanol) filtration (b) of *Miscanthus* biocrude.

Both acetone and MEK resulted in similar amounts of ash removal (deashing)—80% and 83%, respectively. However, EtOH only reduced the ash content by around 65%, even though washing with ethanol resulted in more filtered solids. Physical pre-treatment with significant reduction in ash inorganics is beneficial for the demineralization (acid washing) procedure, as acids will not come in direct contact with the inorganic solids ( $\text{K}_2\text{CO}_3$ , etc.) present in HTL biocrudes, and thereby the efficiency of demineralization will increase because of fewer possible side reactions. The carbonaceous solids (i.e., char) in HTL biocrude should also be removed because they do not have any role to play in



the further downstream processing (i.e., demineralization and hydrotreatment) of HTL biocrudes.

Furthermore, TGA analysis was carried out to observe the impact of solvent-assisted filtration. From Figure 2, it can be observed that the weight loss curves of raw biocrude and all three pre-treated biocrudes remained almost the same. These findings show that, depending on the solvent, most of the carbonaceous and inorganic solids could be effectively removed without the loss of hydrotreatable carbon.



**Figure 2.** Thermogravimetric curve of the raw and three pre-treated *Miscanthus* biocrudes.

Of the three solvents, acetone and MEK performed quite similarly, while the use of ethanol resulted in a larger loss of carbon, along with a smaller reduction of ashes in the biocrude. Therefore, acetone was selected as the optimal solvent owing to its higher volatility and was utilized further for the physical separation of *Miscanthus* biocrude (i.e., the first step in the demineralization process).

### 3.2. Demineralization

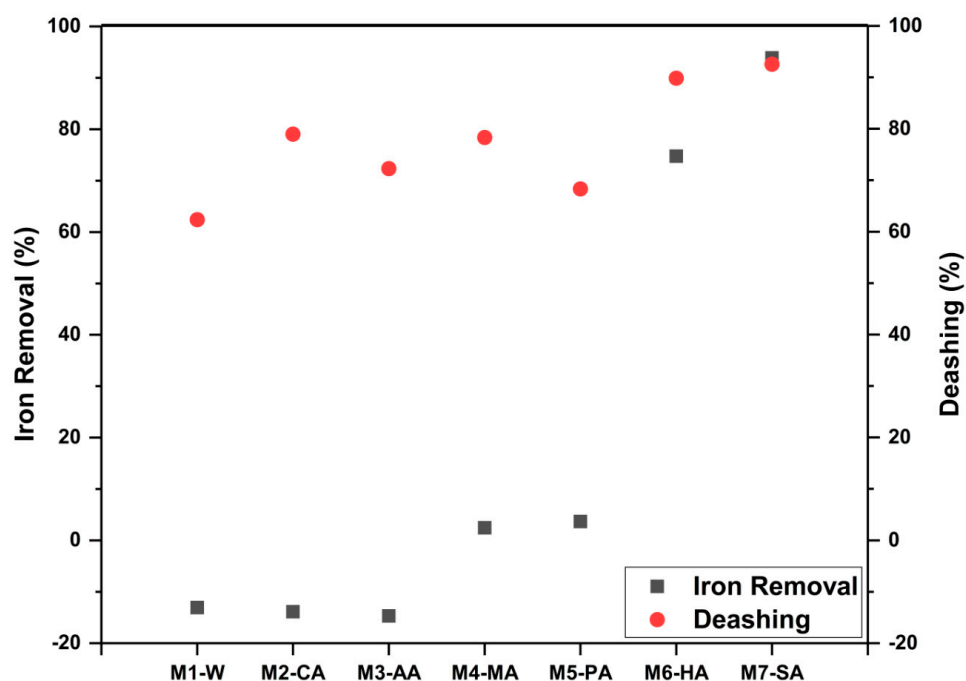
Table 3 shows that acetone-assisted separation of raw *Miscanthus* biocrude resulted in an 80.4% reduction in ash content (deashing). Despite the substantial removal of inorganics, the ICP-OES results indicate that filtered biocrude still contained concerning amounts of K (4221 µg/g) and Fe (245 µg/g), along with small amounts of Mg (47.6 µg/g), Ca (38.9 µg/g) and Zn (9.7 µg/g). This filtered biocrude was then subjected to demineralization via acid washing.

Table 3 shows the demineralization in deionized water and both organic and inorganic acids. In general, deionized water (M1-W) was ineffective for Ca, Fe and Zn. However, K and Mg were largely removed already after washing with deionized water (M1-W), which was able to reduce the ash content from filtered biocrude by 62.2%. This indicates that all K and some Mg were still present after filtration (M-Sep), and could easily be dissolved and removed along with deionized water. However, both filtration and deionized water had almost no effect on the removal of Fe. This is probably because Fe, as well as Ca and Zn, are incorporated in the organic matrix (organometallics) of *Miscanthus* biocrude, and therefore need further treatment (acid washing) for their removal.

**Table 3.** ICP-OES results of *Miscanthus* biocrude before and after physical filtration and demineralization. The ash content is reported by following the ASTM D482-13.

Sample	S	Ca	Cr	Cu	Fe	K	Mg	Mn	P	Zn	Ash
	(µg/g)										
M-Raw	791	3821	<30	<30	292	6059	908	86.5	1217	28.8	23,445
M-Sep	830	38.9	<30	<30	245	4221	47.6	<3	n.d.	9.7	4589
M1-W	862	40	<30	<30	277	<500	12.3	<3	9.7	10.4	1726
M2-CA	916	23.9	<30	<30	279	n.d.	3.2	n.d.	n.d.	6.9	962
M3-AA	864	<15	<30	<30	281	<500	4.1	<3	n.d.	8.5	1296
M4-MA	867	<15	<30	<30	239	n.d.	1.8	n.d.	10.1	6.1	991
M5-PA	875	27.3	<30	<30	236	<500	5.9	<3	593	10.9	1450
M6-HA	857	<15	<30	<30	61.9	n.d.	1.6	n.d.	n.d.	5.1	462
M7-SA	3300	<15	<30	<30	<15	n.d.	2.1	n.d.	n.d.	8.2	337

During acid washing (Figure 3), all demineralizing agents (organic and inorganic acids) reduced the ash content to some extent, whereas 0.1 M sulfuric acid (M7-SA) effectively reduced the ash content by 92.7% (337 µg/g) and 98.6% (337 µg/g) when compared with filtered biocrude (M-Sep) and raw biocrude (M-Raw). The present results are in good agreement with the previous literature [15], where 99% deashing (a reduction from 37,000 µg/g to 370 µg/g) was achieved after the demineralization of raw HTL biocrude produced from forestry residue under supercritical conditions. Moreover, the sulfuric acid solution (0.1 M) reduced 93.9% of Fe (<15 µg/g) and 95.6% of Mg (2.1 µg/g) content and was the strongest demineralizing agent among all utilized acids. However, Zn remained the least affected during acid washing, and merely 15.5% (i.e., 9.7 µg/g to 8.2 µg/g) was removed with 0.1 M sulfuric acid.



**Figure 3.** The overall efficiency for the removal of iron content and deashing of *Miscanthus* biocrude.

Figure 3 illustrates that under the given acidic concentration of 0.1 M, all the employed organic acids (M2-CA, M3-AA and M4-MA) and phosphoric acid (H5-PA) proved to be ineffective for the removal of Fe. Furthermore, the negative values for Fe removal (M1-W, M2-CA and M3-AA) could possibly indicate that Fe was certainly not removed, while the concentration of biocrude likely decreased due to organic losses during acid washing. However, hydrochloric acid (M6-HA) to some extent and sulfuric acid (M7-



SA) to a large extent were not only effective for the removal of Fe, but also for all other metals initially present in *Miscanthus* biocrude. ICP-OES along with ash analysis clearly showed encouraging results with 0.1 M sulfuric acid (M7-SA), which effectively reduced the metallic content along with other inorganics and could ensure the long-term, continuous hydrotreatment of HTL biocrudes.

### 3.3. Biocrude Properties

In order to evaluate the effect of demineralization, elemental analysis was carried out, and the results of the raw, acetone-filtered and acid-washed *Miscanthus* biocrudes are documented in Table 4. Elemental composition revealed that after demineralization the properties of biocrude in terms of carbon, hydrogen and HHV remained almost the same, and the obtained results do not differ from acetone-filtered biocrude. On the other hand, after acid washing, the nitrogen content in the demineralized biocrudes slightly increased. This is possibly due to the organic loss (removal of organics from *Miscanthus* biocrude to washing agents) during the demineralization process, which increases the overall nitrogen concentration.

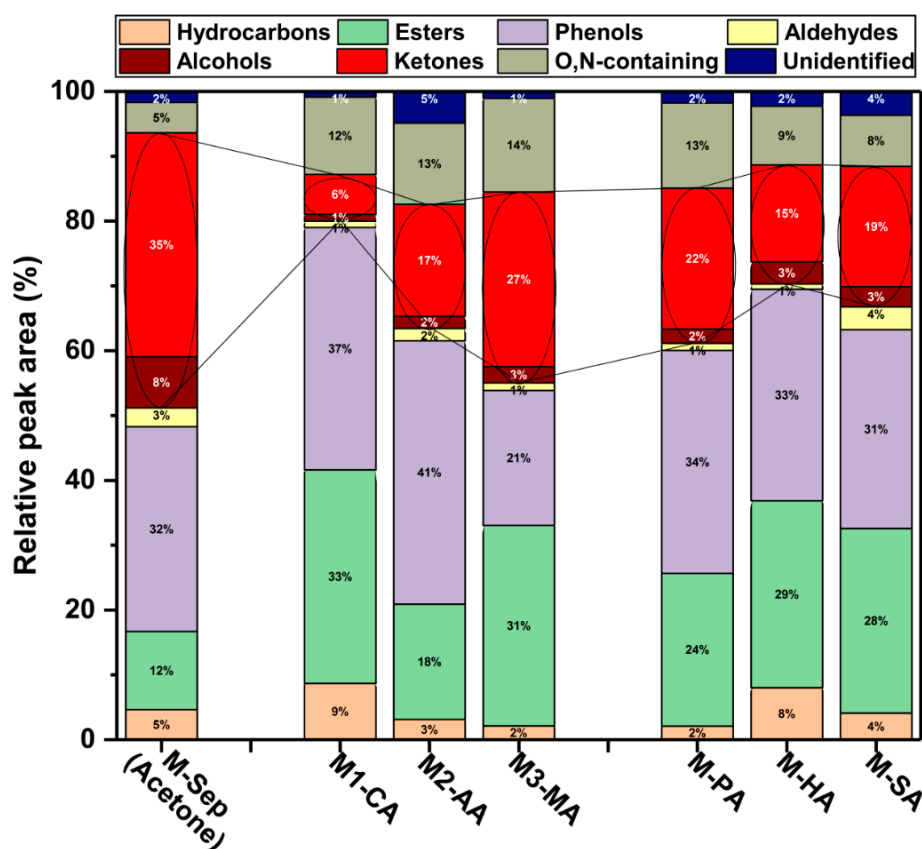
**Table 4.** Elemental composition (%), H/C atomic ratio and higher heating value (HHV) of *Miscanthus* biocrude before and after physical filtration and demineralization. Additionally, the total organic carbon (TOC) and total nitrogen (TN) in the aqueous phase of utilized washing agents after the demineralization of biocrude. Oxygen was calculated by difference.

Sample	Elemental Composition (%)				H/C (-)	HHV (MJ kg <sup>-1</sup> )	TOC (%)	TN (%)
	C	H	N	O				
M-Raw	74.9 ± 1.1	6.8 ± 0.2	0.96 ± 0.03	17.3 ± 1.1	1.09	32.4	-	-
M-Sep	78.1 ± 1.4	7.8 ± 0.1	1.09 ± 0.01	13.6 ± 1.4	1.19	35.1	-	-
M1-W	79.6 ± 0.7	7.6 ± 0.1	1.74 ± 0.02	11.1 ± 0.7	1.15	35.5	0.9	0.025
M2-CA	78.9 ± 0.9	7.4 ± 0.3	1.54 ± 0.46	12.2 ± 1.0	1.12	34.9	1.7	0.051
M3-AA	79.1 ± 2.2	7.7 ± 0.2	1.88 ± 0.25	11.4 ± 2.2	1.16	35.4	1.0	0.023
M4-MA	79.9 ± 1.1	7.5 ± 0.2	2.31 ± 0.04	10.3 ± 1.1	1.12	35.6	0.6	0.017
M5-PA	77.8 ± 1.3	7.7 ± 0.2	2.09 ± 0.25	12.4 ± 1.3	1.18	34.9	0.9	0.059
M6-HA	77.3 ± 0.6	7.6 ± 0.2	1.64 ± 0.36	13.5 ± 0.7	1.17	34.5	1.1	0.051
M7-SA	78.4 ± 0.9	7.6 ± 0.2	1.53 ± 0.02	12.5 ± 1.0	1.16	35.0	1.0	0.058

Subsequently, after each experiment TOC and TN of the aqueous phase (separated washing agents) were quantified and are reported in Table 4. It can be observed (Table 4) that demineralization was associated with organic loss in terms of both carbon and nitrogen. However, while deionized water was ineffective for demineralization, a slight organic loss (0.9% TOC and 0.025% TN) was still observed, possibly due to the presence of polar oxygenates (alcohols, ketones and phenolic derivatives, etc.). TOC and TN results also confirm the speculations made about the negative values for Fe removal (M1-W, M2-CA and M3-AA) in Table 3 and Figure 3. The 0.1 M sulfuric acid (M7-SA) accounted for a TOC (1%) and TN (0.058%), similar to those obtained after employing other inorganic acids (M5-PA and M6-HA), but it led to the highest degree of demineralization. This indicates that the 0.1 M H<sub>2</sub>SO<sub>4</sub> solution (M7-SA) was not only the strongest demineralizing agent, but it also corresponded to optimal organic loss vs. demineralization (Tables 3 and 4).

In order to further investigate the effect of demineralization, GC-MS analysis was carried out to obtain insight into the volatile fractions (up to a boiling point of ca. 350 °C) of acetone-filtered and demineralized *Miscanthus* biocrudes. Figure 4 shows the sample composition in terms of different chemical families and their abundance based on relative peak areas. The volatile fraction showed that filtered biocrude was mainly composed of oxygenates (89%) along with some O,N-containing compounds (5%) and hydrocarbons (5%) predominantly cyclo-paraffins. The majority of the compounds in *Miscanthus* biocrude were ketone and phenol derivatives, representing 35% and 32% of the chromatogram area, respectively. In medium to low abundance, esters (12%), alcohols (8%) and aldehydes (3%) were also present in the *Miscanthus* biocrude. The presence of ketones, phenols (e.g.,

2-cyclopenten-1-one and its alkyl derivatives), esters (fatty acid methyl esters), alcohols and aldehydes are in good accordance with previous literature [26].



**Figure 4.** Chemical composition (relative peak area (%)) in terms of families of compounds after the GC–MS analysis of acetone-filtered and demineralized *Miscanthus* HTL biocrudes.

After demineralization through acid washing (Figure 4), a remarkable result is an immediate decrease in the concentration (relative peak area) of ketones and alcohols. Significant amounts of ketones and alcohols were reduced after utilizing different organic and inorganic acids, most importantly 0.1 M citric acid (from 35% to 6% and 8% to 1%) and 0.1 M sulfuric acid (from 35% to 19% and 8% to 3%) respectively. However, the concentration of other compounds (e.g., hydrocarbons, phenols and esters) remained almost the same or slightly increased. This seems to have been caused by the significant loss of ketones and alcohols during demineralization, which in turn increased the concentration of other compounds detected by GC–MS. This observation is in line with the ICP–OES results (Figure 3), where the concentration of iron increased after demineralization with 0.1 M citric acid and 0.1 M acetic acid. GC–MS results confirm that the negative values for Fe removal (Figure 3) were primarily due to organic loss. Figure 3 also illustrates that 0.1 M citric acid accounted for the highest organic loss (i.e., loss of ketones and alcohols) as compared to other acids. This is most likely due to the presence of three carboxyl functional groups (tricarboxylic acid), which removed the organic compounds from highly unsaturated *Miscanthus* biocrude due to possible side reactions. The overall results (Tables 3 and 4, Figures 3 and 4) show that 0.1 M sulfuric acid was the strongest oxidizing agent and it effectively demineralized the biocrude with contained organic loss.

Furthermore, FT-IR spectroscopy was performed to characterize the impact of demineralization (acid washing) on bulk biocrude, especially the O-containing, N-containing, aliphatic and aromatic functional groups. Figure 5 shows a large stretching vibration at  $3300\text{ cm}^{-1}$ , related to O–H functional groups, and indicates the presence of a high oxygen content in the form of phenols and alcohols. The presence of C–H ( $3310\text{ cm}^{-1}$  and

750 to 850  $\text{cm}^{-1}$ ) and C–C (1605  $\text{cm}^{-1}$ ) aromatic stretching vibrations confirms the high aromaticity of biocrude. The peak signals from 2850 to 2960  $\text{cm}^{-1}$  are attributed to C–H alkyl stretching vibrations. The stretching vibrations at 1695  $\text{cm}^{-1}$ , 1200 to 1260  $\text{cm}^{-1}$  and 1390 to 1460  $\text{cm}^{-1}$  are related to C=O (ketones, carboxylic acids, etc.), C–O (ethers, etc.) and C–H (symmetric and asymmetric bending) functional groups, respectively [31]. The signals at 1510  $\text{cm}^{-1}$  and 1120  $\text{cm}^{-1}$  could be associated with N–H and C–N stretching vibrations and are indicative of nitrogen compounds.

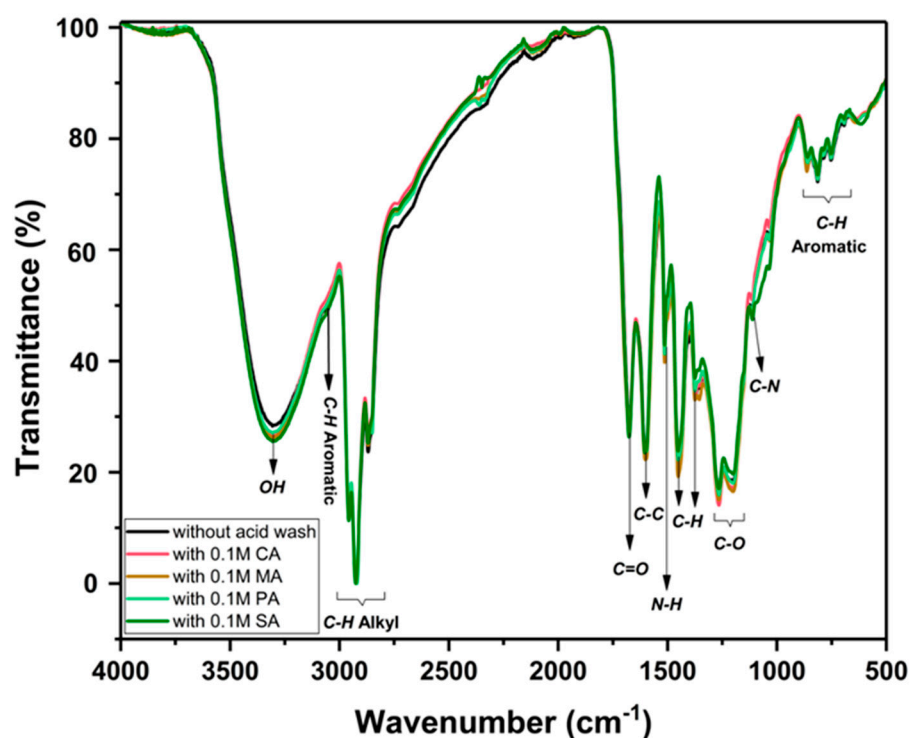


Figure 5. FT-IR spectral analysis of *Miscanthus* biocrude with and without acid washing.

From the FT-IR results of *Miscanthus* biocrude before and after acid washing, it is clearly evident that the peak structure remains the same. From this, it can be concluded that demineralization with a 0.1 M acidic concentration had no effect on the different functional groups. These results are consistent with the other analytical results, which also highlight that at 0.1 M acidic strength demineralization was viable along with some inherent organic losses due to the presence of highly polar organic constituents present in HTL biocrude.

#### 4. Conclusions

The high content of inorganics in HTL biocrudes precludes long-term continuous hydroprocessing, and therefore their removal is essential. In this work, demineralization via acid washing was explored by employing six different organic and inorganic acids with a 0.1 M concentration. Out of all the employed acids, 0.1 M  $\text{H}_2\text{SO}_4$  showed the most promising results (92.7% demineralization). GC–MS analysis showed that organic loss is inherent to demineralization, primarily because of oxygenates (e.g., ketones and alcohols). Furthermore, the FT-IR spectra remained intact during demineralization. Therefore, we anticipate the prospects of demineralization as an effective route for the removal of the high inorganic content present in lignocellulosic biocrudes.

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