Production of biocrude from organic waste: Influence of feedstock composition on hydrodenitrogenation reactivity in biocrude upgrading

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Hydrothermal liquefaction (HTL) process of protein-rich biomass produces biocrude with a high nitrogen content that hinders its use as a biofuel intermediate. Nitrogen compounds in the biocrudes are mainly present as fatty acid amides (FAAs) and nitrogen-containing polycyclic aromatic compounds (NAs), having different hydrodenitrogenation reactivity during the biocrude upgrading process. Therefore, it is crucial to shift reaction pathways towards the formation of less recalcitrant compounds and reduce the nitrogen content of the biocrudes. Herein, the impact of the chemical composition, in particular a lipid content, on the biocrude yield, nitrogen content and types of nitrogen species has been studied using macromolecular model compounds. By comparing the hydrodenitrogenation (HDN) reactivity of FAAs and NAs, it was found that the latter are more recalcitrant compounds compared to the FAAs and that the higher lipid content inhibits the generation of NAs. These results suggest that lipids-rich waste can be supplemented with food waste to produce the biocrudes highly suitable for conventional hydrotreatment processes.

Keywords: hydrothermal liquefaction, hydrotreatment, food waste, nitrogen, bio-oil, fatty acid amides.

1 Introduction

About one-third of food produced for human consumption is wasted globally [1], while approximately 88 million of food waste is accumulated only in the European Union per year [2]. Majority of the food waste are mainly ended up in landfills [3] and this has led to serious environmental concerns, as different microorganisms cause serious bacterial contaminations and infectious diseases due to their nutritional composition [4]. Moreover, the food waste causes the greenhouse gas emissions of about 4.4 Gt CO_2 equivalent per year [5], accounting for 12.9% of the global CO_2 emissions for energy production reported by the IEA World Energy Outlook 2021 (34.156 Gt CO_2 equivalent per year) [6].

Hydrothermal liquefaction (HTL) is a promising approach to minimize the generation of organic food waste and recover energy [7]. Generally, HTL operates at the sub- and supercritical region of water (250–400 °C; 200–300 bar) for a short reaction time [8]. The HTL process provides two main advantages: (i) no requirement for drying the wet feedstock, which is an energy intensive process; (ii) unique attributes of subcritical water, such as a high ionic product and lower dielectric constant [9]. Under HTL conditions the biomass is depolymerized into four different products, namely biocrude oil, aqueous, solid residue, and gas phases [9, 10]. Among these fractions, the biocrude oil is of great interest, as it can be used as drop-in fuels after catalytic upgrading process. Food waste consists of three main macromolecular fractions, namely carbohydrates, proteins and lipids [11]. It has been reported that about 20-40 wt.% of nitrogen in the protein can migrate into the biocrude fraction [12], causing a high nitrogen content (>10 wt.%). In comparison, the crude fossil fuels are characterized by much lower one (>1 wt.%) [12]. Several studies on real petroleum feeds showed that lower than 50 ppm of nitrogen in the feedstock can deactivate catalytic active sites in conventional refinery units [13-15]. Consequently, the existing conventional refinery infrastructures are not suitable for the upgrading of waste-derived oils, especially for hydrodenitrogenation (HDN), while constructing new biorefinery units for the biocrudes is not

economically feasible due to the high capital investments, longer implementation period, higher risks and uncertainty regarding the process efficiency [16]. In addition, little is known about the HDN reactivity of nitrogen compounds of the biocrudes [17]. Optimization of the HTL reaction parameters, such as reaction temperature, operating reaction time, heating rate, etc., is typically not effective, as the low nitrogen content always accompanies with the lower bio-oil yield [18-20]. On the other hand, engineering the feedstock composition for balancing the biocrude quantity and quality (lower O and N contents) is highly relevant to meet the minimum specifications of the upgrading process at the existing refinery units.

In this context, it is important to comprehend the behavior of proteins under hydrothermal conditions and their contribution into the biocrude qualities. In our previous work [21] we investigated the mechanism of the nitrogen moieties generation under HTL conditions employing amino acids (leucine, phenylalanine) as protein model compounds in the presence of organic acids and alkali catalysts. Our results showed that the addition of acetic acid into the system greatly increases the biocrude yield as well as the carbon yield due to the transference of hydrophilic amino moieties from the aqueous phase after acetylation reaction forming more hydrophobic amides. Most importantly, we reported that with the addition of lipids the generation of fatty acid amides (FAAs) competes with the formation of nitrogen- containing polycyclic aromatic compounds (NAs) by Maillard reaction, observed in the presence of polysaccharides [21, 22]. Likewise, Fan, Y. et al. (2020) [23] confirmed the existence of the strong counteraction between amidation and Maillard reaction products, using lactose, lysine and palmitic acid as model compounds of carbohydrate, protein and lipid, respectively. As both studies have been performed with only surrogate model mixtures, further investigations are still needed using more complex mixtures in order to gain the exhaustive understanding about how the chemical composition of biomass affect the specimens of the nitrogen in the final biocrude and their HDN reactivity during the hydrotreatment process of the food waste-derived biocrudes.

In the present study we performed the HTL experiments by employing macromolecular model compounds (albumin, starch, tripalmitin) to demonstrate the competition between the formation

FAAs and NAs. Moreover, we studied the influence of lipid content on the biocrude yield and nature of nitrogen species in the biocrude by quantifying the relative contents of FAAs and NAs. To the best of our knowledge, the impact of chemical composition of biomass waste on the nature of nitrogen species (FAAs and NAs) has not been previously semi-quantified. Last but not least, we also evaluated the HDN reactivity of the two main nitrogen compound classes, FAAs and NAs, in the biocrude produced from the food waste. The results obtained in the present study are important to build better fundamentals for formulating the feedstock composition to produce the biocrude with the higher yield as well as quality, and, most importantly, make the biocrude components less problematic for the existing refinery infrastructures, thus avoiding the additional investment costs.

2. Materials and methods

2.1 HTL experiments

HTL experiments were carried out in a Parr 2L batch reactor (4520 series) at 300 °C for 60 minutes with a heating rate of 2.5 °C/min. The detailed experiment procedure has been described elsewhere [21, 22]. The elemental composition of the albumin, starch and tripalmitin is given Table S1. Shortly, 7 g of the feedstock was mixed with 300 g of water solution and placed into the reactor. For the binary and ternary mixtures of albumin with starch and tripalmitin, equivalent masses of each component (4 g) were employed with the same ratio of the feedstock to water. Before running experiments, the reactor was purged with nitrogen to remove any residual air. After 60 minutes of reaction time, the reactor was cooled with a cooling rate of 11 °C/min by running cold water in an internal coil of the reactor.

The gas yield was determined by the ideal gas law taking into account the residual pressure. The gas fraction was then collected in a gas sample bag and its composition was analyzed by Gas Chromatograph (GC). The gas phase was found to consist mainly of CO_2. The biocrude extraction

has been done using ethyl acetate and the solvent was removed by rotary evaporation. The biocrude and aqueous phases were stored at 5 °C until further analytical characterization.

2.2 Characterization of HTL products

The composition of the gas fraction was analyzed by Gas Chromatograph (Agilent 7890A) equipped with a carboxen 1006 Plot column (30 m x 0.32 mm, average thickness 30 μm). The method used for the gas analysis has been described elsewhere [21, 22].

The chemical composition of biocrudes were determined using a GC-MS with a Finnigan Trace DSQ (Thermo) quadrupole mass spectrometry, interfaced to a Finnigan Trace GC Ultra. The separation of biocrude components has been done using a DB-5 MS (Agilent J&W) fused silica, non-polar capillary column (30 m x 0.25 mm ID x 0.25 m). Helium was used as a carrier gas (1 ml/min). The method was described well in previous studies [21, 22]. Shortly, about 1 mg/ml of biocrude samples in diethyl ether were prepared. The oven temperature was set at the temperature of 60 °C for 2 minutes, followed by a heating ramp of 10 °C/min to the final temperature of 320 °C. The acquisition of mass spectra was done in electronic ionization mode with a mass range of 50-650 Da.

The content of free fatty acids was quantified by GC-FID equipped with Supelco Petrocol EX2887 (5m x 0.53 mm ID, thickness 0.1 μm). Helium was employed as a carrier gas (40 cm/sec). BSTFA (N,O-bis(trimethylsilyl)trifluoroacetamide) was used as a derivitization agent for silylation reaction of fatty acids (palmitic, stearic, mono- and dioleic acids) present in the biocrudes. After the addition of about 100 μl of BSTFA and 200 μl of pyridine to biocrude samples, the solutions were heated at 70°C for 40 min. After silylation of fatty acids, the samples were diluted with 1 ml of dichloromethane, followed by addition of 50 μl of tetradecane (4 mg/ml in hexane) and 25 μl of tricaprin (8000 ppm in pyridine) as internal standards. The oven temperature was set at the temperature of 50 °C for 2 minutes and heated up to the final temperature of 350 °C with a heating rate of 10 °C/min. Elemental composition of biocrude and solid fractions was analyzed using an elemental analyzer Flash 2000 Thermo Fisher.

Fourier transform ion cyclotron resonance mass spectrometry was utilized to analyze the composition of biocrude samples. The analysis was carried out using a 7 T FTICR MS (LTQ-FT Ultra Thermo Scientific), equipped with ESI (Electrospray) ion source. The mass spectra were mainly acquired in positive mode (ESI+). The typical conditions for the ESI+ analysis were described in details elsewhere [21, 22, 24]. Generally, the spectra were collected simultaneously with a low resolution linear ion trap (m/z 100-1000) and with a 7 T ultrahigh resolution FTICR cell with a mass range of m/z 100-1000. The resolution was fixed at 400.000 (m/z 400) and the ion accumulation time was defined by the automatic gain control, which was set to 10^6. About 100 scans were collected and averaged for each analysis for the improvement of the signal-to-noise ratio. Data acquired were processed by Xcalibur software (Thermo Scientific). Since a single accurate mass could generate the great amount of potential different combinations of elements, some restrictions are required to the element ranges . In the present study, the restrictions were selected based on the elemental analysis of biocrude samples with the error range of ± 2.5 ppm: 0-60 ^{12}C, 0-2 ^{13}C, 10-100 H, 0-6 N, 0-1 ^{31}S, 0-6 O. The assignment of molecular formula was performed first below 400 Da due to the lower number of possible combinations for a single mass and then the mass peaks above 400 Da were assigned through the Kendrick mass [25]. The list of corresponding molecular formulas with the masses were categorized into groups using a custom-built software ISOMASS [26] and the mass peaks related to isotopes were determined and removed [24].

Then relevant peaks were grouped based on several parameters, in particular, the number of heteroatoms (N, O , S) and the unsaturation degree, assigned as DBE (double bond equivalents) [27, 28]. The DBE value for each molecular formula $C_cH_hN_nO_oS_s$ was defined as DBE=c-h/2+n/2+1. The molecular formulas were specified to about 90 % of the peaks with the relative intensities higher than 0.1 %.

2.3. Biocrude hydrocracking upgrade

The biocrude samples were upgraded by a hydrocracking treatment carried out under the reaction conditions typically used for the fossil heavy oil treatment [29]. The biocrude sample was added into a stirred reactor together with an oleo-soluble catalyst precursor (Mo^{IV} 2-ethylhexanoate). During the upgrading process, the catalyst precursor converts to highly dispersed molybdenum sulfide (MoS_2) nanoparticles [29].

The reaction occurs at 430°C and 160 bar of hydrogen for 3 hours with 3000 wppm MoS_2 catalyst concentration. At the end of the reaction, the mixture was extracted with tetrahydrofuran (THF), filtered and directly analyzed.

2.4. Product yield determination

The yields of biocrude and solid fractions were determined according to Equation 1:

$$X_{fraction}=Mass_{fraction}/Mass_{feedstock} * 100\% \quad (Eq.1)$$

High heating values of biocrudes and upgraded oils were defined by Dulong's formula, where C, H and O represent the weight percentage of the carbon, hydrogen and oxygen, respectively.

$$HHV\ (MJ/kg) = 0.338 \cdot C + 1.428 \cdot (H - O/8) \quad (Eq.2)$$

Energy Recovery (ER) in the biocrude samples was determined by the following formula:

$$ER = X_{biocrude} \cdot HHV_{biocrude} / HHV_{feedstock} \quad (Eq.3)$$

The nitrogen and oxygen removal are calculated by the following formula:

$$O_{removal} = (O_{initial} - O_{final}) / O_{initial} \cdot 100\% \quad (Eq.4)$$

$$N_{removal} = (N_{initial} - N_{final}) / N_{initial} \cdot 100\% \quad (Eq.5)$$

3 Results and discussions

3.1 HTL of binary mixtures with starch and tripalmitin

The nitrogen content in biocrudes is mainly originated from the protein source. Still, the presence of lipids or carbohydrates can promote or inhibit the migration of nitrogen into the biocrude

fraction. To investigate the interaction mechanisms between biomass fractions, representative macromolecular model compounds, such as albumin, starch and tripalmitin, were tested in both water and water-acetic binary solvent system. Table 1 lists the biocrude yields, element analysis, HHV and ER values of biocrudes produced from binary mixtures HTL.

Table 1. Biocrude yields, elemental analysis, HHV and ER values of biocrudes from albumin and binary mixtures of albumin/starch and albumin/tripalmitin.

	Albumin	Albumin/Starch	Albumin/Tripalmitin
Biocrude yield, wt.%	7.4±1.5	6.3±0.21	70.5±3.6
	Element analysis, wt.%		
C	72.6	71.0	74.3±0.6
N	6.6	6.2	2.2±0.07
H	9.1	7.5	11.4±0.3
S	3.5	2.6	<0.1
O*	7.9	12.7	12.1
Solid yield, wt.%	0.11±0.01	0.1±0.01	0.15±0.07
HHV, MJ/kg	35.6	32.7	38.2
ER, %	10.3	9.06	82.9

** calculated by difference, %*

The biocrude yield produced from albumin and its nitrogen content was in agreement with the previous study performed with the egg albumin at 300°C [30]. The solid yield was negligible, thus implying a full conversion of albumin under hydrothermal conditions. It is worth noting that the yield of the biocrude fraction produced from protein fraction of different feedstocks vary widely based on its amino acid distribution. When the peptide bonds in the protein undergo

hydrolysis, some amino acids with hydrophobic side chains (phenylalanine, tryptophan, etc.) are partitioned to the biocrude phase. On the other hand, hydrophilic amino acids (serine, asparagine, etc.) contribute to the generation of water soluble compounds [22].

The Albumin/Starch binary mixture produced lower biocrude yield than that from the albumin alone. However, the nitrogen content of the biocrude was not reduced correspondingly even if the albumin content in the binary mixture was twice less compared to the individual experiment with the albumin. This indicates the occurrence of the interaction reactions between starch and albumin decomposition products, causing the generation of more nitrogen compounds in the biocrude fraction.

It should be pointed out that the experiments with albumin and albumin/starch binary mixture have been also performed in an acetic acid-water solution (5/95 % wt.%) (Table S2). As previously reported for model amino acids [21], also in the present study a significant improvement of the biocrude yield was observed due to the selective acetylation of water soluble amines forming more hydrophobic amides.

The binary mixture of albumin/tripalmitin resulted in the highest biocrude yield due to the contribution of fatty acids produced from the tripalmitin under HTL conditions and their derivatives into the biocrude phase. In this case, the decreased nitrogen content can be attributed to two main factors: the dilution of protein derived fragments by long carbon chains of fatty acids that are quantitatively partitioned into the biocrude phase and the reaction between the acidic moiety of palmitic acid and water soluble amines to give hydrophobic amides [32].

Energy recovery is an important indicator for the efficiency of the HTL process. In this context, the greatest ER was observed for the albumin/tripalmitin binary mixture due to the highest biocrude yield and HHV values. In contrast, co-feeding albumin with starch resulted in the slightly reduced ER compared to that from albumin only owing to its lower biocrude yield and HHV, which is consistent with previous literature [34, 35]. The presence of starch also negatively affected both oxygen and nitrogen contents of the biocrude. In general, the biocrude with higher heteroatom contents is more difficult to upgrade into transport fuels.

3.2 Characterization of main chemical species in biocrudes produced from albumin and binary mixtures.

The biocrude samples produced from albumin and albumin/starch mixture were analyzed by FTICR MS ESI+, as basic nitrogen species are more efficiently ionized in this ionization condition. The mass spectra of biocrudes contained thousands of different peaks and each of them is related to a specific molecular formula. The spectra were then elaborated and the molecular formulas were categorized into groups based on their heteroatoms using a petroleomic approach. Fig.1 depicts the main class components of biocrude products produced from the albumin and albumin/starch mixture. The abundance of one or two nitrogen atom containing compounds (N1 and N2, respectively) was observed for the biocrude produced from the albumin HTL.

For the albumin and starch mixture HTL the N2 class was clearly predominant in the biocrude followed by N1, O1N2 and O1N1 class components.

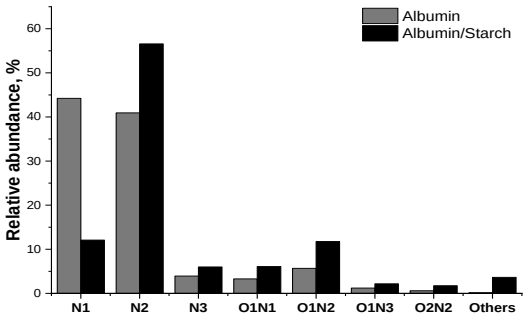

Fig. 1. Heteroatom class components of biocrudes from albumin and albumin/starch mixture.

In order to determine the possible structures of the biocrude components the abundance plots of double bonds equivalents DBE (the sum of rings and double bonds) versus carbon number (Cn) for the main heteroatom classes are depicted in Fig. 2. In the case of the biocrude obtained from

albumin, the main N1 class distribution corresponded at DBE= 4 and Cn=17-20; DBE=8 and Cn=20-23. Concerning N2 class, a broad distribution of species ranging from Cn=20-26 and DBE=7 was observed. The N1 species could be tentatively assigned to aniline and pyridine derivatives with a single ring (DBE=4) or functionalized with a benzene moiety (DBE=8). The N2 class could be assigned to condensed pyrazine or pyrimidine derivatives (DBE=7).

Generally, NAs are generated through Maillard reaction; however, their formation was also observed when amino acids were treated solely [39, 40]. For instance, the degradation of ^{13}C-labelled serine in the absence of any sugars led to the generation of different α-aminocarbonyl intermediates that are common precursors to pyrrols, pyrazines and pyridines via Knorr pyrrole synthesis [39]. The other mechanism for the formation of pyrazines can also occur through the intra- and intermolecular cyclization of amino acids followed by dehydration reactions [12, 34, 38].

The biocrude from the albumin/starch mixture contained mainly N2 homologues series of compounds with the same DBE values of 7 and 11 with Cn=16-26, indicating a higher degree of unsaturation and functionalization. These species could be indicative for quinazoline and naphthyridine derivatives. Based on the FTICR MS analysis, it was shown that NAs, mainly N1 and N2 containing compounds, can be produced from the albumin without any carbohydrate source; however, in the presence of starch, the formation of N2 class components with higher DBE values is enhanced via reactions of amines with oxygenated derivatives (aldehydes, ketones) generated by sugars. Some hypothesized structures based on the elemental analysis and DBE values are illustrated in Fig. S1.

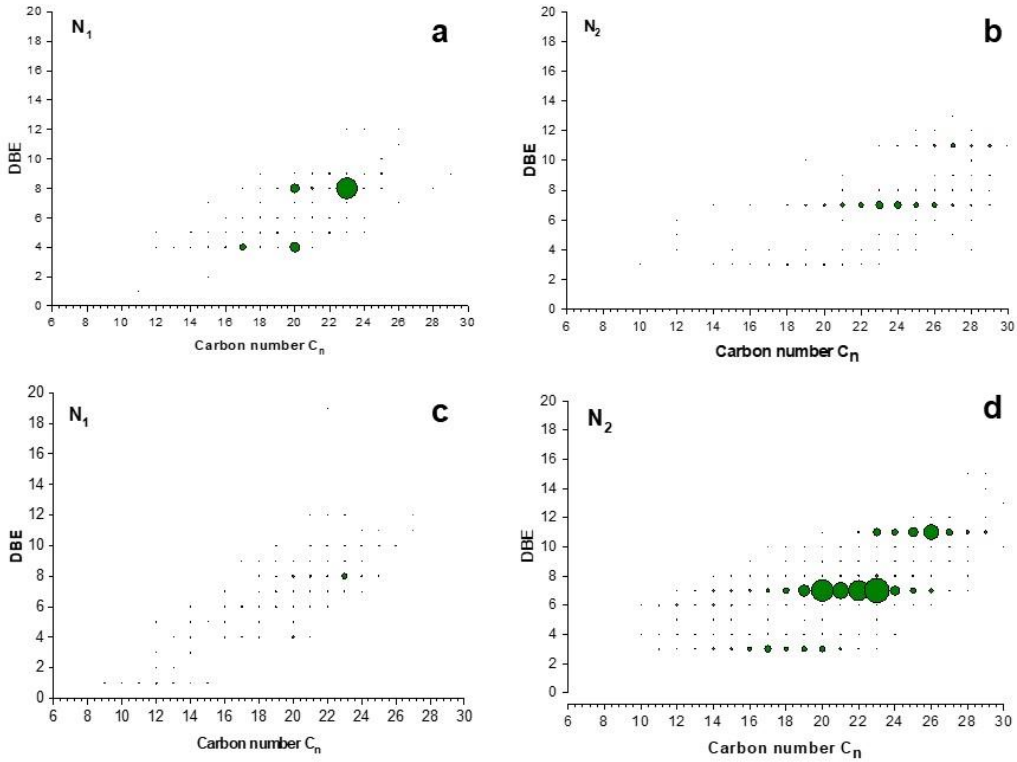

Fig. 2. C_n vs DBE plots for main classes found in biocrudes from a) N1 classes for albumin; b) N2 classes for albumin; c) N1 class for albumin/ starch; d) N2 classes for albumin/starch.

The predominant nitrogen species in the biocrude produced from albumin/tripalmitin mixture were mainly in the form of fatty acid amides (FAAs). Therefore, GC-FID was employed for the quantification of FAAs. Under hydrothermal conditions, tripalmitin underwent hydrolytic cleavage to form palmitic acid, corresponding to 72 wt.% of the biocrude. The amidation reaction took place between palmitic acid and ammonia and amines, resulting in the formation of about 4 wt.%FAAs (Fig. S2).

These results confirm that Maillard reaction is the main reaction pathway that takes place in the binary mixture of protein and carbohydrate, thus generating NAs, while the presence of lipids shifts the reaction pathway towards the formation of FAs and FAAs, which are expected to be less resistant to upgrading process compared to the NAs.

3.3 HTL of ternary mixture

In order to verify the influence of the lipid content on the nitrogen distribution in the biocrudes, comparative experiments were carried out with the ternary mixture containing two different lipid contents of 20 wt.% and 33 wt.%. Two ternary mixtures of albumin/starch/triolein with the weight ratios of 1:1:0.5 and 1:1:1 were processed under identical HTL conditions. Triolein was selected herein in replace of tripalmitin, as oleic acid is the main component of waste cooking oils [41]. Table 2 represents the yields, HHV and ER values of biocrudes.

Table 2. Biocrude yields, elemental analysis, HHV and ER of biocrudes from HTL of ternary mixtures

	Albumin/Starch/Triolein 20 wt.%	Albumin/Starch/Triolein 33 wt.%
Biocrude yield, %	25.0±2.9	36.1±1.5
Biocrude yield without triolein contribution, %	7.1	6.4
Solid yield, %	2.1	1.0
Element analysis, %		
C%	74.0±0.7	74.5±0.6
N %	3.8±0.1	3.0±0.05
H, %	10.5±0.4	11.1±0.2
O, %	11.4	11.4
S, %	0.3±0.04	0.1
HHV, MJ/kg	36.7	38.0

ER, %	37.17	51.2

As expected, the higher biocrude yield and lower nitrogen content were obtained with the higher lipid content mainly due to the direct contribution of fatty acids to the biocrude. As result of this, the ER was substantially improved as well. In this case, the synergistic effect of the addition of lipid to albumin on the biocrude yield, previously reported for the binary mixture, was not prominent. In fact, most of the biocrude is derived from the hydrolysis of the lipid fraction with formation of oleic acid. If it is subtracted, the yields decrease to 6-7%, which are similar to the cases of the binary albumin/starch or albumin alone tests. This can be explained by the occurrence of hydrolysis of three macromolecular fractions, albumin, starch and triolein, at different temperatures. In fact, starch is rapidly hydrolyzed to produce oligosaccharides and monosaccharides at 180−250 °C [42], while the hydrolysis of lipids, for instance, soybean, linseed, and coconut oils proceeds at 260−280 °C [43]. Thus, starch-derived products are present in the reaction mixture since the first stages of the process and they limit their effect on the formation of amides, that would have increased the biocrude yield due to their solubility in the oil phase.

Deep characterization of the products was thus carried out. Given the poor resolution of the GC-MS analysis for polar nitrogen compounds, FTICR ESI+ was utilized to characterize the FAAs and NAs species of the biocrudes. It should be pointed out that by ESI+ the presence of FAs was not detected, as they are selectively ionized in the ESI- mode.

In order to determine the effect of the lipid content on the formation of the NAs and FAAs in the biocrudes produced from the ternary mixtures , the relative contents of FAAs and NAs were determined by FTICR-MS, taking into account their relative intensities in the mass spectra normalized with respect to that of an internal standard (caffeine) and also considering dilution factors. The distribution of FAAs in the biocrude products from ternary mixtures is illustrated in Fig.3. As it can be seen from Fig. 3, the biocrude produced from the 33% lipid containing ternary

mixture contained more FAAs compared to that from the mixture with the 20% lipid content. The ratio of the total relative peak intensity of FAAs in the biocrudes from the mixtures with 33 % and 20 % lipid contents was estimated as 1.51, thus indicating that the high-lipid mixture produced a higher amount of FAAs.

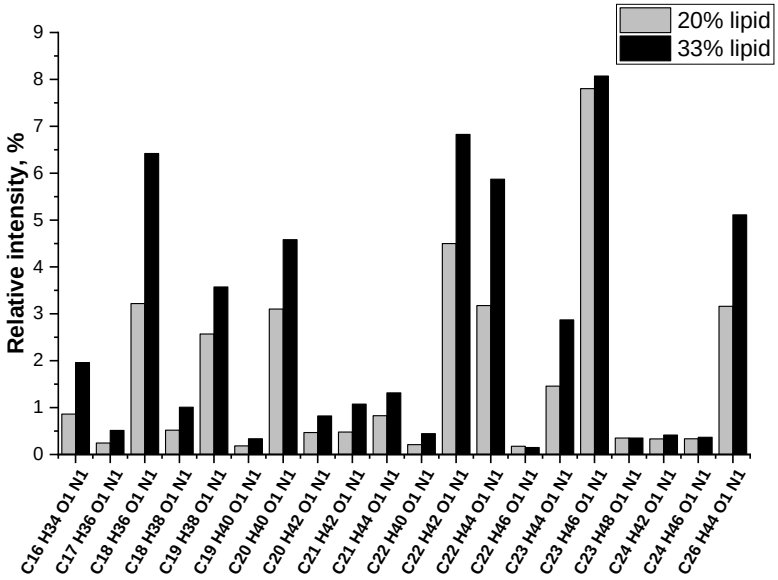

Fig. 3. FTICR ESI+ based distribution of main FAAs species as protonated ions for ternary mixture with 20 % and 33 % triolein contents.

For the semi-quantitative analysis of NAs, the mass spectrum peaks that are relevant to the nitrogen-containing heterocyclic and aromatic compounds were considered by elaborating the compounds only with a DBE value higher than 4. Fig.4 illustrates the abundance plots of DBE versus Cn for the NAs. It can be seen that the NAs in the biocrudes from the ternary mixtures were present in forms of N1, N2 and O1N1 class components at DBE=4-9 and Cn=8-20 and their relative abundances were more significant for the mixture with the 20% of lipid content. In fact, the ratio of the total peak intensity of NAs between 20% and 33% triolein containing mixtures was 0.47 (Total Peak area of NAs for 20% triolein/Total Peak area for 33% triolein), thereby confirming the lower content of the NAs in the biocrude obtained from the mixture with the higher

lipid content. These results confirm the positive impact of the lipids on the promotion of amidation reactions, forming FAAs and inhibiting the formation of NAs, the latter being more recalcitrant for the hydrotreatment process.

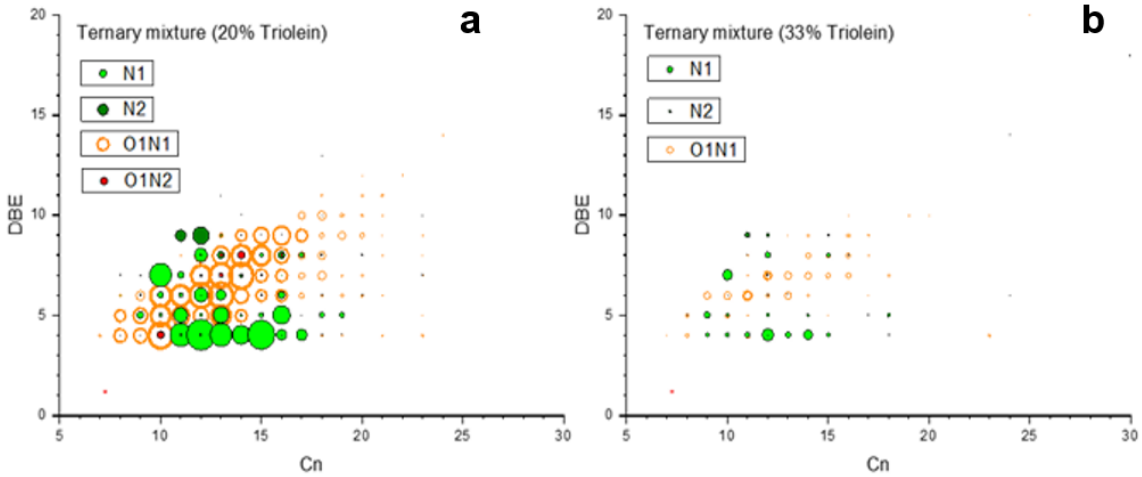

Fig. 4. Cn vs DBE plots for aromatic nitrogen classes (DBE >4) for biocrudes from ternary mixtures: a) 20% and b) 33% triolein content.

3.4 Hydrotreatment of biocrude produced from organic food waste

In order to validate the hypotheses elaborated using model compounds, the composition of the biocrudes produced from the ternary mixture of albumin/cellulose/tripalmitin and from a real municipal organic food waste were characterized by FTICR MS with APPI and compared considering the number of common products and their intensities. According to the results, only about 44% common products were present in both model and biomass waste biocrudes [44]. Even though the employment of the ternary mixtures can help to understand the interaction mechanisms that occur under HTL conditions and optimize the process, they may not be fully reliable for the next upgrading stage via hydrodeoxygenation and hydrodenitrogenation.

Therefore, in order to accurately evaluate the hydrodenitrogenation reactivity under relevant hydrotreatment conditions, and particular the effect of FAAs and NAs content, the two biocrude samples were produced starting from real food wastes with the different lipid contents. A standard sorted household organic food waste was selected with the dry matter of 35%, carbon content of 42% and lipid content of 20%. The comparison was made with a supermarket food packaging and expiring waste with the dry matter of 50%, 55% of carbon content, and 31% of lipid content (due to the presence of meat,cured meats and dairy products packaging).

The HTL of sorted household and supermarket wastes resulted in the biocrude yields of 35% and 58%, respectively. Afterwards, the HTL oils were upgraded by conventional hydrocracking process that is typically employed for the refinery upgrading of fossil heavy oil, such as the vacuum distillation residue, also referred to as the bottom-of-the-barrel [29]. The yields of upgraded oils were 92 and 93 % for the biocrudes obtained from organic waste with 20 and 33 % lipid contents, respectively. As shown in Fig. 5, the upgrading of the biocrude from the 33% lipid containing food waste resulted in the increased yields of diesel (170-350 °C) fraction as expense of vacuum gas oil VGO (350-500 °C) and heavy oil (+500 °C) fractions compared to those from the food waste with the 20% lipid content.

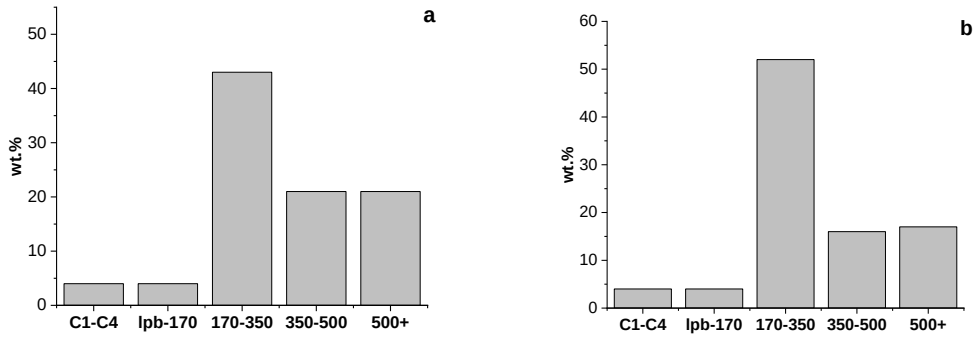

Fig. 5. Distillation cuts for upgraded oils from: a) household food waste; b) supermarket food waste.

The characterization of the biocrudes before and after the upgrading process is given in Table 3 [45]. It can be seen that the upgrading of the household waste HTL oil resulted in the removal of

around 75% of oxygen, 64% of sulphur and 60% of nitrogen and, as a result of the removal of heteroatoms, the HHV increased from 34.8 to 43. MJ/kg, similar to that of fossil fuels. In the case of the household waste HTL oil, the main difference was the denitrification efficiency that increased up to 71%.

Table 3. Element analysis of biocrudes produced form the organic food waste [45].

	HTL oil from sorted household organic waste	Upgraded HTL oil	HTL oil from supermarket food waste	Upgraded HTL oil
		Element analysis, %		
C	72.0	82.0	72.5	83.0
H	9.0	12.3	9.3	12.2
O	12.5	3.1	12.3	3.1
N	5.8	2.3	5.2	1.5
S	0.75	0.27	0.68	0.27
HHV, MJ/kg	34.8	43.3	35.6	44.9

The upgraded oil produced from household waste was analyzed by GC-MS to determine the type of residual nitrogen containing species (Fig.S4). The native biocrude was found to contain FAs, FAAs and some NAs. After the hydrotreatment, the main peaks were related to the linear saturated hydrocarbons with the carbon numbers ranging from C14 to C30 were detected; however, the elemental analysis clearly showed that nitrogen was still present in the upgraded oil.

The nitrogen compounds that are not detectable by GC-MS due to the low volatility and high polarity, were additionally characterized by FTICR MS with the APPI (Atmospheric pressure photoionization) in positive ion mode (Fig. 6). The classes were determined and compared for the biocrudes and the upgraded oils, normalizing the abundances according to the elemental analysis

results.The class distribution confirmed the efficient oxygen removal, as only trace amounts of compounds related to the O1 and O1Nx classes (FAAs) were detected. On the other hand, the amount of NAs belonging to N1, N2, N3 classes, decreased slightly, thereby confirming that the NAs are more difficult to remove by the hydrotreatment process. Similar results were obtained with the supermarket food waste upgraded oil, confirming the NAs belonging to N1, N2, N3 classes are the most recalcitrant, under the given hydrocracking conditions. In this case, the relative abundance of the Nx species was lower than that from the oil with the lower lipid content (even if by a semi-quantitative comparison, due to complexity of the mixture), thus confirming the effect of lipids on the distribution of nitrogenous products, which are shifted more towards the FAAs components. This is in fully agreement with the lower nitrogen content measured with the elemental analysis.

Based on these results, blending of the protein-rich biomass with acyl donor species, such as oleaginous biomass, microalgae, waste cooking oils and fat fractions from animal waste, can be one of the most optimal solutions to inhibit the Maillard reactions and promote the formation of nitrogen compounds with the higher HDN reactivity, thereby producing the biocrudes with specifications that can meet the requirements of the existing refinery facilities.

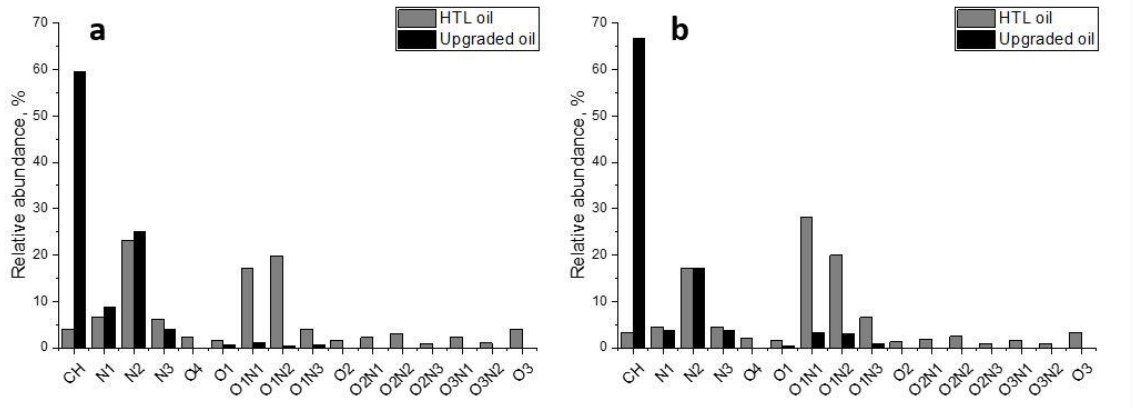

Fig. 6. Main molecular classes distribution of HTL oil and upgraded oil.

The relative abundances of the classes have been normalized according to the elemental analysis results for a) household food waste; b) supermarket food waste [45].

4. Conclusion

HTL tests carried out on model molecules have given general indications that interactions between proteins and lipids lead to an improved biocrude yield and a lower content of nitrogen-containing aromatic compounds, compared to that observed with protein and carbohydrate mixtures. The presence of lipids in the HTL feedstock favors the formation of fatty acid amides, which can be converted into hydrocarbons, thereby resulting in the more efficient removal of nitrogen in the biocrude upgrading process. These results suggest that HTL feedstock should be supplemented with a lipids-rich waste biomass to produce a biocrude more suitable for upgrading by conventional hydrotreatment processes.

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