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CIRCULAIR

Full report on biocrude conditioning, along with mass and carbon balances

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Authors: D. Castello[1]; L. K. R. Lajapathi Rai[1]; A. Achour[1]; S. Chiaberge[2]

Affiliations:

[1]AAU Energy, Aalborg University, Pontoppidanstræde 111, 9220 Aalborg Øst, Denmark

[2]ENI S.p.A., Renewable, New Energies and Material Science Research Center, via Giacomo Fauser 4, 28100 Novara, Italy

Abstract

This deliverable presents the findings on the conditioning of hydrothermal liquefaction (HTL) biocrude to enable its suitability for continuous catalytic hydrotreating. Raw HTL biocrude, i.e. the untreated product from the liquefaction plant, is typically a mixture of solids, oil, and aqueous phases, and poses challenges for upgrading due to its high solid and inorganic content. A scalable conditioning process was developed involving solvent extraction and demineralization. Acetone was identified as the optimal solvent for biocrude recovery, and a multistep extraction procedure was implemented to efficiently separate solids. This method achieved near-complete biocrude recovery and significantly reduced ash content, though still not down to a level that is suitable for hydroprocessing. Further inorganic removal was explored via washing with acidic aqueous solutions and solid sorption. While sulfuric acid washing achieved low ash levels, it also resulted in substantial carbon losses to the aqueous phase and in the additional need to dispose of this liquid. Sorption using materials like alumina proved more effective, reducing the ash content to acceptable levels (down to about 200 ppm) with high carbon recovery and no liquid waste. Characterization of conditioned

biocrudes confirmed minimal alteration in molecular composition. Overall, the proposed process, and particularly sorption with Al_2O_3, shows promise for scalable biocrude conditioning. Future work will focus on integrating this approach into continuous systems and optimizing sorbent regeneration.

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Phone	+49 89 307 484961
E-mail	Valentin.Batteiger@bauhaus-luftfahrt.net
Website	www.project-circulair.eu

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Glossary

Acronym	Signification
APCI	Atmospheric pressure chemical Ionization
CTMDP	2-Chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane
DAF	Dry ash free
DBE	Double bond equivalent
EDTA	Ethylenediaminetetraacetic acid
FTICR-MS	Fourier Transform Ion Cyclotron Resonance - Mass Spectrometry
GC	Gas Chromatography
GC-MS	Gas Chromatography - Mass Spectrometry
ICP	Inductive Coupled Plasma
KF	Karl-Fischer
MS	Mass Spectrometry
NCCs	Nitrogen containing compounds
NMR	Nuclear Magnetic Resonance
OES	Optical Emission Spectrometry
TOC	Total Organic Carbon
HTL	Hydrothermal liquefaction

Executive summary

The present public report “Full report on biocrude conditioning, along with mass and carbon balances” reports on the preliminary findings from the CIRCULAIR project concerning the conditioning of HTL biocrude, in order to improve its quality to a level that can be suitable for the subsequent continuous catalytic hydrotreating. This concerns the removal of solids and inorganics, which have a detrimental effect on the catalysts.

Raw HTL biocrude, i.e. the product of the HTL process not subjected to any other treatment, is usually obtained as a mixture of solids (char and inorganics), oil and aqueous phase. Depending on the initial feedstock, these properties can give to the raw biocrude the appearance of an oily sand, with similarities to the fossil “oil sands”, though from a different origin. Raw biocrude from manure and straw, as investigated in CIRCULAIR, is therefore unsuitable for direct upgrading through hydrotreating, due to potential reactor plugging from the solids and catalyst poisoning due to its high inorganic content. A suitable conditioning process has to be developed in order to allow the production of HTL-based drop-in fuels via hydroprocessing. This conditioning process needs to solve two main issues:

- **Solid removal:** A suitable method needs to be implemented to separate the oil fraction (biocrude) from the other phases (mainly solids and also aqueous phase) in raw biocrude, which is generally achieved by extraction.
- **Inorganics removal:** Even after solid removal, the pretreated biocrude oil can still contain high levels of inorganic material (ash) that can deactivate the subsequent catalytic processes. Hence, a demineralization process is essential (e.g. acid washing or adsorption). However, demineralization normally takes place along with the loss of some organic carbon. Such losses should be minimized in order to preserve the final fuel yields.

This public deliverable reports on the development of both steps, by showing results from experimental tests run at laboratory scale, in the perspective of establishing a process that can be scaled up to treat larger amounts of biocrude. The experimental activities were carried out on HTL biocrudes from two different feedstocks: an equal mixture (50:50) of straw and manure, and 100% manure.

As far as solid removal is concerned, solvent extraction was implemented. The activities were first addressed to select the right solvent, which was identified with acetone. Indeed, this solvent was able to extract the maximum amounts of biocrude for the raw material, as it was obtained from trials in a Soxhlet extractor. However, the interest of this project is to apply solvent extraction to larger batches, hence providing a scalable solution. Standard filtration is hardly scalable to the required amounts of biocrude, as the high solid content (~ 18-25%, according to the different batches considered) would result in frequent filter plugging. Therefore, a multistep procedure was developed that is based on subsequent steps of biocrude dilution in solvent, settling, filtration of the supernatant and re-dilution of the settled solids. Results showed that, adopting a 1:5 dilution ratio, it is possible to recover nearly all extractable biocrude (i.e., the amount of biocrude that could be obtained by Soxhlet extraction) after two subsequent steps. This procedure is relatively simple and can be replicated on larger scale.

The developed procedure for biocrude extraction was also able to decrease the overall inorganic content (ashes) in the oil from 98,200 ppm down to 3,100 ppm for 50:50 manure/straw and from 178,700 ppm to 2,200 ppm for 100% manure biocrude. Though the removal was considerable, the resulting levels are still much higher than what can be accepted for direct downstream processing, as these inorganics are likely to poison the catalysts during hydroprocessing. Two alternative treatments were then investigated to further reduce inorganic content: acid washing and adsorption.

As far as acid washing is concerned, 0.1 M solutions of sulfuric acid, EDTA and citric acid were adopted to remove the remaining inorganics. For 50:50 manure/straw biocrude, sulfuric acid washing achieved the lowest inorganic content of 550 ppm, followed by EDTA (2,700 ppm) and citric acid (2,200 ppm). However, acid washing resulted in substantial losses of carbon to the washing medium, which was characterized by elevated values of TOC (23-30 g/L). Therefore, though effective for demineralization, acid washing results in poor carbon balances and in the production of a liquid waste, which discourages its application.

Therefore, treating biocrude with sorbents was investigated as an alternative treatment method. Several sorbent materials were investigated, including alumina, silica-alumina, zeolites, resins and molecular sieves. The obtained results showed levels of ashes between 83 and 1,760 ppm, but with generally higher carbon recoveries in the biocrude (always > 90%). The tests were also carried out with the filtered biocrudes from 100% manure, obtaining similar results, with 865 ppm ashes after H_2SO_4 washing and 533 ppm after sorption on Al_2O_3, which turned out to be the best option among those considered.

The conditioned biocrudes underwent characterization by several techniques, including ICP-OES, GC-MS, FTICR-MS and NMR. Analyses showed that the conditioning process does not alter the molecular composition of the biocrudes in an appreciable way. For 50:50 manure/straw the different adopted techniques did not show any modifications in the relative abundance of the different chemical species, while for 100% manure slight differences were observed, since the acid or sorbent treatment removed some basic nitrogen-containing compounds. In both cases, anyway, changes are minimal, which is a positive aspect, signalling that the treatment is not depleting the properties of the biocrude to treat.

In conclusion, the overall proposed process, including extraction and sorption proved to be effective for biocrude conditioning in view of its subsequent upgrading. In particular, treatment with solid sorbents, and especially Al_2O_3, turned out to be a promising alternative for biocrude conditioning, also considering that, unlike acid washing, this approach does not produce a liquid byproduct needing further treatment and disposal. Future work should consider the actual implementation of this treatment approach in a continuous system, including an accurate determination of its kinetics and alternatives for sorbent regeneration.

1. Introduction

Hydrothermal liquefaction (HTL) is a promising technology for converting biomass into biocrude oil, offering a sustainable alternative to traditional fossil fuels. However, raw HTL biocrude presents significant challenges for further processing. It often resembles oil sands in consistency, characterized by a highly viscous nature and a substantial inorganic content. These inorganic materials can deactivate catalysts used in subsequent upgrading processes, making the purification of HTL biocrude a critical step to ensure its viability as a fuel source. This study investigates the use of solvent extraction as a method to effectively separate oil from raw HTL biocrude and reduce its inorganic content. We hypothesize that selective solvents can efficiently extract the desired oil fraction while removing the inorganics to a certain extent. Our research focuses on two key areas to achieve this goal.

Firstly, the study aims to identify suitable solvents with varying polarities, such as acetone, ethyl acetate, and toluene, to evaluate their effectiveness in extracting oil from raw HTL biocrude. The optimization process involves determining the optimal biocrude-to-solvent ratio to maximize oil yield, balancing extraction efficiency with practical considerations for industrial application. Secondly, the study explores methods to reduce the inorganic content of the pretreated biocrude. This involves testing acidic solutions, such as sulfuric acid, EDTA, and citric acid, as well as water. Additionally, we investigated a novel approach using various sorbent materials and compared the results to the acid wash method. Addressing the challenges in determining accurate mass and carbon balances during these processes is also a key component of the research. Mass and carbon balance calculations are integral to this analysis, providing insights into the recovery efficiency and overall effectiveness of the solvent extraction process.

By investigating these aspects, the study aims to develop a scalable and efficient method for separating oil from raw HTL biocrude and reducing its inorganic content. Successfully addressing these challenges will facilitate more effective downstream catalytic processes and enhance the practical application and sustainability of HTL-derived biofuels.

2. Description of biocrude conditioning process

2.1. Process concept

This study explores a two-step biocrude conditioning process designed to improve the quality of biocrude oil derived from hydrothermal liquefaction (HTL), with the ultimate goal of producing high-grade transportation fuels via appropriate hydroprocessing steps. Key objectives include maximizing oil recovery efficiency and meticulously removing catalyst-deactivating impurities and inorganic substances. These objectives are illustrated in Figure 1.

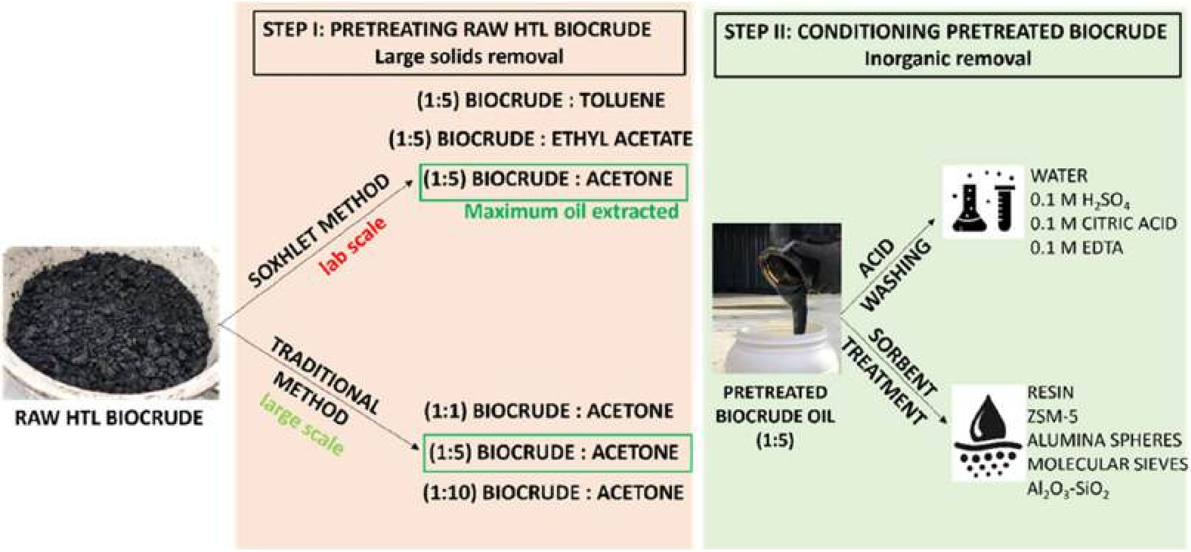

Figure 1: Two-step process for conditioning the biocrude.

2.2. Process development

2.2.1. Solvent selection for biocrude extraction

The selection of an appropriate solvent for extracting biocrude from the HTL matrix was investigated by means of a Soxhlet extraction technique. Here, acetone, ethyl acetate and toluene were tested as extracting solvents (Figure 2). The effects of these solvents were evaluated under controlled conditions: a solvent to biocrude ratio of 1:5, a temperature of 60 °C and an extraction time of 12 hours. Results indicated that acetone achieved the highest total extraction yield of pretreated biocrude (Section 3.1.1), while toluene produced the lowest yield. Therefore, acetone was identified as the optimal extraction solvent for the continuation of this project.

Figure 2: Procedure for Soxhlet extraction.

2.2.2. Establishment of a scalable extraction procedure

Once the best solvent was determined, it was necessary to develop a methodology to perform biocrude extraction on a larger scale. Soxhlet extraction is indeed a useful laboratory method, but it is not suitable to handle the amounts of biocrude expected in the CIRCULAIR project. Additionally, due to the high amount of solids present in the biocrude, filtration does not appear viable, as it would imply frequent plugging of the filter itself.

In order to solve these issues, a multi-step procedure was adopted that is based on diluting the raw biocrude with solvent and then letting the solid settle overnight. In this approach, the largest part of solids settles in the bottom of the tank due to gravity. The supernatant is relatively free of solids and can be easily filtered, to obtain solid-free biocrude after removing the solvent. At the bottom of the settling tank, solids, including some biocrude, remain. Therefore, this residue can be dissolved again in the solvent and the process is repeated as above, increasing the amount of recovered biocrude. A graphical representation of this scheme is shown in Figure 3.

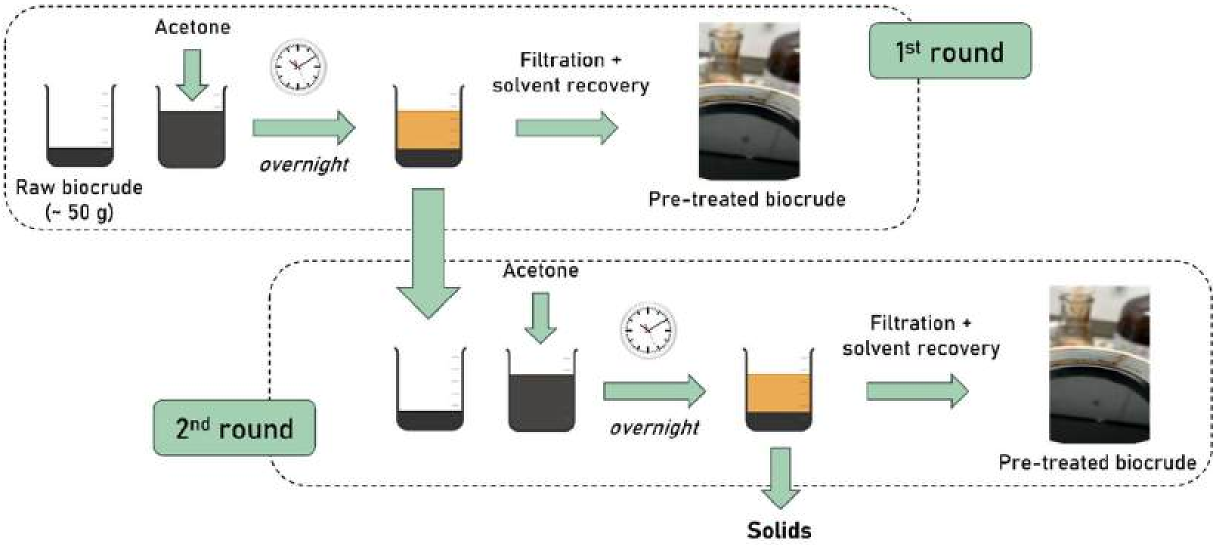

Figure 3: Scheme of the adopted separation method based on solvent extraction and solid settling.

In order to establish this scheme, it is important to determine the optimal biocrude-to-solvent ratio. To this end, various acetone to HTL-biocrude ratios of 1:1, 1:5, and 1:10 were examined. It is hypothesized that the observed increase in extraction yields of treated biocrude with higher solvent ratios could be attributed to improved permeability of HTL biocrude, facilitating more efficient mass transfer through diffusion processes. Moreover, as the solvent reduces the overall viscosity, solids settling is enhanced. On the other hand, the usage of solvent must be limited, since its removal and recovery are an energy-intensive process.

In order to determine the efficiency of the procedure, carbon recovery was determined as follows:

$$\mathrm{C}\ \%(\mathrm{DAF}) = \frac{\mathrm{Carbon}\ (\%)}{100 - \mathrm{Ash}\ (\%)}$$

$$\mathrm{Carbon}\ \%(\mathrm{dry\ basis}) = \frac{\mathrm{Carbon}\ (\%)}{100 - (\mathrm{Ash} - \mathrm{moisture})\ (\%)}$$

where DAF (dry ash-free basis) represents the oil's composition excluding the weight of mineral ash and moisture; Moisture refers to the water content present in the oil; Ash refers to the residue remaining after burning the oil at 775°C and Dry basis: refers to biocrude oil excluding the water content.

2.2.3. Demineralization process

Demineralization and removal of inorganic elements through acid washing are established practices in petroleum refineries, wastewater treatment, HTL biocrude processing, and plastic recycling. Addressing the elimination of impurities in HTL biocrude that can negatively affect catalysts has been a significant focus of prior research, as noted by Haider et al. (2023). This preliminary study follows a similar approach as detailed in our previous work (Figure 4a). Here, three different acidic solutions at a concentration of 0.1 M were utilized, adopting sulfuric acid, citric acid and EDTA. For comparison purposes, also washing with pure water was carried out. The selected demineralization agents were adopted in order to have both organic and inorganic acids, following the most common approaches in the field. Moreover, the choice of sulfuric acid could be beneficial, due to its relatively low price and the possibility of adding small amount of sulfur to the oil, which are useful if sulfided catalysts are used during the hydrotreating process.

As an alternative method, the utilization of solid adsorbents was investigated. Adsorbents such as aluminum oxides, zeolites, and activated carbon have demonstrated efficacy in capturing alkali and alkali earth metals, heavy metals, transition metals, and half-metals in existing refinery settings (Danmaliki & Saleh, 2017). These materials exhibit high adsorption capacities and can be regenerated, making them suitable for industrial applications (Burakov, 2018). For the first time, the current research also emphasizes the removal of impurities in HTL biocrude (Figure 4b). Adsorption experiments were conducted in batches under same conditions (50 °C, steering at 400 rpm for 4h), comparing five different sorbents:

- Resins: Amberchrom™ 50WX8, hydrogen form, 100-200 mesh (Sigma-Aldrich).
- Molecular Sieves: 13X pellets, 1.6 mm diameter (Sigma-Aldrich).
- Alumina Spheres: 2.5/210 µm (purchased from SASOL).
- ZSM-5 Zeolite: (Thermo Fisher Scientific).
- Silica-Alumina (Siral 30) (SASOL).

To date, no studies have specifically addressed the removal of inorganics from real HTL biocrude. Comparative evaluation of these two methods not only considers their efficiency in impurity removal, but also evaluates scalability with minimal carbon lost and environmental impact.

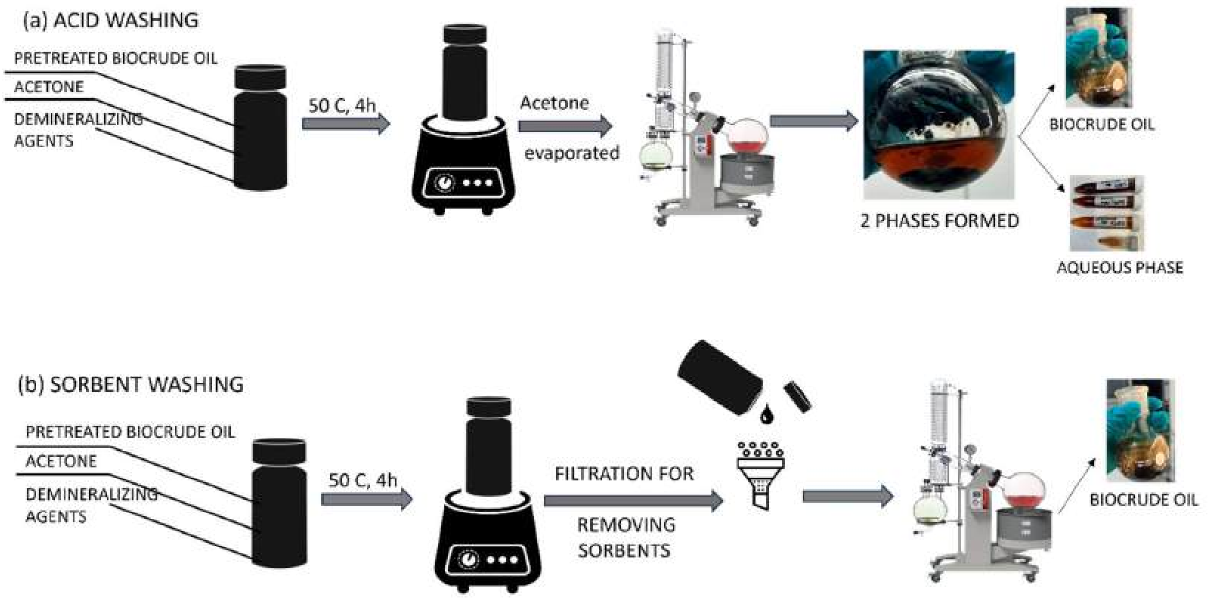

Figure 4: Acid washing experiment setup (a), and sorbent washing experiment setup (b)

2.3. Analytical techniques

Characterizing pretreated HTL biocrude oil and the resulting solids after solvent extraction involves several key analytical techniques.

In order to determine the elemental composition of biocrude samples, CHN analysis was carried out by means of an instrument FlashSmart (Thermo Fisher Scientific). Tocophenol nicotinate was utilized as a standard. The instrument determines the weight percentage of carbon, hydrogen and nitrogen, while oxygen content was obtained by difference. By determining these elemental compositions, CHN analysis offers a comprehensive view of the sample's elemental makeup. This information is important for calculating precise carbon balances, which are critical for understanding the overall efficiency of the HTL process. In the case of the solid fraction after extraction, oxygen was not reported, since its determination by difference would not be meaningful due to the very elevated amount of inorganics in this fraction.

To complement elemental analysis, water content determination by means of Karl-Fischer (KF) titration was employed, using a TITROLINE 7750 instrument. This technique precisely determines the water content within pretreated biocrude oil and acid-washed oil samples. AQUASTAR Water Standard 1% Reference Material for KF Titration, containing 1-methoxy-2-propanol, was used as the reference for accurate measurements. This meticulous water determination plays a vital role in correcting the dry basis weight of the oil. This correction ensures that subsequent analyses are based on accurate, water-free weight data, leading to more reliable results.

To quantify the organic carbon content within the aqueous phases following pretreatment and acid washing, an Hach Lange's DR3900 Spectrophotometer was employed for Total Organic Carbon (TOC) Analysis, utilizing the LCK 386 kits. These TOC data, integrated with CHN analysis results, are crucial for establishing precise mass and carbon balances.

Ash content measurement is conducted according to the ASTM D482-19 standard, which involves determining the inorganic residue remaining after the combustion of the biocrude samples at 775°C in a muffle furnace. The ash content provides insight into the amount of non-combustible material present in the biocrude and solids. This measurement is critical for evaluating the purity of the pretreated biocrude and the effectiveness of the demineralization process. The ash content analysis helps in assessing the quality of the biocrude and its suitability for further refining or catalytic processing.

ICP-OES (Inductively Coupled Plasma – Optical Emission Spectrometry) is an analytical technique used to determine the concentration of elements, mainly metals, in a sample. A ThermoFisher iCap6300 was employed for the analysis of Bio-Crudes.

The biocrude samples were first treated through microwave digestion with nitric acid and hydrogen peroxide, to obtain an aqueous solution. Thanks to the single cavity technology, it is possible to work at high power density, and with continuous sequential sampling, the system enables fast digestions in just a few minutes, with automatic loading/unloading and reproducible results.

The sample is then nebulized and introduced into a high-temperature Argon plasma (between 6000 and 10,000 K), where the atoms are excited. The excited atoms emit characteristic radiation, which is detected by an optical spectrometer and correlated to the amount of the element present. The technique offers high sensitivity, typically in parts-per-billion (ppb) range, making it suitable for trace element analysis.

To determine the possible changes to the molecular composition of the biocrudes, a number of different analytical techniques were employed. Gas chromatography with mass spectrometry (GC-MS) was carried out, utilizing a Trace 1300 ISQ QD - Single Quadrupole by Thermo Scientific. Biocrude samples were diluted in dichloromethane and relative peak areas were determined from the resulting chromatogram, in order to classify the measured compounds. The identification of the different chemical species was carried out by using NIST libraries.

GC-MS is very effective in the identification of several compounds. However, being a gas chromatographic technique, its detection is limited to those compounds that are vaporized at measuring conditions, therefore those with boiling points up to ca. 300 °C. This is an actual limiting factor for a product like HTL biocrude, whose composition mostly includes heavy molecules, with boiling points that are often higher than this threshold. Therefore, characterization was carried out also with more sophisticated techniques like FTICR-MS (Fourier Transform Inductive Cyclotrone Resonance Mass Spectrometer). This kind of analysis was carried out at Eni with an LTQ FT Ultra instrument by Themo Scientific, with an atmospheric pressure chemical ionization (APCI) ion source. Samples were diluted to 1 mg/mL in acetone:acetonitrile 1:5. Mass spectra were acquired with a resolution of 200k and elaborated with software PeakbyPeak by Spectroswiss to assign molecular formulas to roughly 10000 peaks per each biocrude sample.

^{13}C, and ^{1}H-NMR spectra were recorded with a 400 Avance Bruker NMR (400 MHz) in deuterated acetone: around 10 mg of the sample were dissolved in 0.6 ml of acetone-d6.

^{13}C-NMR spectra were acquired with power gated decoupling from proton (ZGPG).

The reference signal is acetone at 29.5 ppm for ^{13}C-NMR and at 2.05 ppm for ^{1}H-NMR.

For ^{31}P-NMR phosphitylation of the -OH groups have been performed using 2-Chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (CTMDP) as reactant after solubilization of the sample in a mixture of $CDCl_3$ and pyridine. ^{31}PNMR has been performed for the characterization of the reacted hydroxyl groups. Cyclohexanol (145 ppm) has been used as an internal reference.

Together, these techniques provide a comprehensive analytical framework for evaluating the performance and efficiency of HTL biocrude conditioning, by offering detailed insights into the elemental composition, water content, organic carbon, and inorganic residues of the samples.

3. Conditioning of manure/straw biocrude

This section presents the preliminary results of the conditioning process consisting of two distinct steps: (1) Biocrude extraction and (2) Demineralization.

3.1. Step 1: Biocrude extraction

The first step is represented by biocrude extraction. The activities involved first the selection of a suitable solvent for biocrude and then in establishing a scalable procedure that can be adopted to pre-treat larger amounts of biocrude (20-40 kg) as foreseen in the course of the CIRCULAIR project.

3.1.1. Solvent selection

The preliminary phase of this study involved selecting an appropriate solvent for extracting conditioned biocrude from the raw HTL-biocrude. This step was evaluated via the Soxhlet extraction method. Acetone, ethyl acetate and toluene were chosen as the initial extracting solvents due to their diverse polarities and solvent characteristics. The performance of each solvent was assessed under similar and controlled conditions.

The preliminary results indicated that acetone yielded the highest extraction of 63 wt.% of pretreated biocrude (Figure 5), demonstrating superior effectiveness compared to ethyl acetate (52 wt.%) and toluene (26 wt.%). Toluene, in contrast, yielded the least due to its low polarity, which might strongly affect its overall extraction efficiency. Based on these findings, acetone emerged as the optimal extraction solvent for the next steps of the project.

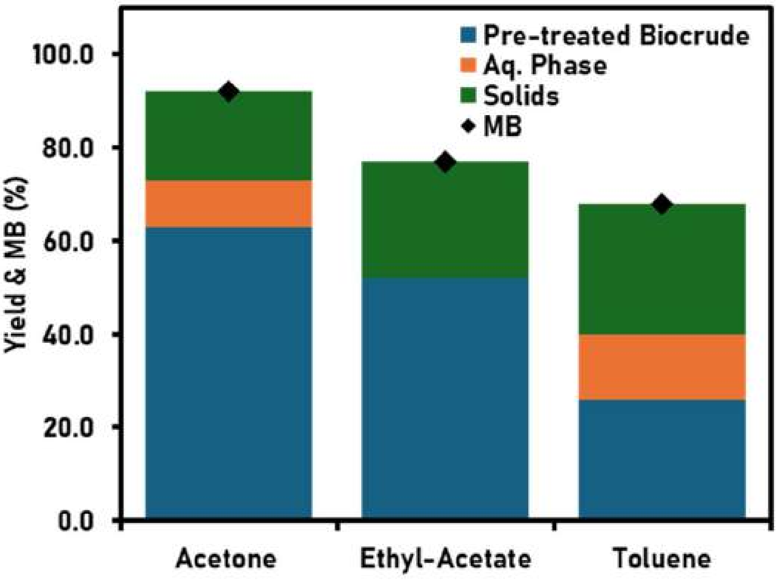

Figure 5: Mass balances and phase distributions (% w/w) for solvent extraction with acetone, ethyl acetate and toluene (1:5)

In the preliminary phase of this study, we explored how different ratios of HTL-biocrude to acetone affect the yield of pretreated biocrude. The ratios examined were 1:1, 1:5, and 1:10. Each ratio was assessed to determine its impact on extraction efficiency and the remaining solid content. Figure 6 illustrates the relationship between different acetone ratios and their impact on the extraction yield and solid content in biocrude.

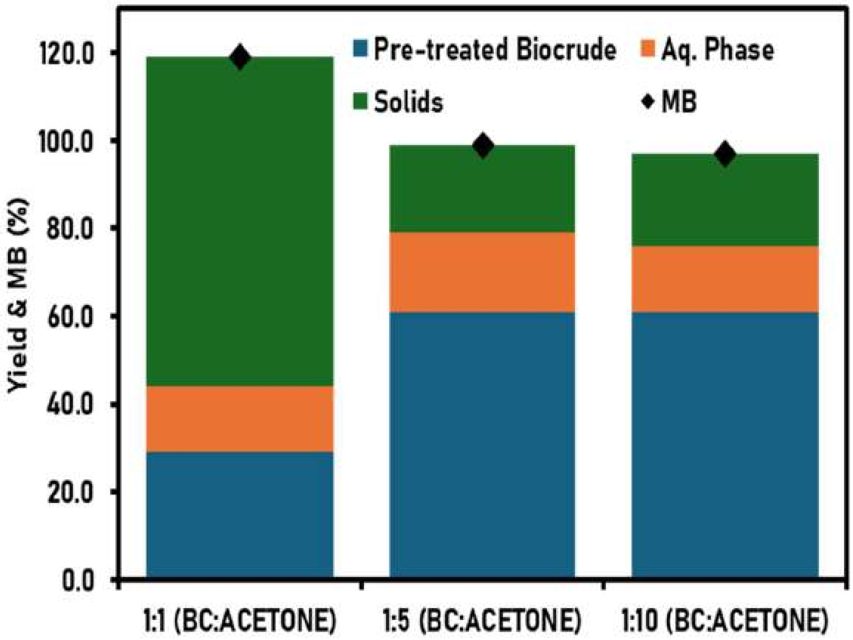

Figure 6: Mass balance and phase distribution (% w/w) in various biocrude-acetone mixtures (1:1, 1:5, 1:10)

The findings indicated that the 1:5 and 1:10 ratios provided the highest oil extraction yields, being able to recover around 61% after two rounds of extraction, which is close to the result obtained in the Soxhlet, which we assumed as a benchmark. These ratios also resulted in a relatively low solid content of 20%, and 21%, respectively. The higher acetone concentration in these ratios likely enhances the permeability of HTL biocrude, which facilitates more effective mass transfer and solvation of biocrude components. This improved efficiency underscores the benefits of using a higher solvent concentration in the extraction process. Conversely, the 1:1 ratio yielded a lower oil recovery of 29% after two rounds and a significantly higher solid content of 75%. After the first round of extraction at this ratio, 94% of solids remained, suggesting that a substantial portion of biocrude was not extracted due to limited solvent diffusion and saturation.

This outcome indicates that the 1:1 ratio is less effective and selective for biocrude extraction, as it does not provide sufficient solvent to adequately solvate and mobilize the biocrude components. While the 1:10 ratio demonstrated a slightly higher extraction efficiency, it also requires a larger volume of solvent, which might pose economic and environmental challenges for large-scale applications. The increased solvent usage could lead to higher operational costs and greater environmental impact, making this ratio less practical despite its effectiveness in laboratory settings.

The 1:5 ratio, however, emerged as the most balanced and practical option. It offers a favorable compromise between maximizing oil yield and minimizing solid content and solvent usage. Achieving an oil extraction efficiency of 61% after two rounds, while maintaining a solid content of 20%, makes this ratio the most viable for scaling up the process. Assuming the output of Soxhlet as a benchmark, the investigated extraction procedure allowed recovering around 97% of biocrude, which is a very remarkable result.

3.1.2. Mass and carbon balances and inorganics removal

Following the Hydrothermal Liquefaction (HTL) process, it is essential to conduct a comprehensive carbon balance for the system. This was performed on a batch of biocrude obtained from Aarhus University from HTL runs on straw/manure 50:50 at 325 °C. In Figure 7 the mass balance obtained from the extraction procedure is presented. As it can be observed, this sample presented high share of aqueous phase, probably due to the intrinsic difficulty of phase separation after HTL.

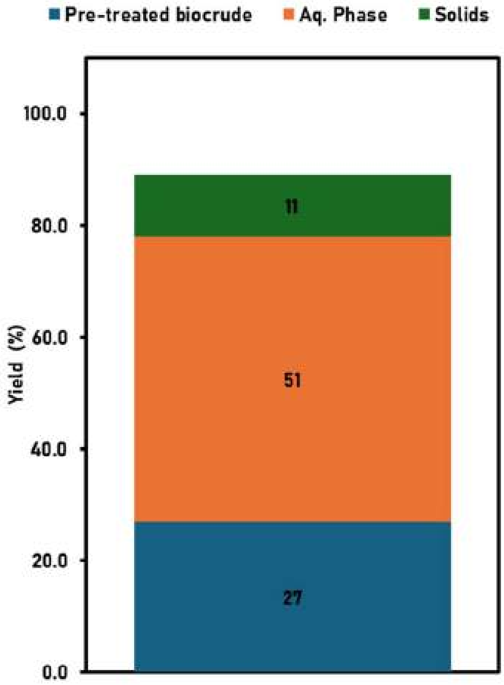

Figure 7: Distribution of the product from solvent extraction of 50:50 manure/straw raw HTL biocrude.

The overall elemental analysis and carbon distribution is summarized in Table 1. It can be observed that the majority of carbon resides in the biocrude with approximately 44.2% found in the oil phase. The solid residue contains 10.3% of the carbon, while the aqueous phase holds 12.3%.

Table 1: Elemental analysis for carbon balance assessment in the pretreated biocrude oil.

Properties	Biocrude	Solids	Aqueous
C (wt.%)	70.2	52.9	NA
H (wt.%)	7.3	5.1	NA
N (wt.%)	3.0	2.6	NA
O (wt.%)	19.5	NA	NA
H/C atomic (-)	1.239	1.157	NA
O/C atomic (-)	0.208	NA	NA
Carbon Balance (%)	44.2	10.3	12.3
Ash content (ppm)	3 100	570 000	NA

The raw HTL biocrude exhibited a high inorganic content, reaching approximately 98,200 ppm. This level of inorganics could pose a significant threat to catalysts used in subsequent refining processes. Solvent extraction is able to greatly reduce the inorganics content in the biocrude. From our measurements, 3,100 ppm ashes remained in the biocrude after treatment. This remarkable reduction indicates that the largest amount of inorganics in the raw product is contained in the separated solids.

Despite the significant reduction in the ash content, these results are still far from the quality requirements of an oil for hydrotreating, for which inorganic contents in the order of a few hundred ppm are advisable. Therefore, a subsequent demineralization treatment is made necessary.

3.2. Step 2: Demineralization

To further reduce inorganic content and enhance catalyst performance, two demineralization methods were evaluated and compared from the pretreated biocrude. The focus was on finding effective removal techniques to minimize contaminants.

3.2.1. Acid washing

Figure 8 illustrates inorganics removal and carbon recovery using various acid solutions.

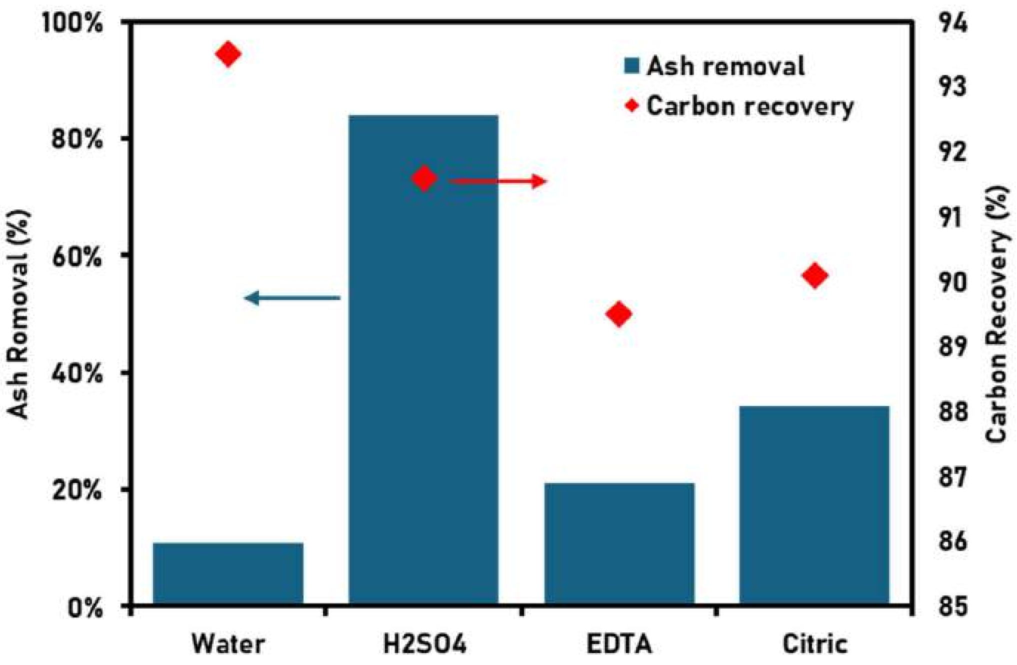

Figure 8: Acid wash washing: Carbon recovery and ash removal

Sulfuric acid wash proved to be the most effective, reducing inorganic content to 550 ppm (83.9 % removal relative to the pretreated biocrude, Table 1). EDTA wash and citric acid wash also showed substantial reductions in inorganics, lowering levels to 2,700 ppm and 2,200 ppm, respectively (Table 2). These acids present viable alternatives for demineralization, offering considerable impurity reduction. As expected, water washing resulted in an inorganic content of 3,050 ppm, with negligible removal of ashes from the starting material.

A challenge in these processes was accurately determining mass and carbon balances, especially during acid washing. The presence of a small amount of aqueous phase in the acid-washed oil sample presented a challenge in accurately performing the mass and carbon balances. In Table 2, Total Organic Carbon (TOC) analysis revealed significant carbon presence in the aqueous phase of acid-washed samples, indicating about 10 % loss of carbon material during washing. In summary, sulfuric acid wash offers the most effective demineralization, while the performance of the other acids is much less significant. Balancing effective inorganic removal with minimizing carbon loss is crucial for optimizing demineralization processes for industrial applications.

Table 2: Elemental analysis for carbon balance assessment of acid-washed samples.

Properties	Water	H_2SO_4	Citric acid	EDTA
C (wt.%)	69.7	71.2	72.5	73.1
H (wt.%)	7.7	7.3	7.4	7.5
N (wt.%)	2.9	2.8	3.0	3.0
O (wt.%)	19.6	18.7	17.1	16.4
H/C (-)	1.321	1.235	1.227	1.228
O/C (-)	0.211	0.196	0.177	0.168
Carbon recovery (wt.%)	93.5	91.6	90.1	89.5
Carbon in aqueous (wt. %)	6.5	8.4	9.9	10.5
TOC in aqueous (mg/L)	19040	23725	28535	30215
Ash in oil (ppm)	3050	550	2250	2700

3.2.2. Sorbent treatment of biocrude

Ash removal from HTL-biocrude via sorbents was investigated as a potential alternative to acid washing. Figure 9 illustrates how adsorbents effectively reduce inorganic content and minimize carbon loss in pretreated HTL biocrude.

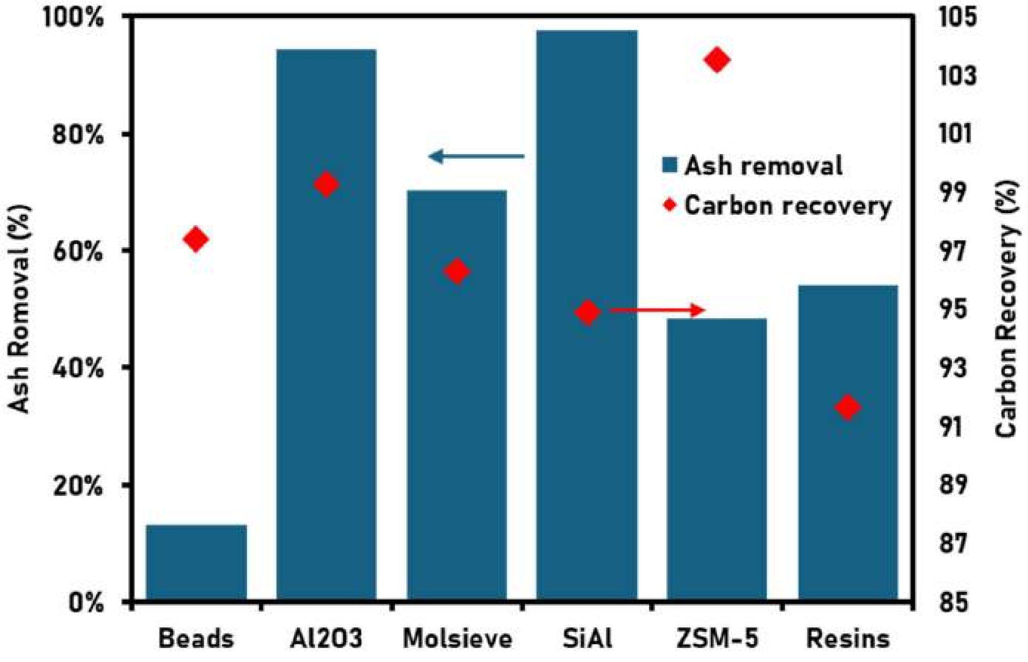

Figure 9: Sorbent washing: Carbon recovery and ash removal

Sorbents, selected based on findings from Olsson Månsson et al. (2023), underwent evaluation using a muffle furnace to measure residual ash content post-treatment. Results indicate a significant reduction in inorganic compounds of up to 98%, particularly notable with Al_2O_3-SiO_2 and alumina sorbents, which also showed better carbon recovery. In general, as it can be observed in Table 3, sorbent washing turned out to be an effective method to remove inorganics from the biocrude. This underscores the role of adsorbents in enhancing biocrude purity alongside solvent extraction.

Table 3: Sorbent washing efficiency on ash removal, carbon recovery, and elemental composition

Properties	Glass beads	Al_2O_3	Mol-Sieves	Al_2O_3-SiO_2	ZSM-5	Resins
C (wt.%)	69.5	71.4	71.0	71.8	69.6	71.1
H (wt.%)	7.4	7.7	7.6	7.6	7.4	7.6
N (wt.%)	2.8	3.0	2.5	2.7	2.9	2.7
O (wt.%)	20.3	18.0	18.9	17.9	20.2	18.6
H/C (-)	1.269	1.289	1.275	1.265	1.276	1.274
O/C (-)	0.219	0.189	0.200	0.187	0.217	0.196
Carbon recovery (wt.%)	97,4	99,3	96,3	94,9	103,5	91,7
Ash in oil (ppm)	2978	190	1016	83	1764	1575

Decision factors between acid washing and adsorbent use include cost-effectiveness, environmental impact, and specific processing requirements. Overall, sorbents may play a crucial role in demineralizing HTL biocrude, improving its quality while optimizing carbon management and process efficiency.

3.2.3. Comparison of the two demineralization alternatives

In Figure 10, the two different alternatives for biocrude demineralization are compared in terms of ash removal efficiency versus carbon recovery in the oil phase.

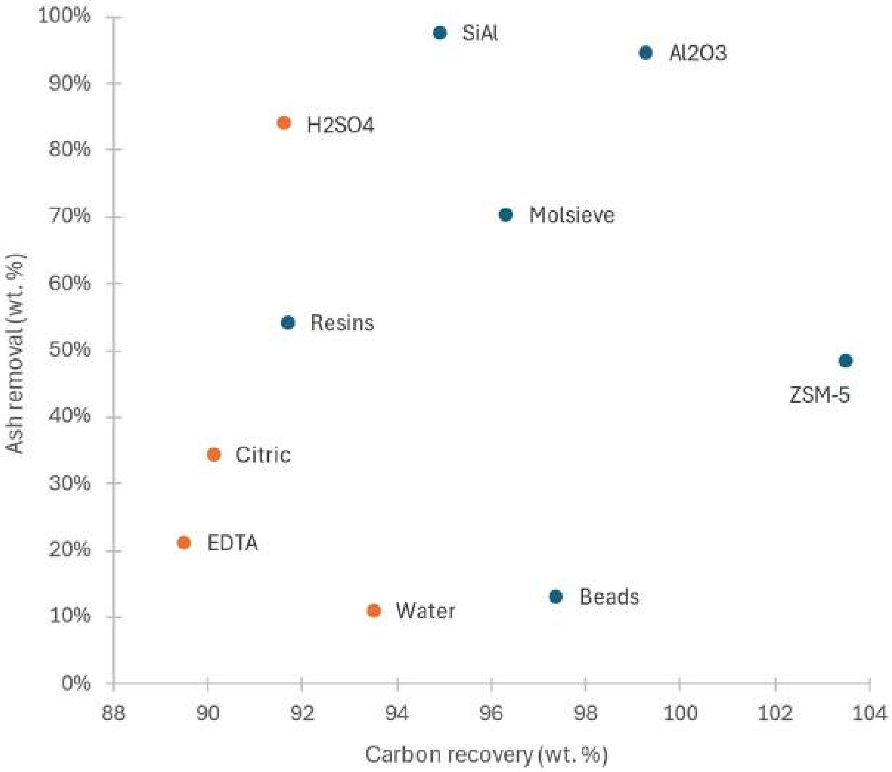

Figure 10: Comparison of the different demineralization alternatives in terms of carbon recovery and ash removal efficiency for 50:50 manure/straw biocrude. Carbon recovery rates above 100% are attributed to measurement uncertainties.

Technologies based on sorbent washing show generally higher carbon recoveries compared to those based on acid washing, which are penalized by the considerable carbon losses to the aqueous phase. This represents a remarkable advantage of sorbent washing, which does not involve the production of a liquid by product stream and therefore can result in a more efficient process in view of scale up.

Sorption has also an optimal performance in terms of ash removal, with the highest efficiencies achieved by alumina and SiAl, which show removal performances slightly superior compared to the strongest acid employed (sulfuric acid). Based on these data, the best result, bringing together carbon efficiency and ash removal performance, was obtained with Al_2O_3 spheres, representing a good candidate for a biocrude demineralization process.

3.3. Detail on inorganic removal

In Table 4 the inorganic elements concentrations in filtered and treated samples from 50:50 manure/straw biocrude are reported, as measured by ICP-OES.

Table 4: Concentration of inorganics (ppm) in the filtered and demineralized 50:50 manure/straw biocrude samples, as detected by ICP-OES. The overall ash value is obtained by incineration.

Sample	Ash	Na	K	Ca	Fe	Ni	P
Biocrude	3424	6	2200	90	46	5	5
Acid washing							
Water	3050	25	90	140	90	14	4
Sulfuric acid	550	10	<10	90	100	8	8
Citric acid	2250	20	95	280	195	29	10
EDTA	2700	9	37	110	80	8	6
Sorbent treatment							
Glass beads	2978	8	390	50	15	3	8
Alumina	190	4	332	22	39	5	3
Alumina-silicate	83	8	22	50	46	5	4
Resin	1575	11	<20	70	18	5	5
Mol. Sieve	1016	7	200	79	39	5	5
ZSM-5	1764	16	925	60	45	5	5

The starting biocrude is characterized by a high content of inorganics, among which potassium shows a remarkable presence, followed by calcium and iron. The washing with acids resulted in a remarkable reduction especially of K, while the other elements do not appear much changed compared to the starting biocrude. Apart from the results relative to K, the trends do not seem in line with the ash content measured by incineration.

Regarding sorbent treatment, inorganic removal appears more efficient. Whereas the removal of K is less remarkable than with the acids (except for alumina-silicate and resins), the performance with the other inorganics, especially Ca and Fe, is more effective. However, it should be mentioned that also here the ICP results are not completely in line with those of ashes following sample incineration. Probably, the presence of other inorganic components apart from those investigated, along with the heterogeneity of the samples, could be a possible explanation for this mismatch.

3.4. Chemical characterization of the treated oil

In this section, the biocrude is analyzed in order to reveal possible alterations to its molecular composition induced by the demineralization treatment. To this purpose, samples were analyzed by GC-MS, FTICR-MS and NMR.

3.4.1. GC-MS analysis

Figure 11 shows the GC-MS chromatograms of the filtered 50:50 manure/straw biocrude before and after demineralization via washing with sulfuric acid and treatment on alumina sorbent.

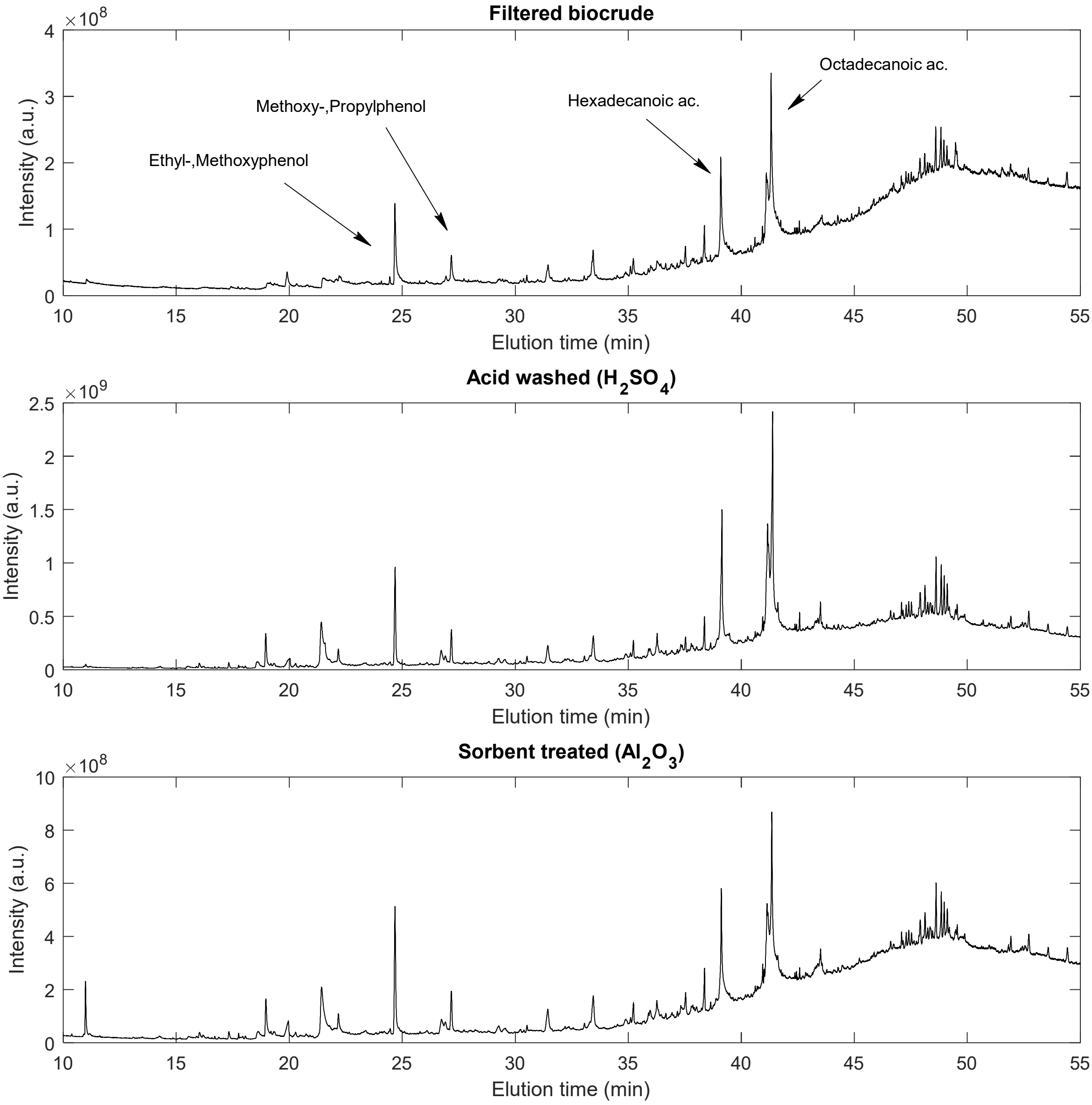

Figure 11: GC-MS chromatograms for the 50:50 manure/straw biocrude samples: (a) Raw biocrude; (b) H_2SO_4 washed; (c) Al_2O_3 sorbent treated.

It can be visually observed that the overall shapes of the chromatograms are substantially the same, indicating that all characteristic peaks of the original biocrude are retained after treatment. Among the noticeable peaks, it can be observed that, on the left-end side of the chromatogram, some alkylated phenolic compounds can be identified. These are normally derived from the lignocellulosic fraction, being phenol the fundamental moiety of lignin. On the right-hand side of the chromatogram some long-chain fatty acids are present, like hexadecanoic and octadecanoic acids, which are probably derived by the manure part, generally rich in lipids. Both acids and sorbents do not look to play any relevant action on these chemical species.

In order to obtain a more comprehensive, semi-quantitative view of the composition, the GC-MS peaks were classified into their different chemical families, considering the relative peak areas as an indirect measure of their abundance. The results of these elaborations are presented in Figure 12.

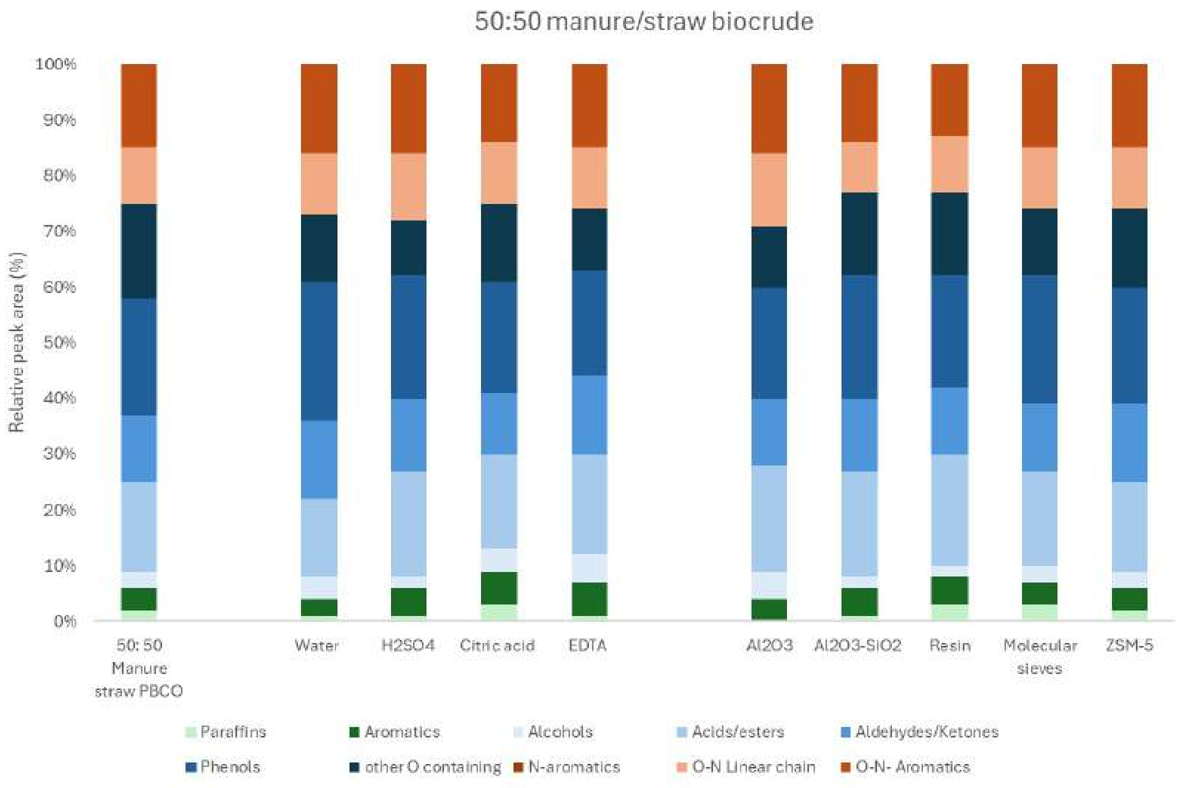

Figure 12: Characterization of the samples from 50:50 manure/straw biocrudes in terms of chemical compounds family, based on GC-MS data.

From Figure 12 it is evident that the different alternatives for demineralization are not causing noticeable shifts in the biocrude composition, at least for the range of compounds that can be detected by GC-MS, i.e. those that can be vaporized at temperatures up to around 300 °C.

All the oils are dominated by oxygenated compounds, especially phenolics and organic acids, in line with the mixed nature (lignocellulosic and lipidic-proteic) of the original feedstock.

3.4.2. FTICR-MS and Nuclear Magnetic Resonance (NMR) characterization

The solvent extracted biocrude obtained from 1:1 manure/straw were characterized by Eni using an integrated analytical approach based on FTICR MS and NMR. The same approach was also employed for the characterization of the pre-treated conditioned bio-crudes that showed the most promising results in term of ash removal (acid wash with sulphuric acid and Al_2O_3 sorbent bed treated biocrudes). The biocrudes were analyzed following the procedure described in Section 2.3. The resulting mass spectra were then elaborated with the PeakbyPeak software (Spectroswiss) and ions were classified into classes considering the number of heteroatoms present in the ion molecular formulas.

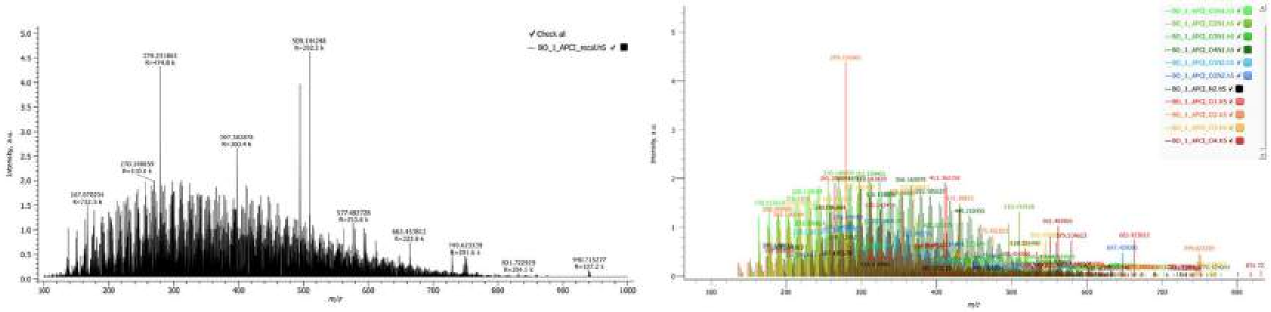

Figure 13: Raw FTICR MS of filtered 1:1 manure/straw HTL biocrude and main classes of compounds determined by accurate mass analysis (petroleomic approach).

The FTICR MS spectra were elaborated to assign the molecular formulas of roughly ten thousand peaks (complex composition). Regarding the filtered biocrude sample, the most important classes are related to Oxygen, Nitrogen containing classes (mainly O_xN_1, with x=1-4, Figure 13). Pure oxygenated species were also detected (likely related to phenols and sterol derivatives).

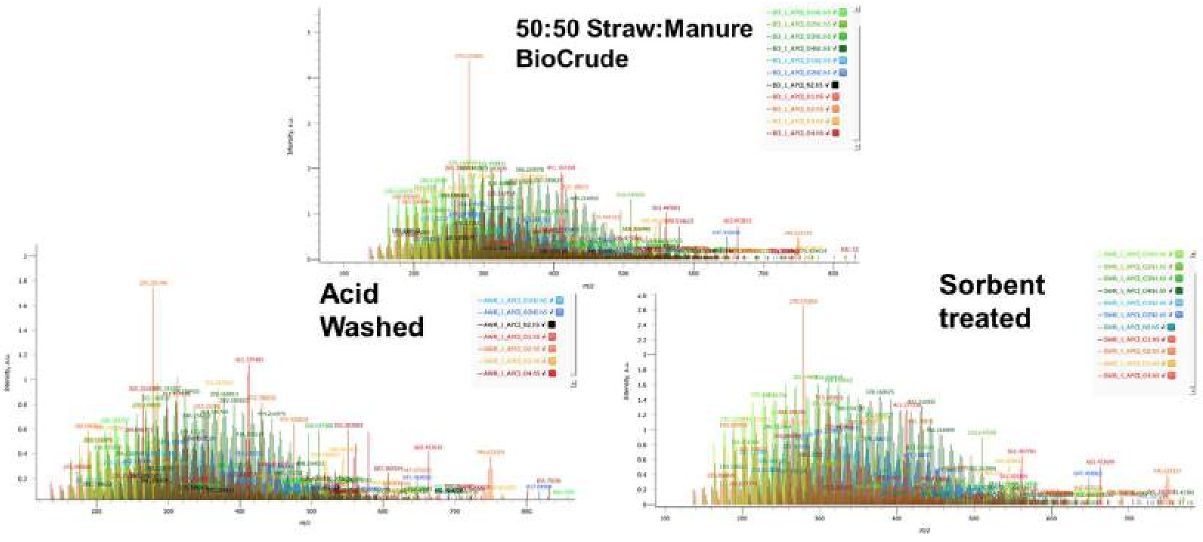

Figure 14: Class colored FTICR Mass spectra of 50:50 Biocrude and respective acid washed (H_2SO_4) and sorbent treated biocrude samples.

Regarding biocrude composition, FTICR MS analysis revealed no sensitive change in the overall bulk composition of the 50:50 manure/straw biocrudes after acid wash and sorbent treatment as it can be seen comparing the spectra of Figure 14.

NMR spectra ^1H and ^{13}C -NMR of the filtered 1:1 manure/straw HTL biocrude are shown in Figure 15 and Figure 16.

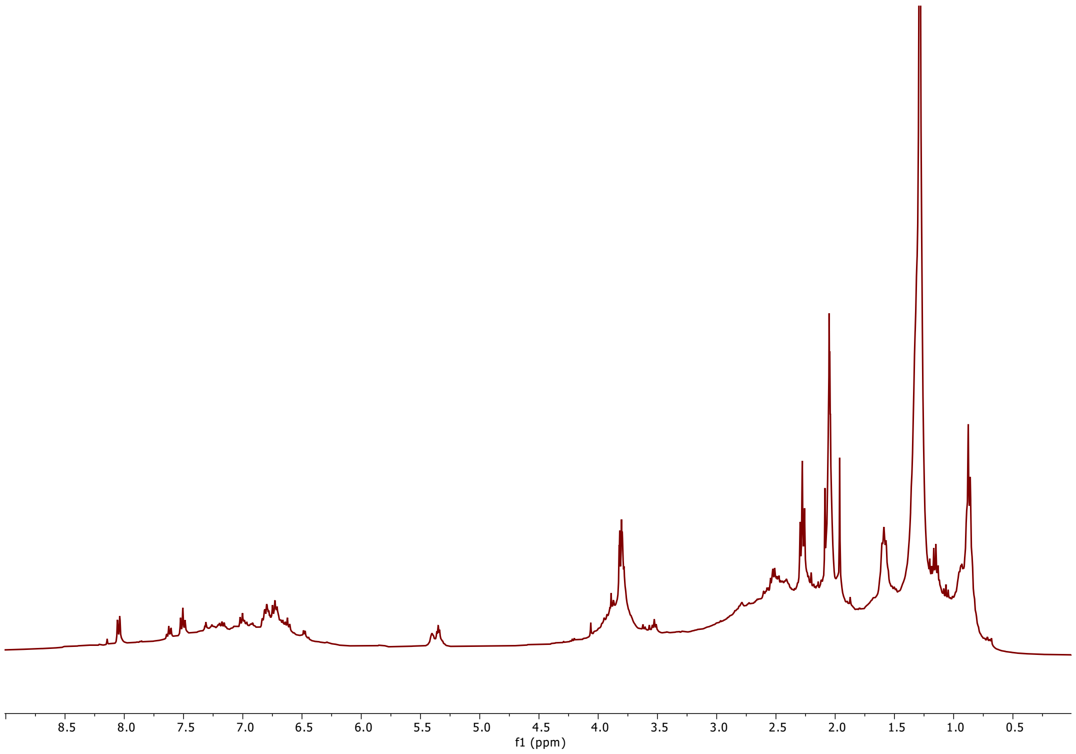

Figure 15: ^1H-NMR spectrum of filtered 1:1 manure/straw HTL biocrude dissolved in deuterated acetone.

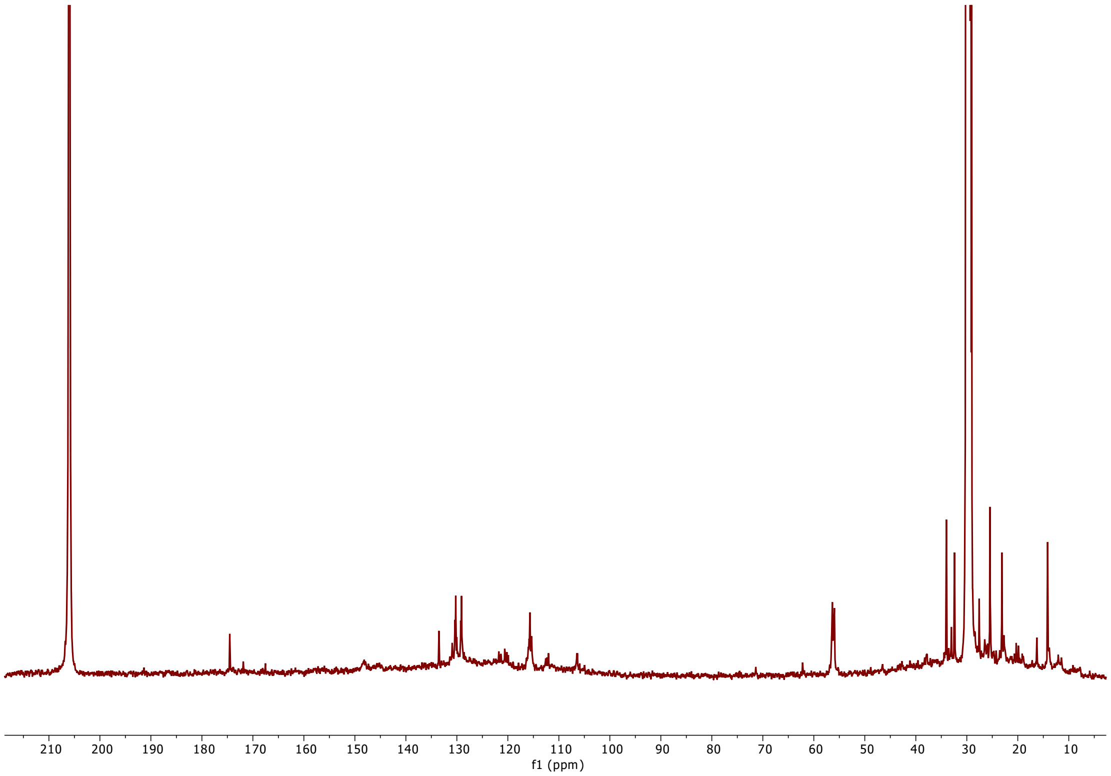

Figure 16: ^{13}C-NMR spectrum of filtered 1:1 manure/straw HTL biocrude dissolved in deuterated acetone.

Protonic signals above 6.0 ppm and carbon signals between 110 and 140 ppm confirm the presence of aromatic compounds. The 175 ppm signal in the ^{13}C-NMR spectrum likely originates from a carbonyl-containing functional group, such as a carboxylic acid, ester, or amide. A peak at 5.5 ppm falls within the typical range for vinylic protons. A cluster of signals between 3.5 ppm and 4.0 ppm for the protonic NMR as well as between 50 ppm and 65 ppm for the carbon one confirms the presence of heteroatoms such as oxygen and nitrogen. Similarly, the acid washed, and sorbent treated bio-crudes were characterized by NMR.

From the comparison of the acquired spectra (^{1}H, ^{13}C) of acid washed, and sorbent treated biocrudes and the starting filtered 1:1 manure/straw HTL biocrude sample, the organic portion of the biocrude seems to be unaffected by the pre-treatments (no significative change in NMR spectra were found).

4. Conditioning of manure biocrude

The same procedure as for the straw/manure biocrude was established also for another biocrude batch, produced from 100% manure. This biocrude presents important differences respect to the previous oil, because the higher share of manure results in a higher nitrogen content. However, similarly to the previous case the initial biocrude has a very heterogeneous aspect, resembling more a sort of "oil sand", therefore requiring a thorough extraction process (Step 1).

Differently from the case of straw/manure biocrude, for the 100% manure sample only the best performing alternatives among those tested for 50:50 manure/straw oil were tested. Therefore, following biocrude extraction, demineralization (Step 2) was carried out only with H_2SO_4 for acid washing, and with Al_2O_3 for sorption treatment. Each of these tests was also compared with blank experiments, using water washing and glass beads treatment, respectively.

4.1. Step 1: Biocrude extraction

The received 100% manure raw biocrude batch was processed using the procedure described in Section 2.2.2. The procedure was carried out on a batch of ca. 47 kg of raw material and it gave the results reported in Figure 17. Here, it is possible to observe the mass balance after the extraction operations and the yields of solid, aqueous and oil phases that were obtained. It is apparent that a large part of the separated batch was represented by aqueous phase. The separation of the aqueous phase from the raw products is an actual issue with this type of biocrudes, since water often remains trapped withing the viscous matrix of biocrude or forms to some extent an emulsion with it. As a result, relevant amounts of water are still present in the raw product, in this case, it summed up to 62 wt. %.

Regarding the other fractions, solids represent 25% and biocrude only around one third of the raw biocrude batch.

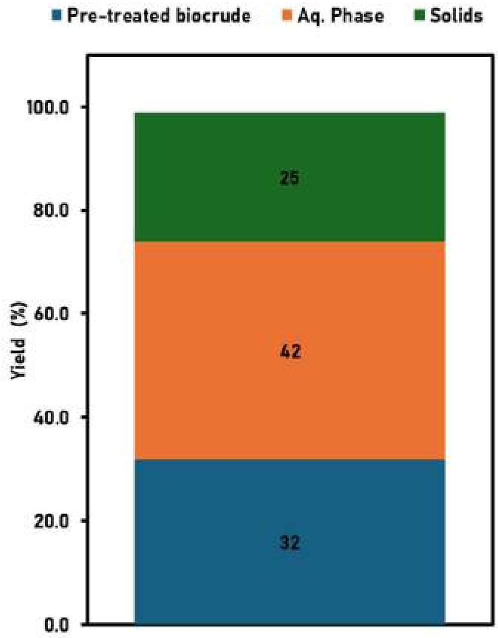

Figure 17: Distribution of the product from solvent extraction of 100% manure raw HTL biocrude.

In Table 5, the elemental analysis of the produced fractions are reported, along with their ash content (for biocrude and solids) and the calculated carbon balance. To this regard, the raw product had a measured carbon content of 59.6%. It should be mentioned that the reported carbon balances are complicated due to the very heterogeneous nature of the raw starting product, consisting of three phases. Therefore, results of carbon balances can be considered as indicative of the distribution among the phases, but their absolute numbers are influenced by the uncertainties in the analysis of the heterogeneous raw starting products.

Table 5: Elemental analysis for carbon balance assessment in the pretreated 100% manure biocrude.

Properties	Biocrude	Solids	Aqueous
C (wt.%)	77,1	45,8	13,8
H (wt.%)	8,0	4,7	NA
N (wt.%)	4,1	2,2	NA
O (wt.%)	10,8		NA
H/C atomic (-)	1,245		NA
O/C atomic (-)	0,105		NA
Carbon Balance (%)	41.4	19.2	9.7
Ash content (ppm)	2 209	420 000	NA

4.2. Step 2: Demineralization

Similarly to what was observed for the 50:50 manure/straw biocrude, the sole filtration, despite the great reduction in the amount of ashes, is still not able to reduce the inorganics to values that are compatible with catalytic processing. Therefore, a subsequent inorganics removal step was conducted, according to the two different alternatives: acid washing vs. sorption. Differently from the previous case, for the 100% manure biocrude only the best performing options were investigated, i.e. H_2SO_4 for acid washing and Al_2O_3 for sorption. In each case, the results were compared with the relative blank test.

4.2.1. Acid washing

As far as acid washing is concerned, the results, encompassing elemental composition, carbon balance and ash removal, are shown in Table 6.

Table 6: Elemental analysis for carbon balance assessment of acid-washed 100% manure biocrude samples.

Properties	Water	H_2SO_4
C (wt.%)	80,0	78,5
H (wt.%)	7,8	7,6
N (wt.%)	3,6	3,8
O (wt.%)	8,6	10,1
H/C (-)	1,170	1,162
O/C (-)	0,081	0,096
Carbon recovery (wt.%)	93,6	86,0
Carbon in aqueous (wt. %)	6,4	14,0
TOC in aqueous (mg/L)	15 000	32 800
Ash in oil (ppm)	2229	865

It can be observed how H_2SO_4 is able to promote a good ash removal, removing around 61% of the ashes originally present in the biocrude. The ash-removing action is confirmed by the comparison with the blank test, whose ash content appears basically unchanged compared to that of the original biocrude. No significant changes can be detected in terms of elemental composition of the biocrude.

The residual ash content is however still relatively large and would require further treatment or the adoption of *in-situ* measures during the upgrading process. The aqueous solution after washing has a remarkable organic content, as it can be observed by its TOC value. The quite relevant carbon loss to the aqueous phase (14.0%, compared to 8.4% observed for the 50:50 manure/straw biocrude) might be due to the specific nature of the organic compounds involved, or it may also be attributed to the higher interaction of the basic nitrogen compounds with the acidic solution.

4.2.2. Sorbent treatment of biocrude

The other alternative to demineralization is sorption treatment. In Table 7 the results relative to glass beads (blank) and Al_2O_3 spheres are presented.

Table 7: Sorbent washing efficiency on ash removal, carbon recovery, and elemental composition for 100% manure biocrude samples.

Properties	Glass beads	Al_2O_3
C (wt.%)	72,0	72,0
H (wt.%)	8,1	8,0
N (wt.%)	3,9	3,9
O (wt.%)	16,1	16,0
H/C (-)	1,350	1,340
O/C (-)	0,167	0,167
Carbon recovery (wt.%)	87,8	85,0
Ash in oil (ppm)	1990	533

The treatment with alumina spheres causes a remarkable reduction in the ash content, obtaining values around 500 ppm, lower than with sulfuric acid treatment. Also in this case, the performance is less effective than for 50:50 manure/straw biocrude, which might be due to the specific nature of the inorganics but also to the different interactions between biocrude and material. It can be hypothesized that, also in this case, basic nitrogen-containing compounds could have more interactions with the solid material, which is acidic in nature.

4.2.3. Comparison of the two demineralization alternatives

The investigated demineralization processes can be compared by reporting their ash removal efficiencies versus their carbon recovery. The result is shown in Figure 18.

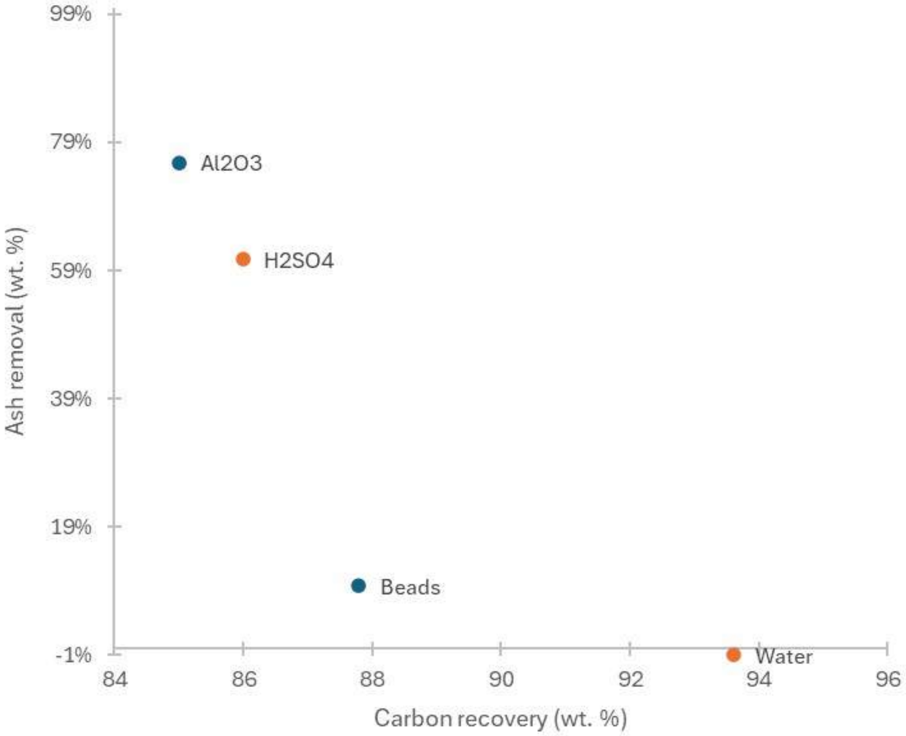

Figure 18: Comparison of the different demineralization alternatives in terms of carbon recovery and ash removal efficiency for 100% manure biocrude.

Sorbent treatment with Al_2O_3 sets the best inorganics removal performance, compared to sulfuric acid. However, the latter seems to have slightly better carbon recovery, despite the observed remarkable losses to the aqueous phase. Therefore, during Al_2O_3 processing significant amounts of organic compounds are adsorbed to the surface of the material, reducing its carbon efficiency. This aspect should be better addressed and optimized, if a scale-up of this technology will be carried out.

4.3. Detail on inorganics removal (ICP-OES)

The filtered biocrude sample, as well as the demineralized ones, were analyzed by means of ICP-OES to determine the concentration of each inorganic element. Results are reported in Table 8 and are compared with the overall ash value obtained by incineration.

Table 8: Concentration of inorganics (ppm) in the filtered and demineralized 100% manure samples, as detected by ICP-OES. The overall ash value is obtained by incineration.

Sample	Ash	Na	K	Ca	Fe	Ni	P
Biocrude	2209	8	130	150	180	6	11
Acid washing							
Water	2229	<30	<50	90	160	6	10
Sulfuric acid	865	3	7	55	12	5	2
Sorbent treatment							
Glass beads	1990	19	150	470	350	6	10
Alumina	533	9	17	55	90	5	0,5

For the filtered biocrude prior to demineralization treatment, ICP shows a remarkable presence of K, Ca and Fe, as well as non-negligible amounts of P. The influence of demineralization is particularly evident by comparing the results of treated samples with their respective blank tests. Sulfuric acid is revealed to be particularly effective in the removal of iron and potassium and, in general, performs very well on all the investigated elements. Alumina also shows a good removal of inorganics, especially if the test is compared with the blank run that was carried out with glass beads. Results are generally less good than with sulfuric acid, especially as far as Fe removal is concerned.

Interestingly, based on ICP values, alumina is less performing than sulfuric acid, while the ash determination via incineration gives a more favorable result to the former. This could be an indication that alumina is able to remove other elements which were not quantified by ICP. However, it should be also mentioned that these samples are quite heterogeneous and local variations in their compositions are possible, determining oscillation in the analytical measurements.

4.4. Molecular characterization of the treated biocrudes

The treated samples underwent characterization by means of GC-MS, FTICR-MS and NMR, in order to investigate how the demineralization process may affect the molecular structure of the biocrude.

4.4.1. GC-MS analysis

Figure 19 shows the GC-MS chromatograms of the 100% manure biocrude before treatment and after acid washing and sorption treatment.

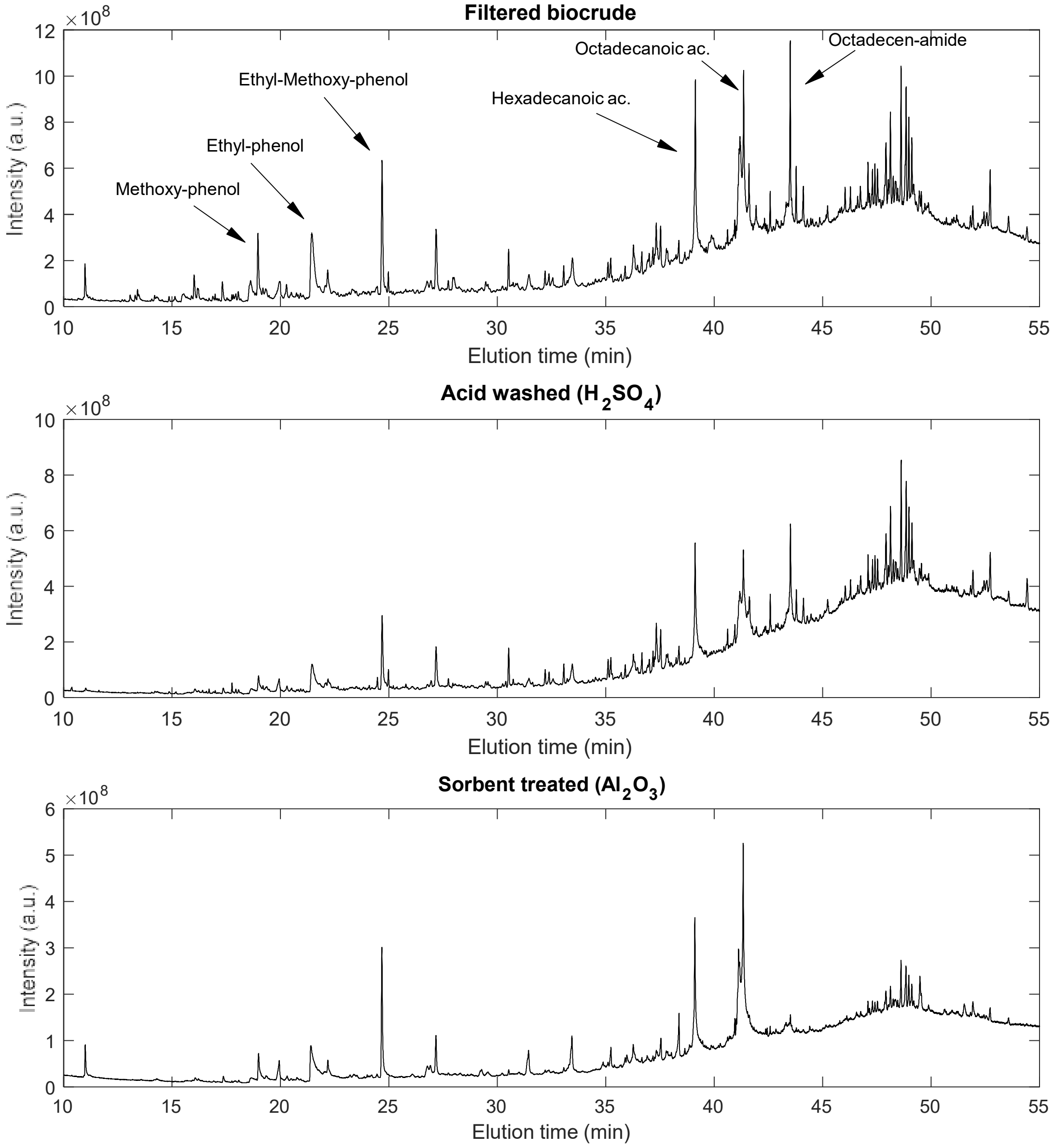

Figure 19: GC-MS chromatograms for the 100% manure biocrude samples: (a) Raw biocrude; (b) H_2SO_4 washed; (c) Al_2O_3 sorbent treated.

Similarly to the case of 50:50 manure/straw biocrude, the demineralization process does not seem to alter the composition of the 100% manure biocrude. The most apparent peaks are generally preserved after treatment. In particular, the peaks relative to phenolic compounds are clearly visible on the left part of the chromatogram, while at higher elution times the peaks of fatty acids (hexadecanoic and octadecanoic acids) and fatty amides are evident.

Peaks were also processed and classified in families of chemical compounds, obtaining the graph in Figure 20.

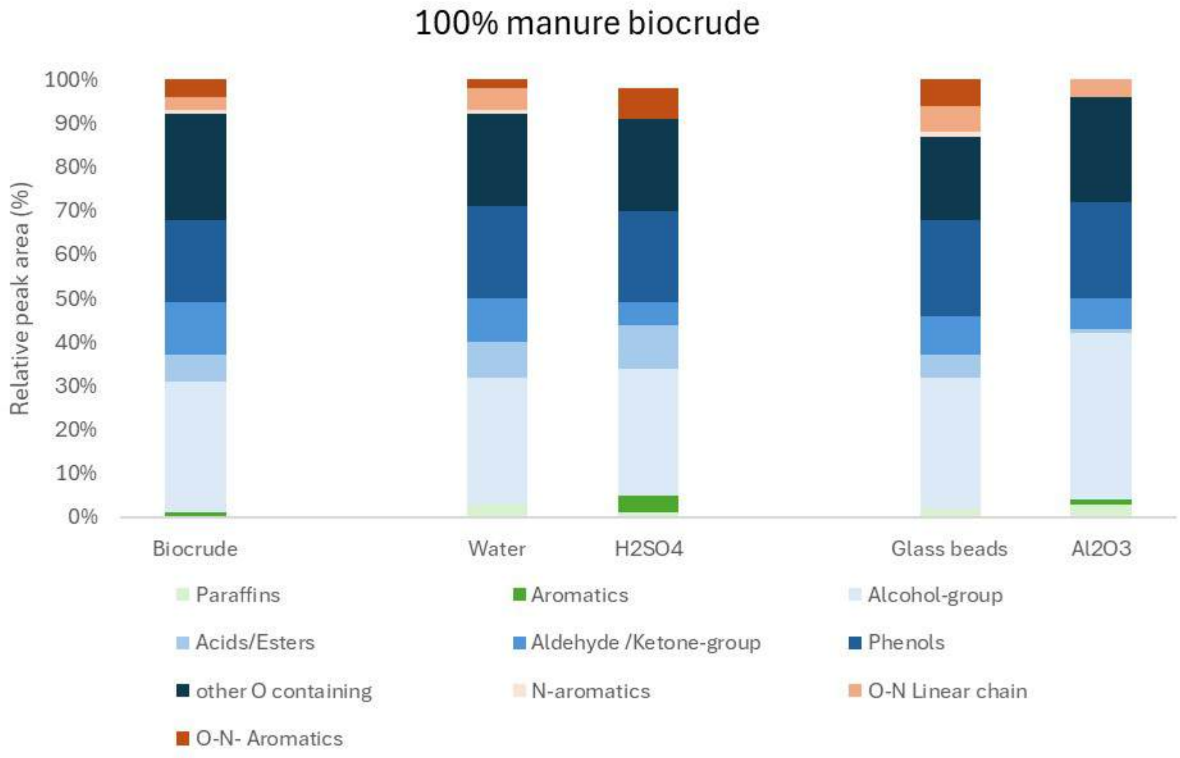

Figure 20: Characterization of the samples from 100% manure biocrudes in terms of chemical compounds family, based on GC-MS data.

The biocrude compositions seem to be dominated by oxygenated compounds, especially aromatic ones. In general, the composition of the treated samples is basically identical to that of the starting biocrude. The only slight exception is represented by the sample treated with sulfuric acid, showing a higher share of acids and esters.

It must be pointed out that GC-MS detection range is limited to the relatively low molecular weight compounds, i.e. those able to vaporize up to ca. 300 °C. For HTL biocrudes, being characterized by a much heavier boiling point distribution, this leaves out a considerable part of the sample. Therefore, the results of GC-MS, though useful to understand general trends, should not be considered indicative of the whole biocrude sample.

4.4.2. FTICR-MS and Nuclear Magnetic Resonance (NMR)

The 100% manure biocrude and the respective acid washed and sorbent treated samples were analyzed with FTICR MS and NMR by Eni to have a more detailed characterization.

In Figure 21 the FTICR analysis revealed more Nitrogen containing species than 50:50 manure:straw biocrude. The main compounds are likely related to acid amides (O_1N_1 class), and N containing heterocyclic aromatic compounds (NCCs). Fatty acids are present as O_2 Class, steroles and steranes as class O_1 and CH, respectively.

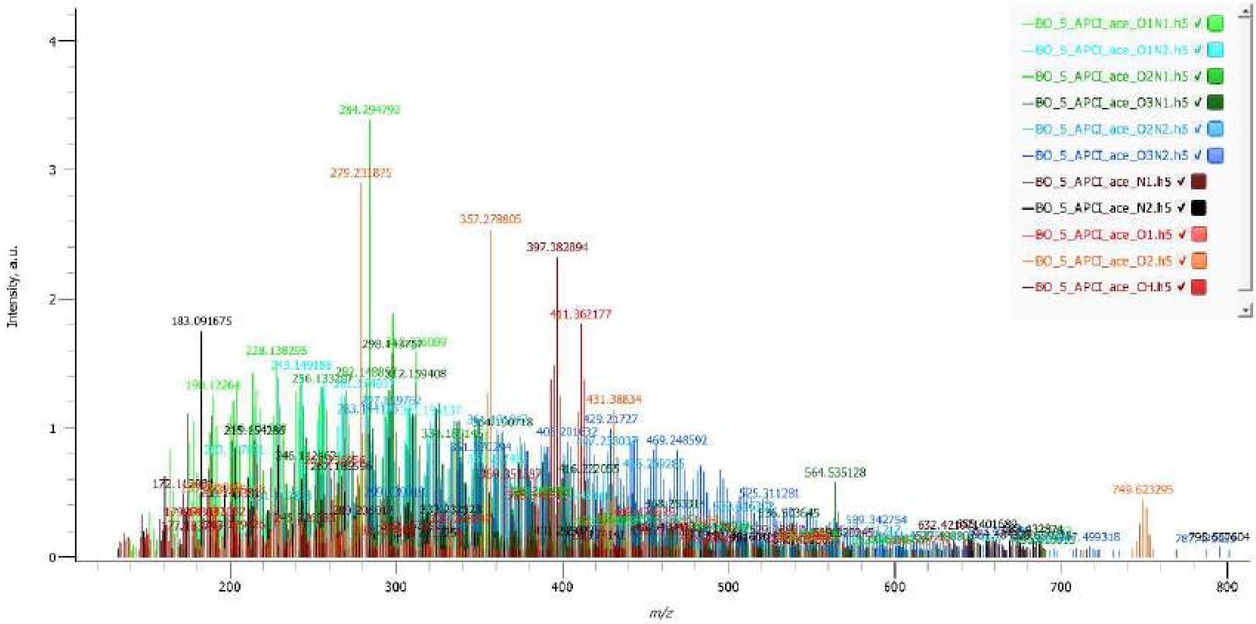

Figure 21: Class attributed APCI Mass spectrum of 100% manure extracted biocrude.

Regarding the biocrude composition after treatment (acid wash and sorbent treatment), a slight reduction of low molecular weight nitrogen containing aromatic compounds, especially for sulfuric acid washed biocrude. The detailed class distribution plots (Carbon number vs Double Bond Equivalents - DBE) of Figure 22 show in detail the differences of distributions at the molecular level.

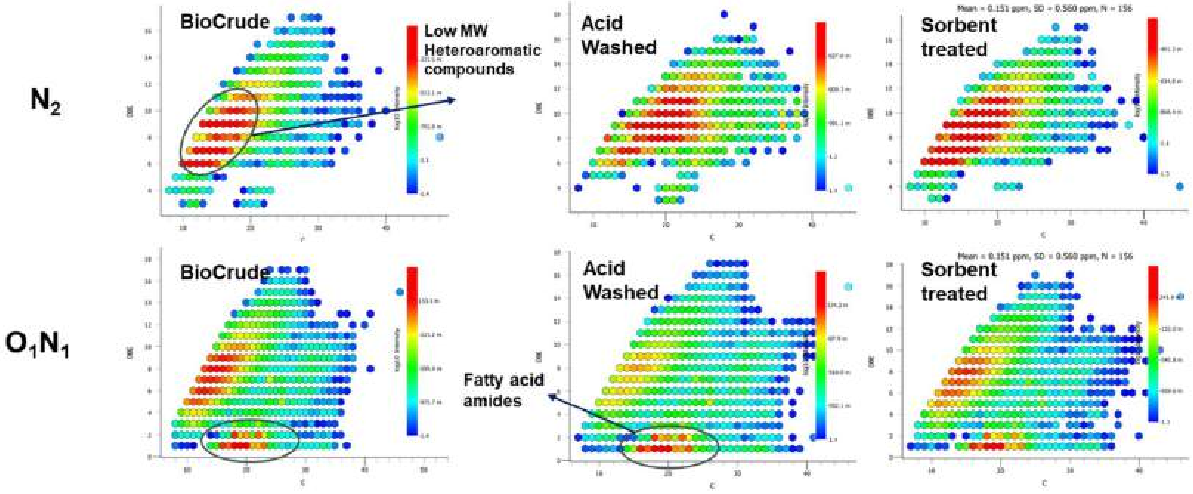

Figure 22: C_n vs DBE compound distributions for N containing classes N_2 and O_1N_1 of sample 100% Biocrude compared with the respective acid washed and Sorbent treated bio-crudes.

The amount of N_2 compounds with low Carbon numbers and lower DBE (6-9 in particular) were reduced after acid wash and the most intense species are in the C_n range 15-30, but with similar DBE range. This proves that acidic washing removes the most basic compounds (with low C_n), that are the ones with the highest N/C ratio. Similar results are also obtained for NCCs related to O_1N_1 species. In the meantime, the amount of fatty acid amides seems not affected (no change in distribution and respective peak abundances). Conversely, the sorbent treatment does not cause a significative change in the distribution of organic compounds.

To monitor the possible changes among the hydroxyl groups after the treatment, a phosphitylation of the -OH groups have been performed using 2-Chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (CTMDP) as reactant after solubilization of the sample in a mixture of $CDCl_3$ and pyridine. ^{31}PNMR has been performed for the characterization of the reacted hydroxyl groups. Cyclohexanol (145 ppm) has been used as an internal reference.

As shown in Figure 23, both samples before and after treatment show the presence of aliphatic -OH (145-150 ppm), phenolic -OH (137-140 ppm) and carboxylic -OH (135-136 ppm), with the former two being present in a larger amount and in the same order of abundance.

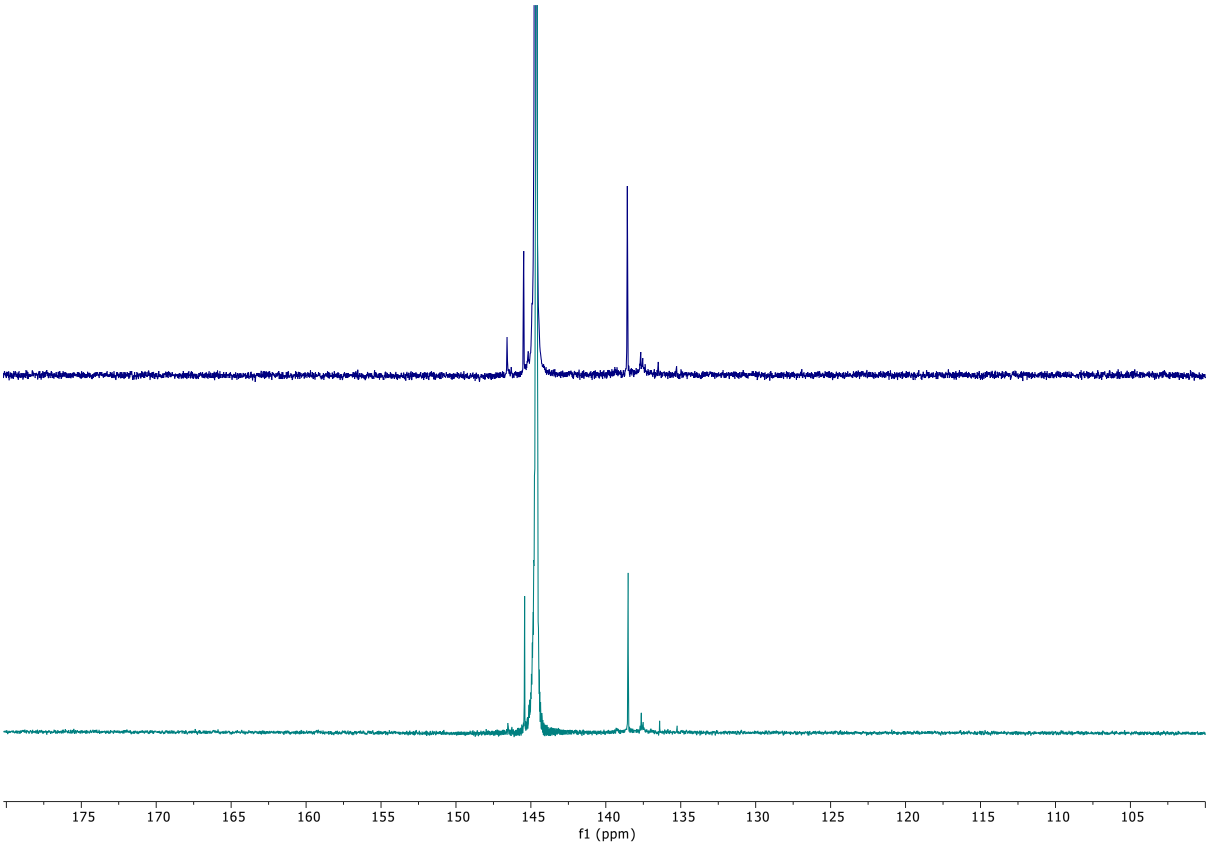

Figure 23: ^{31}P-NMR spectra of 100% manure filtered biocrude (blue) and the same biocrude after washing with H_2SO_4 (aqua). Samples were dissolved in a mixture of deuterated $CDCl_3$ and pyridine.

From an initial comparison over all the acquired spectra (^{1}H, ^{13}C and ^{31}P) the organic portion of the 100% manure HTL biocrude sample does not seem to be significantly affected by the treatments, the slight changes observed by FTICR MS analysis are probably not detectable by NMR spectroscopy.

5. Conclusions and outlook

This study emphasizes effective methods for improving the purity of HTL biocrude in order to make it upgradable by means of hydroprocessing. Raw biocrude produced from HTL cannot undergo direct processing, especially as far as solids and inorganics are concerned. Raw biocrude has often a similar appearance like an "oil sand", from which biocrude needs first to be extracted and then de-metallized to reduce its inorganic content.

Acetone, identified as the most efficient solvent, demonstrated superior oil extraction efficiency. A multi-step approach for biocrude extraction was developed, based on gravity-driven settling of solids. The experiments showed that, using a 1:5 ratio of biocrude to acetone, it is possible to recover almost all the extractable biocrude in two steps of this settling treatment. This procedure can be easily scaled up and allows treating larger amounts of biocrude by avoiding direct filtration, which is not realistic at larger scales. The performed experiments also proved that the procedure can be applied to raw HTL biocrudes from different origins. In this case, a mixed biocrude from 1:1 straw and manure and another one from 100% manure, both characterized by an elevated amount of solids, apart from still very high amounts of aqueous phase.

The extraction procedure can be considered as the natural complement of the HTL production process, helping in obtaining an actual separation of the main product phases. Indeed, phase separation after HTL is not trivial and needs to be appropriately engineered, in order to obtain a product stream that could be effectively handled and transported to the upgrading facility. Biocrude extraction should be therefore implemented as part of the HTL process itself, as an enhanced way to separate its products, each of them to be valorized in the most appropriate manner.

The obtained biocrude after extraction is however still high in inorganics (around 2000-3000 ppm), therefore needing a further treatment step, since the subsequent biocrude hydrotreating requires feeds with a much lower inorganic content, typically as high as a few hundred ppm, in order to extend the catalysts lifetime. Therefore, a further demineralization step is needed to achieve this target. This part of the process can be seen as an actual pre-treatment prior to upgrading, to be established at the bio-refinery location.

The two explored alternatives, i.e. acid washing and treatment with solid sorbents, were both effective in reducing the residual inorganics content. However, significant differences were observed with the different acids and sorbent used. In general, the most effective results were obtained with strong acids, like sulfuric acid, and with sorbents like Al_2O_3 and silica-alumina. Both approaches proved to be able to reduce ashes to an order of magnitude of a few hundred ppm, although the most promising results were obtained with Al_2O_3, able to obtain conditioned oils with 190 and 533 ppm for manure/straw and manure HLT biocrudes respectively.

Despite their relatively good effectiveness in reducing the inorganics content, both treatments did not affect the molecular composition of the oils in a relevant way. This was especially true for the mixed manure/straw biocrude, for which no significant differences at molecular level were found before and after treatment, as observed by advanced characterization techniques like GC-MS, FTICR-MS and NMR. Some minor differences were instead observed in the case of the 100% manure biocrude, characterized by a higher nitrogen content, in which case the treatment with either acids or sorbents resulted in a slight decrease of nitrogen-containing compounds. This can be explained by the acid-base interactions of the basic nitrogen compounds with the acidic media utilized for the treatment. However, none of these effects can be considered as substantial and, in any case, both acid and sorbent treatment give similar outcomes. These slight modifications induced by the pre-treatment should be therefore taken into account for those biocrudes characterized by an elevated nitrogen content.

A remarkable finding is the higher performance of sorbent treatment when inorganics removal efficiency is put in relation with carbon recovery. Here, processes based on acid washing are disfavored, because they are based on the utilization of an aqueous solution which removes part of the organics as soluble products, as it can be detected by analyzing the TOC of the aqueous solutions after washing. However, also during sorbent treatment some organics are retained on the surface of the sorbent itself, the overall effect seems to be more evident for the acids. In addition, the production of a liquid stream to be treated represents an undesirable aspect of acid washing, as this byproduct will likely need specific wastewater treatment, hence adding costs to the overall process.

The adoption of a sorbent-based treatment process is therefore a viable alternative for an industrial implementation in an HTL-based biorefinery. In a practical realization, it can be implemented as a sorption column filled with the desired material (e.g. Al_2O_3 spheres) where biocrude can be passed through right before the first step of hydrotreating. A precise description of the adsorption kinetics and the alternatives for the regeneration of the spent sorbent material are important future work to be carried out and which can eventually lead to a comprehensive evaluation of the complete oil conditioning process prior to upgrading.

6. References

- Haider M, et al., (2023), Understanding the demetallization of nitrogen-rich hydrothermal liquefaction biocrudes by FTICR mass spectrometry: Recalcitrant effect of metalloporphyrins and basic nitrogenates, Fuel (2023) 334, https://doi.org/10.1016/j.fuel.2022.126755
- Danmaliki G, et al., (2017), Effects of bimetallic Ce/Fe nanoparticles on the desulfurization of thiophenes using activated carbon, Chemical Engineering Journal (2017) 307 914-927, https://doi.org/10.1016/j.cej.2016.08.143
- Alexander E, et al., (2018), Adsorption of heavy metals on conventional and nanostructured materials for wastewater treatment purposes: A review, Ecotoxicology and Environmental Safety (2018) 148 702-712, https://doi.org/10.1016/j.ecoenv.2017.11.034.
- Emma Olsson et al., (2023), Removal of Inorganic Impurities in the Fast Pyrolysis Bio-oil Using Sorbents at Ambient Temperature, Energy Fuels 2024, 38, 1, 414–425, https://doi.org/10.1021/acs.energyfuels.3c02473