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Hydrothermal liquefaction (HTL) of Animal by-products: Influence of operating conditions

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ABSTRACT: Hydrothermal liquefaction (HTL) of Animal By-Products (ABP) is a promising technology for their recycling and disposal. Different operating parameters have been studied to determine their influence on the process. Higher heating values of biocrudes ranging between 35-39 MJ/kg have been obtained showing a maximum yield of 61% at 225^{o}C. At low HTL temperature, the products are similar to those of rendering process and the biocrude is mainly formed by triglycerides and fatty acids in a 90:10 ratio, approximately. By increasing temperature, the free fatty acid yield increases, as well as amides and heterocyclic compounds as a result of the triglycerides and protein reactions. Between 250 and 290^{o}C a great difference in the composition of the biocrude obtained is observed. Water content also showed significant effects on the product yields. Large amounts of foams were obtained at low water contents that were minimised when it is increased. This is a very important feature to be considered for scaling up the phase separation process. Glycerine amount in the aqueous phase was remarkable, as a consequence of fat hydrolysis. Increasing pH to 9 increases the extraction of organics into the aqueous phase, whereas operating at pH 5 yields similar amounts of biocrude as compared with neutral pH, with a higher percentage of fatty acids. Reusing of the aqueous phase is necessary for the viability of the process and leads to increasing amounts of dissolved organics in the aqueous phase with the number of cycles, reaching a saturation level after three-four recycling rounds.

KEYWORDS: Hydrothermal liquefaction; Animal by-products; Biocrude; Influence of variables.

ABBREVIATIONS: ABP, animal by-products; HTL, hydrothermal liquefaction; PAP, processed animal protein; HHV, high heating value; TGA, Thermogravimetric analysis; GC-MS, gas chromatography – mass spectrometry.

HIGHLIGHTS

HTL process as a promising alternative to animal by-products treatment.

Temperature, water content and pH greatly affect HTL yields obtained.

High yields of valuable biocrude are obtained at moderate temperatures.

Process water recycling is crucial for the viability of ABP HTL process.

1. INTRODUCTION

Animal by-products (ABP) are materials of animal origin that people do not ingest. In the European Union (EU), the over 20 million tons that are being generated annually emerge from slaughterhouses, plants producing food for human consumption, dairies and fallen stock from farms (Food safety Europen Commission Website, n.d.).

ABP have typically a moisture content of around 40-70 % ((AMSA, 2015; 'EFPRA | Providing Information on Europe's Rendering Industry,' n.d.; Leon et al., 2018)). This amount of water increases the energy demand of the sterilisation rendering process (Meeker, 2006).

ABP are categorised according to their risk using the basic principles in Regulation (EC) 1069/2009. To accomplish the European legislation, a rendering process is used to treat animal by-products. This process consists in heating the waste at 133^{o}C during 20 minutes at a 3 bar pressure, achieving, thereby, the drying of the material and the separation of the fat fraction from the bone and protein fraction. The solid products obtained by rendering are called meat and bone meal (MBM) if the ABPs are classified in categories 1 and 2 (high risk), and processed animal protein (PAP) if the ABPs are classified in category 3 (low risk and suitable for human consumption). MBM is treated mainly by incineration in cement kilns (Cascarosa et al., 2013; Soni et al., 2009). Several studies have been published about pyrolysis, combustion and gasification of MBM (Cascarosa et al., 2012; Feng et al., 2018; Skodras et al., 2007).

Hydrothermal liquefaction (HTL) is a promising method to convert any type of biomass into high value-added chemicals (Villadsen et al., 2012; Zhou, 2014). HTL is a thermochemical process that produces solid, liquid biocrude and gas, involving the use of water at temperatures around 200-300^{o}C and moderate to high pressure (5-30 MPa) in a pyrolysis process (Elliott et al., 2014; Kruse et al., 2013; Peterson et al., 2008). The yield of gases obtained is very low. The operating conditions of the HTL process (low temperature and high pressure) restricts the generation of this fraction, maximising the yield of biocrude (Elliott et al., 2014; Gai et al., 2015b).

The references found show the usefulness of this process to convert different raw materials into biofuel or valuable products. As Tekin et al. (2014) indicated in their review of hydrothermal biomass processing, the number of scientific studies related to conversion of biomass in hydrothermal liquefaction has increased in the last years, mainly in the algal biomass field. Thus, for example, it is possible to find a large number of references reporting lignocellulosic feedstock HTL (Castellví Barnés et al., 2015; Jones et al., 2014a; Liu et al., 2013; Singh et al., 2014; Zhong and Wei, 2004; Zhu et al., 2014); wood chips (Berglin et al., 2012), residual biomass and wastes (Cheng et al., 2014; Neveux et al., 2015) and algae (Chen et al., 2014; Dimitriadis and Bezergianni, 2017; Jazrawi et al., 2013; Jones et al., 2014a; López Barreiro et al., 2013; Patel and Hellgardt, 2015; Zhu et al., 2013). Very few scientific studies have been found regarding HTL of food processing residues: Zheng et al. (2015) studied the alkaline hydrothermal liquefaction of swine carcasses; Yin et al. (2010) investigated the production of bio-oil by HTL of cattle manure and Goto et al. (2004) studied the hydrothermal liquefaction of municipal organic waste. Gollakota et al. (2018) published a review where 100 feedstocks treated by HTL for the obtaining of biocrude are listed. Most of them are different species of microalgae, but other raw materials such as wood, garbage or swine manure have been also included.

However, no HTL studies on specific animal by-products have been found despite the potential advantages, from an economical and microbiological point of view, that this process shows when compared with others, such as pyrolysis or rendering, with which it could compete. The use of moderate temperature and high pressure in the HTL process avoids the evaporation of moisture and guarantees the sample inertisation.

Due to the total amount of this type of sub-products generated in Europe annually, the European Community's 7th Framework Programme funded a research project (FP7-ENV.2013.6.3-2603986, 2014) whose objective was the development of three different technologies at pilot plant scale for the treatment and valorisation of animal by-products. One of those technologies was the HTL process. This work has been developed in the context of that project.

Water content, residence time, pH and temperature are the parameters that show higher influence on the HTL process. Most of the literature found report results in the 240-350^{o}C temperature range.

Thus, the main objective of this work is to study the effect of: water content, total ABP mass, initial pressure, residence time, reactor headspace (empty volume in the reactor), pH, temperature and aqueous phase recycling on the yields and composition of the different fractions obtained. Especial attention has been paid to temperature, focusing on the low temperature range, and to the possibility of the aqueous phase recycling since it has been revealed as a critical aspect for the economic viability of the HTL process.

2. MATERIALS AND METHODS

2.1. Raw material

Different materials have been used in the present study:

a) raw waste from porcine and bovine origin in a 60:40 ratio (including, skin, fat, tendons, bones,...) supplied by a manufacturing company of animal by-products. Samples were homogenised by grinding under cryogenic conditions. A lab scale blade mill, freezing the sample with liquid nitrogen was used. The grinding process was run until the mesh size of the sample was 0.710mm.

b) waste (porcine and bovine residues) supplied by a butcher shop at two different seasons. By comparing visually with the previous raw waste, that one from the butcher's is easier to manage, with lower percentage of tendons and skin and higher percentage of fat and bones. The grinding process followed was similar to that of waste a).c) A mixture of PAP and fat obtained from the rendering process of sample a). The percentages of PAP, fat and water mixed to prepare this sample (55.7% PAP, 7.2% fat, 37.1% water) were estimated from data of PAP and fat content of porcine and bovine samples found in literature (Tacón, 1989) and considering the 60:40 (porcine/bovine) ratio of the raw material used in this paper. . A more detailed explanation of the calculations performed was presented in a previous work (Leon et al., 2018).

The moisture content of the materials was measured by drying at 105°C until constant weigh (EN ISO 18134-1:2015). The ash content was obtained by combustion of the sample at 815°C for

1h (EN ISO 1171:2010). Elemental analysis was carried out with a CHNS Elemental Microanalyser, with Leco Micro TruSpec Detection System. Table 1 shows the characteristics of the materials used.

Each experiment was duplicated. All the data presented in this manuscript correspond to the average of the corresponding values. The error calculated as the differences between the data divided by the average of said data is lower than 10%.

Table 1. Proximate and ultimate (dry-basis) analysis of samples studied (weight %).

	Ash	Moisture	N	C	H	O*	HHV (MJ/kg)
Fat	0.0	0.0	0.0	77.6	12.3	10.2	39.3
PAP	16.2	0.5	12.0	44.7	6.6	20.5	20.5
Grinded real waste	4.3	49.8	3.1	39.3	8.5	44.8	14.2
Butcher waste 1	4.8	26.7	2.7	41.9	9.3	41.3	15.7
Butcher waste 2	5.0	25.4	2.2	43.1	9.8	39.9	16.6

* Determined by difference (100-(N+C+H+ash))

2.2. Hydrothermal liquefaction (HTL) reactor

HTL batch runs were carried out in an electrically heated lab scale reactor (8.5x4.5cm). Figure 1 shows a scheme of the system used. The temperature of the process was controlled by two thermocouples, located one in the furnace and the second at the bottom inside the reactor.

Experiments were conducted as follows: a given amount of sample (consisting in the waste and the amount of distilled water needed to achieve the selected water content) was introduced into the reactor. The reactor was sealed and purged through the corresponding valves with nitrogen gas, and pressurised (10-28 bar) with nitrogen. Temperature and pressure within the reactor were monitored during each experiment. After pressurizing the reactor, it was heated up to the selected temperature (150-290^{o}C) and maintained for the residence time (5-15 min) after reaching the set condition. At the end of the desired residence time, the furnace was turned off and the reactor cooled down to room temperature; pressure decreasing simultaneously. The products obtained were classified into 4 phases: gas, organic phase, aqueous phase and solids. The mass balance was in the range 94.7-100.7% in all experiments. The gas flowed through liquid traps and was collected in a sampling bag. Liquids and solids were removed from the reactor vessel and centrifuged at 1900 rpm and 5 min for separating the different phases (solids, biocrude and aqueous phase).

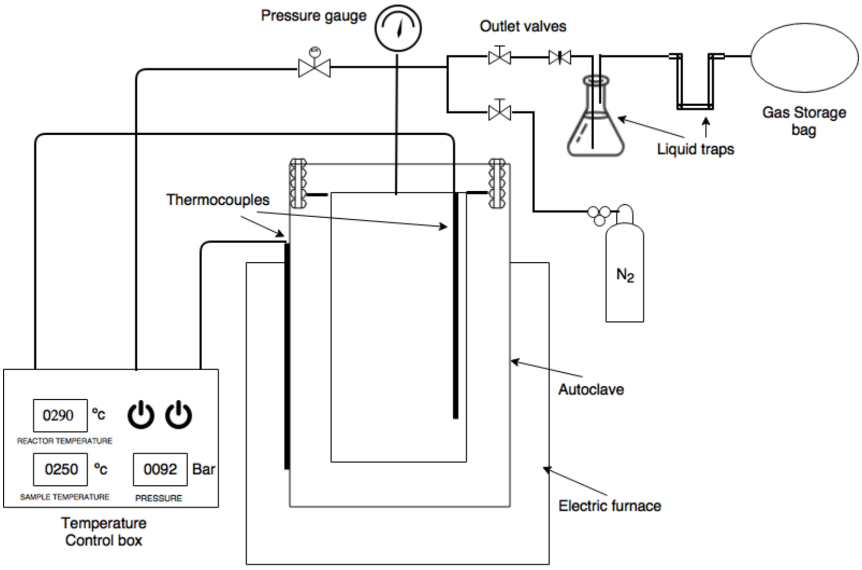

Figure 1 HTL system scheme

2.3. Influence of the pH of the initial solution in the HTL process

In order to analyse the influence of pH value on the product distribution and the composition of the phases, a series of three experiments was carried out under neutral, acidic and alkaline conditions.

Biocrudes have been produced by hydrothermal liquefaction at 250°C and 5 min residence time. In the first case, HTL of animal by-products was performed in distilled water, without any additive. In the other cases, acetic acid or sodium hydroxide were added as additives, to obtain reaction media with pH values of 5 and 9, respectively.

2.4. Aqueous phase recycling in the HTL process

A series of four HTL runs was performed to study the recycling of the aqueous phase in the process. The following conditions were set up: initial pressure 28 bar, final temperature 250°C and 5 min residence time.

The phases were separated by centrifugation and aqueous phase was reused in another HTL experiment, instead of adding fresh distilled water. The process was repeated three times simulating a continuous process with recycled aqueous phase. In each run the ABP/aqueous phase ratio was 40:60. The analysis of the products after each cycle was similar to the other experiments.

2.5. Analytical methods

Similarly to the raw materials used, the elemental analysis of the organic phases was determined by a CHNS Elemental Microanalyzer, with a Micro TruSpec of Leco detector and high heating values were measured using a Leco model AC-350 calorimetric bomb.

Composition of the gas fraction obtained was analysed using a chromatograph (Agilent GC 6890N) with flame ionization detector (GC-FID) for hydrocarbons and a GC-FID with methanizer for CO and CO_2. For quantification of the gas compounds, standards of known concentration were used.

The yield of NH_3, analysed in the runs performed at 250°C, was obtained using H_2SO_4 absorber through the 4500-NH_3·C Nesslerization direct method (Greenberg et al., 1992).

Liquid products obtained in the HTL runs were analysed by gas chromatography with mass spectrometry (GC/MS) (Agilent GC 6890N-HP 5973N MSD). The quantification of the biocrude and aqueous phases was performed with commercial standards. The biocrude fraction was diluted in n-hexane and the aqueous phase in isopropanol. The analysis operating conditions were similar to those used in previous works (Leon et al., 2018). Chromatographic peaks with a relative area higher than 0.5%, in at least one of the samples, were selected and identified in the chromatogram using the NIST 02 and Wiley 7N mass spectral libraries. If the given compound did not correspond to any of the standards injected, the average response factor associated with its main functional group was used. Those components whose match quality was lower than 80% have been grouped and classified as ‘Unidentified’.

A Thermobalance Mettler Toledo was used to characterise the solid and liquid fractions obtained. Approximately 6 mg of sample (solid or liquid) were heated from 25 to 800^{o}C at 10^{o}Cmin^{-1} under N_2 atmosphere. The output of the volatiles from the TGA was connected to a Bruker Tensor 27 FTIR spectrometer through a heated line.

Ecotoxicity analyses of the aqueous phases of some experiments were carried out by using Microtox test. Toxicity was assessed by determining the inhibition of the luminescence of Vibrio fischeri exposed for 15 min. The test was performed according to the basic test procedure (UNE-EN-ISO 11348-3:2009).

3. RESULTS AND DISCUSSION

According to the results obtained, this section has been divided into four parts. First, we present and discuss the results obtained in the analysis of the influence of the following variables: water content, total ABP mass, initial pressure, residence time, reactor headspace and pH, then we discuss the effect of temperature, the comparison of the biocrude obtained with other fuels and, finally, the possibility of the aqueous phase recycling.

3.1. Effect of different operating conditions.

Table 2 summarises the operating conditions of the experiments performed. To study the influence of these variables in the products obtained, the results were analysed and compared from different points of view: fraction yields obtained, TG/DTG curves, FTIR spectra and GC/MS analysis.

3.1.1. Fraction yields

Table 3 shows the fraction yields (on dry-basis) obtained in the runs performed. Appendix 1 shows the elemental analysis and high heating value (HHV) of the biocrude obtained in 3 of these runs.

In some experiments, foams were observed in the gas collection system when the gases were being collected. These foams were weighed and analysed. Their composition, as observed in the thermogravimetric, FTIR and chromatographic analyses, was very similar to the biocrude and therefore they were included in that phase. The formation of foams makes difficult the separation between phases, therefore, it is important to find the conditions that minimise this formation.

Table 2. Summary of the experiments performed

Run	Water content (%)	Total mass (g)*	Initial Pressure (bar)	Residence time (min)	Final pressure° (bar)	Head space (%)	Type of material	T (°C)	pH	Notes
A	50	94	28	15	169	5	raw waste	290	7	-
B	50	95	10	15	120	5	raw waste	290	7	Similar to A, < Initial Pressure
C	50	95	28	5	150	5	raw waste	290	7	Similar to A, < Residence Time
D	50	80	28	5	121	5	raw waste	290	7	Similar to C, < total mass
E	50	80	28	5	110	20	raw waste	290	7	Similar to D, > Head space
F	80	80	28	5	112	20	raw waste	290	7	Similar to E, > Water content
G	50	80	28	5	132	20	PAP + fat + water	290	7	Similar to E, Different Material
H	80	80	28	5	73	20	butcher waste 1	250	5	Similar to I, < pH
I	80	80	28	5	73	20	butcher waste 1	250	7	Similar to F, < T
J	80	80	28	5	72	20	butcher waste 1	250	9	Similar to I, > pH

* material + water

° Consequence of P_{init}, vapour pressure of water at process temperature and volatiles generated in the run.

Table 3. Yield fractions in the HTL runs (% g i/g total (dry-basis)).

Condition studied	Run	Data variable	Gas (%)	Biocrude (%)	Aqueous phase (%)	Solids (%)
Initial pressure (bar)	A	28	5.7	56.1	20.8	19.1
	B	10	1.6	55.6	15.7	26.8
Residence time (min)	A	15	5.7	56.1	20.8	19.1
	C	5	2.7	59.9	20.9	16.1
Total mass (g)	C	95	2.7	59.9	20.9	16.1
	D	80	1.7	63.6	19.9	14.6
Head space (%)	E	20	1.9	67.1	13.4	18.9
	D	5	1.7	63.6	19.9	14.6
Water content (%)	F	80	2.0	60.2	20.1	18.1
	E	50	1.9	67.1	13.4	18.9
Type of raw material	E	real waste	1.9	67.1	13.4	18.9
	G	mixture FAT+PAP	3.8	44.9	35.4	15.0
pH	H	5	0.7	74	20	3.5
	I	7	1.1	73.5	12.5	11.5
	J	9	0.4	41	42	7.0

The results indicated that by increasing **the water content** from 49.6 % (run E) to 80 % (run F), the amount of foams obtained was practically negligible. This was probably due to the fact that by increasing the water content, the percentage of waste in the reactor was reduced and therefore the amount of gases and volatiles generated was also reduced. In that case, the separation between gases and liquids was easier. In addition, although the biocrude yield slightly decreased, its quality was better since the thermogravimetric results indicated that by increasing the water percentage in the sample, the biocrude presented much lower water content (from 20 to 7% approximately), and its separation from the aqueous phase was more easily attained. These aspects could be due to the fact that the biocrude phase is more deoxygenated when the water content in the sample is higher (Appendix 1), resulting in a more hydrophobic phase (Elliott et al., 2014), what is really important since it facilitates the separation of the products. This fact could significantly simplify handling the streams and reduce the cost of the separation step in a larger scale HTL plant.

On the contrary, when the **mixture of rendering products** was used (run G), a significant amount of foams was generated and separation between aqueous and organic phases was more difficult than in the other runs. Additionally, the yield of the biocrude phase was considerably reduced in this run, increasing the organics found in the aqueous phase. This reduction could be due to the fact that in the rendering process the water-soluble compounds are removed and hence they were not introduced in the reactor, consequently, those compounds or those from them derived in the HTL process would not be present and could not be part of the biocrude phase.

The influence of the other parameters, in the range of values studied, was less significant. None of them affected the foam formation although they modified the fraction yields slightly. Thus, it is observed that higher **initial pressure** increases both gas and liquid products, decreasing solid fraction. On another hand, longer **residence time** favours the degradation of the biocrude phase to gaseous products; therefore, as the biocrude yield is the principal objective, operating at short residence times seems to be the better option. Several researchers have investigated the effect of residence time on hydrothermal liquefaction of different materials (Boocock and Sherman, 1985; Karagöz et al., 2004; Qu et al., 2003; Yan et al., 1999). In general, crude yield reaches a maximum before decreasing for very long residence times while gas yield and biomass conversion increase continuously until a saturation point (Akhtar and Amin, 2011).

In the case of modifying the **total mass** loaded and the **headspace** in the reactor, the biocrude yield suffered some variations, probably due to the effect of other variables indirectly involved, such as the heat transfer or final pressure.

The influence of **pH** of the reaction media has been also analysed. A significant modification in the distribution of phases under basic conditions can be observed when comparing with neutral and acidic media. By increasing the pH from 7 to 9, a reduction of biocrude yield and an increase of organics in aqueous phase are clearly observed. Under acidic conditions, the biocrude yield is similar to that obtained at neutral pH although organic percentage in aqueous phase has been increased, reducing the solid phase. Similar tendencies were observed by Yin and Tan (2012) when studying cellulose HTL at 3 different pH values. In that case, more severe reduction of biocrude and increase of aqueous phase were observed under extreme basic conditions (pH = 14) while acidic medium (pH = 3) led to similar aqueous phase and slightly higher biocrude than those yields under neutral pH.

3.1.2. Composition analysis

The thermogravimetric analysis of the biocrudes showed that pressure does not modify the main type of components, while reducing the residence time showed a more significant influence shifting the biocrude DTG curve to higher temperatures. The fact that this shift was not observed when varying pressure means that higher pressure does not involve different composition in the final product. Therefore, from this point of view, it would be enough to use a small initial pressure to assure that, at each temperature, pressure is higher than the vapour pressure of water at that temperature (for example 74.4 bar at 290^{o}C).

More details about the TG/DTG analysis of the samples can be found in Appendix 2.

TGA-FTIR can provide information regarding the type of functional groups and chemical compounds formed in each step (Gómez-Siurana et al., 2014; Marcilla et al., 2009). In this work it was observed that the IR bands obtained (wavenumber) in the different biocrude samples were similar but their relative proportion changed depending on the type of sample and run conditions. Due to the length of the paper the results and discussion of these data is shown in Appendix 3.

GC-MS analysis provides information of the components of the phases obtained.

The composition of the liquid phases is due to the reactions occurring in the hydrothermal processing, including hydrolysis, decomposition, condensation and repolymerisation. Hydrolysis reactions proceed at the early steps of the process while repolymerisation, decomposition and condensation of the intermediates are favoured with the increment of reaction temperature and residence time (Gollakota et al., 2018). The combination of all these reactions leads to a very wide spectrum of compounds in the liquid fractions.

Gai et al. (2015a) inferred a general picture of the HTL process based on the experimental results and previous studies for microalgae. This picture could be similar for ABP. These authors distinguished three ranges of temperature where different reactions can take place. At temperature lower than 100^{o}C, proteins, lipids and carbohydrates are hydrolysed. In the 100-

200^{o}C range, molecules resulting from the previous hydrolysis undergo decomposition processes (decarboxylation and deamination). Above 200^{o}C, further reactions take place to produce molecules such as aliphatic amines, esters, aromatic compounds or pyrrole derivatives.

More than 70 compounds have been identified in the aqueous phase. A Table with the yields of the major compounds obtained in the experiments performed is presented in Appendix 4. Although the main component is the glycerine, coming from the hydrolysis of the lipids, there are many pyrrole derivatives originated from the protein content of the residue.

The main difference observed in the composition of the different aqueous phases lies in the relationship between glycerine and the other major organic compounds identified. For a better comparison of the influence of the operating variables, the compounds detected have been grouped according to their main functional group and Figure A4.1 (Appendix 4) shows the yields of these groups as a function of the parameters studied. The results indicated that increasing pressure and residence time lead to greater amount of heterocyclic organic compounds with a lower proportion of glycerine. On the contrary, water content and total mass in the reactor do not influence on aqueous phase composition. As expected, the use of rendering products instead of real waste as raw material led to quite different composition, showing a significant increase of heterocyclic organic compounds.

A similar study with GC/MS was carried out for the biocrude phase. The list of the major peaks is also shown in Appendix 4.

Additionally, as in the case of the aqueous phase, the components were classified into groups based on the functionalities (Figure 2): fatty acids and esters, nitrogen and oxygen heterocyclic compounds, nitrogen compounds and oxygenated compounds. Using as raw material the waste supplied by the manufacturing company of ABPs, the group with major yield (weight percentage respect raw material) in all the experiments corresponded to heterocyclic organic compounds, followed by nitrogen compounds (mainly amides).

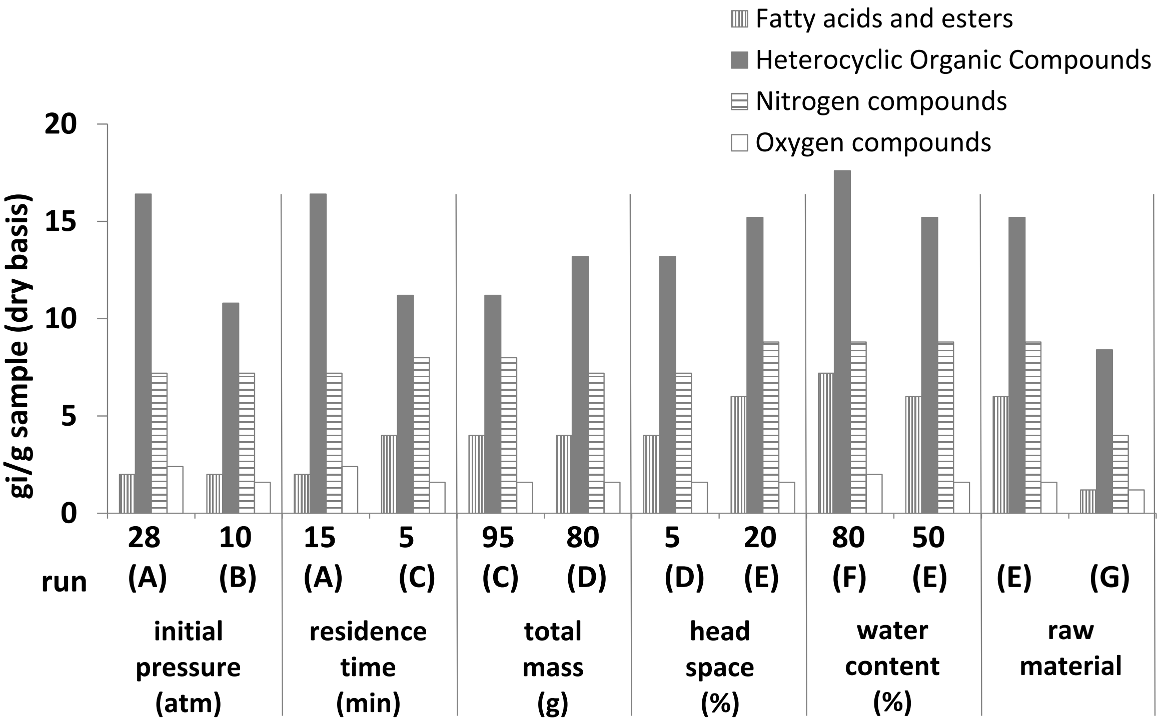

Figure 2. Comparation of compound groups identified in the biocrude phase

From Figure 2, two main ideas can be deduced. On one hand, the large differences of biocrude composition between rendering products and the real waste. A significant decrease in fatty acids was observed from the rendering products. On the other hand, the great influence of long residence time that led to higher heterocyclic organic compounds/fatty acids ratio. It looks like at long residence times the reactions of the fatty acids coming from lipid decomposition are promoted. Parameters such as total mass, headspace or water content did not affect significantly the percentage of compounds grouped by functional groups, although it could be remarkable the high percentage of oleic acid present in the biocrude coming from higher water content.

The main compound in the gas fraction of all HTL runs was carbon dioxide (yield lower than 2%), the others (CO and C_1-C_6 hydrocarbons) being practically negligible. This fact reflects that nearly 100% of the organic products remained in the liquid fraction.

As said previously, Appendix 1 shows data of the elemental analysis and HHV of different biocrude samples. A direct correlation between the HHV and the carbon content for all the samples was detected, whereas the relation with the oxygen content was the opposite. The carbon content in biocrude of run F was higher, with a lower oxygen content, what made that its HHV was also higher, indicating that, as said previously, a higher water content provided a biocrude with better properties.

Appendix 5 shows the composition of the biocrudes obtained in the study of pH. The compounds have been also classified and grouped together according to their functional groups. Figure 3 shows the yields of these groups. It can be seen that, in this case, using the materials supplied by a butchery (butcher waste 1), fatty acids and esters are the major group in all the experiments.

By comparing the influence of the pH value on the composition detected, it must be emphasised the significant differences between acidic and neutral media, despite the similarity between both biocrude yields. Under acidic conditions, the yield of fatty acids and esters in the biocrude is increased, while the other groups, especially the heterocyclic compounds, have been reduced. Consequently, pH is a variable affecting significantly the results obtained and using acidic conditions may be a selection for a real process. Ross et al. (2010) studied the hydrothermal processing of microalgae using alkali and organic acids. In spite of the differences in the raw material and therefore in the product distribution, these researchers also remarked the presence of larger amounts of fatty acids such as hexadecanoic acid and fatty acid amides such as hexadecanamide when adding acetic acid or formic acid to the reaction medium.

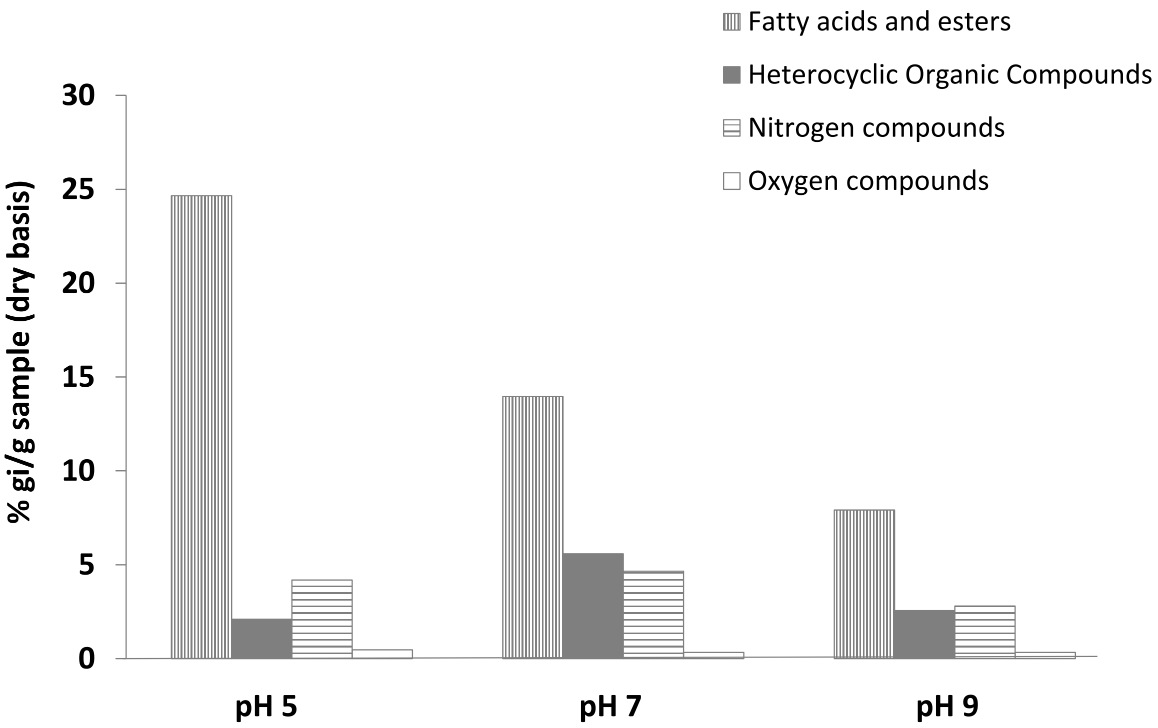

Figure 3. Groups of compounds identified in the biocrudes of HTL runs at different pH

3.2 Effect of temperature.

Six different HTL runs were performed at six different temperatures in the range 150-290°C. Initial pressure was kept at 28 bar and the residence time at the selected temperature was 5 min. The total mass in the reactor was 80 g approximately, with a water content of 80% (the material used was butcher waste 2). Under these conditions, the final pressure reached was in the range 44-110 bar.

3.2.1. Fraction yields and elemental analysis of products

The degradation reactions increase with temperature, leading to a rapid reduction of the solid fraction and to an increase of the other phases. The combination of primary and secondary reactions results in the formation of a slight maximum yield (61%) in the biocrude obtained at 225°C, decreasing down to 54% above this temperature. Other researchers, such as

Akhtar and Amin (2011) and Chen et al. (2014) also reported a maximum with temperature. Appendix 6 shows the yields of the fractions obtained at the temperatures studied as well as the elemental composition and the HHV of the biocrude fractions. The organic matter content in the aqueous phase also increased up to 225°C. From that temperature on, the variation of the yield is very low. The increase of temperature in the HTL process seems to favour the hydrolysis of not only triglycerides but also proteins, what promotes the generation of water soluble compounds (Sato et al., 2004). Gas fraction increases markedly with temperature but the yields obtained are always lower than 3%.

According to these results, the optimal working temperature would be 225-250°C, where the degradation of the raw material is very high, the biocrude yield reaches its maximum value and the solid residue is minimum. Possible applications of the organics in the liquid effluent must be studied (for example as glycerine source and fertilizer).

In the interval of temperatures studied, the biocrude HHV values seem to be independent of the process temperature. This similarity is coherent with the fact that the CHNO elemental analysis of all the biocrudes obtained are very similar, regardless of the type of compounds forming them at each operating temperature.

As in the previous cases, elemental analysis shows that the biocrude composition was mostly carbon (73-77%) followed by oxygen (11-15%) and hydrogen (11-12%). Nitrogen was detected in the biocrudes obtained at temperatures higher than 225°C and increases with temperature (<3% in all the cases), due to the reactions and decomposition processes of proteins (Gai et al., 2015a). From elemental analysis data (dry basis), N/C and O/C ratios can be calculated. These ratios are significantly reduced in the biocrude as compared to those in the raw material.

3.2.2. Analysis of biocrude by TG/DTG

Biocrude was characterised by TG/DTG analysis. Figure 4 shows the DTG of the biocrudes obtained at the different temperatures studied. This figure also includes the DTG curve of a fat sample resulting from a typical rendering process. As can be seen, the HTL biocrudes obtained at low temperatures (150-200°C) follows a DTG pattern very similar to that of the rendering fat. In these cases DTG curve shows a main peak at around 400°C, corresponding to the decomposition of the triacylglycerols, as well as a very small shoulder observed at around 280°C, corresponding to the evaporation of the biocrude lighter fraction mainly formed by free fatty acids.

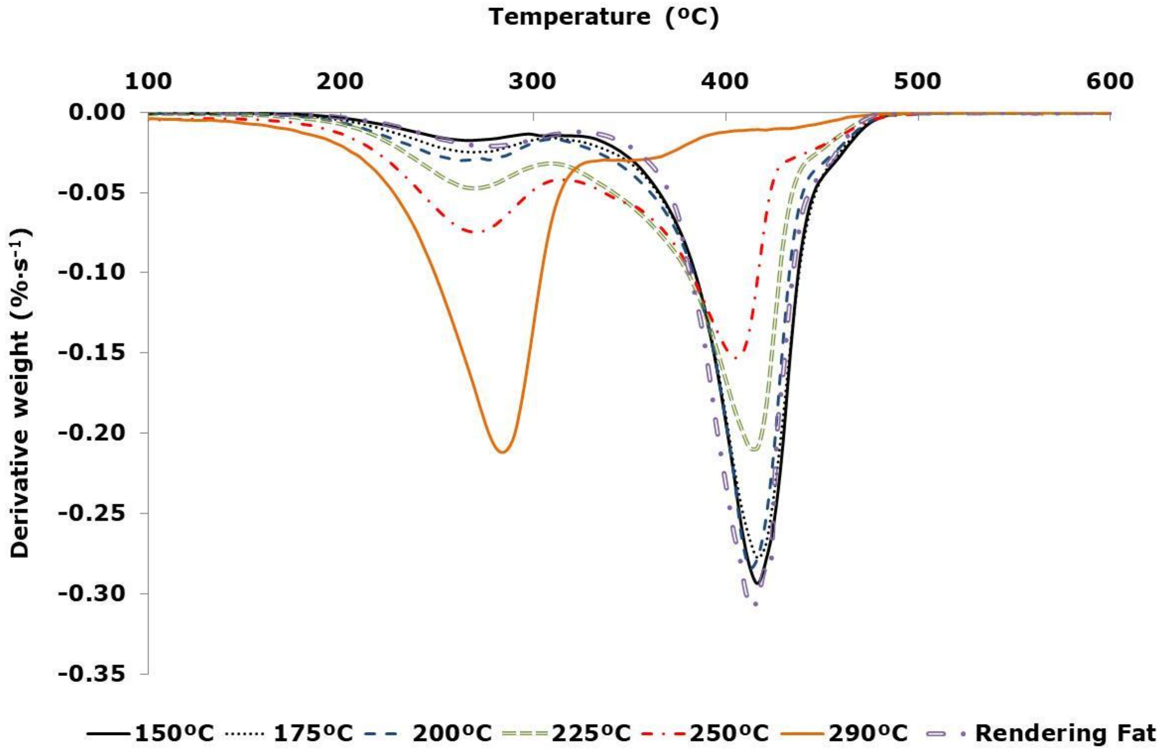

Figure 4. DTG curves of the biocrudes obtained at different temperatures and rendering fat.

The connection of both peaks with triglycerides and fatty acids respectively has been already presented by other authors. For example, Melzer et al. (2013) studied TG/DTG curves of shea butter and jatropha oil and attributed the major sharp peak at 420°C to triacylglycerol decomposition and the minor wider peak in the range 215-300°C to the fatty acids evaporation.

In the present paper, the evolution of both fractions with HTL temperature clearly shows how the increment of this parameter favours the decomposition of triglycerides increasing the percentage of more volatile compounds.

At low temperatures, where the biocrude DTG curve is very close to that of the rendering fat, it is expected that chemical composition of the peak corresponding to the largest fraction is mainly formed by triglycerides. By increasing temperature, the curve differs from that of the rendering fat and, in addition to a greater percentage of fatty acids, other compounds coming from protein degradation can be present in the biocrude composition (Gai et al., 2015a).

From the area of the DTG peaks, the triglycerides/light fraction ratio in the biocrudes obtained can be calculated, moving from values of 90:10 at 150°C, 83:17 at 200°C to 20:80 at 290°C. The marked change observed is produced in a very narrow temperature range of around 40°C. Thus, by increasing temperature from 250 to 290°C, the percentage of triglycerides decreases from 60% to 20%. Therefore, although the HHV of the organic fraction obtained in both cases is very similar (around 38 MJ/kg) the difference in the composition can affect the quality of the fuel (different molecular weight, viscosity, ageing processes in storage conditions, etc.). This fact must be taken into account when process temperature is selected and with the temperature profile to be used in a reactor at large scale.

3.2.3. Analysis of biocrude by GC/MS

In order to obtain more information about the composition of the lightest fraction, the biocrude was analysed by GC/MS.

Appendix 7 compares the chromatograms of the biocrudes obtained at the 6 temperatures studied. These chromatograms give information about the percentage (and type) of components evolved in the process with a boiling point lower than the injector and column temperature. Due to this limitation, GC/MS results can be only associated to the first DTG peak. At first sight, a shortage of peaks at low temperatures (150-200°C) can be observed, detecting almost exclusively peaks corresponding to fatty acids and cholesterol which reach high relative percentages.

The pattern changes at high temperatures, where the complexity of the chromatogram increases by increasing the peaks corresponding to amides and heterocyclic organics, and the percentages of all of them tend to equalise. Increasing HTL temperature yields more compounds extracted from the raw material as well as more degradation reactions taking place, leading to a more complex chromatogram without yielding any specific major compound.

Appendix 7 also shows the yields of the chemical compounds identified in the biocrudes obtained as well as in the aqueous phases. As can be seen, oleic acid (9-octadecenoic acid) is the major compound in all the organic samples analysed. Another remarkable feature is the increase in amide yields with temperature. As in the previous cases studied in this paper, it is worthy to remark the glycerine yields in the aqueous phases, especially at high temperatures, as a result of the hydrolysis of the triglycerides.

Figure 5 shows the yields of the main functional groups obtained in the biocrudes. As can be observed, except the minority group formed by aldehydes and alcohols (oxygenated compounds) which is almost independent of HTL temperature, the other groups increase significantly by increasing this parameter. At low temperatures, the biocrude is very similar to the rendering product and the GC/MS analysis detects only fatty acids in a low yield.

These results show that the oil fraction obtained can be used as source of chemicals, fatty acids and amides mainly. Thus, the options of the biocrude are not limited to its use as fuel, but also as a precursor of chemical products of interest. Further investigation will be necessary to optimise the use of this fraction (selective separation methods and refining treatment).

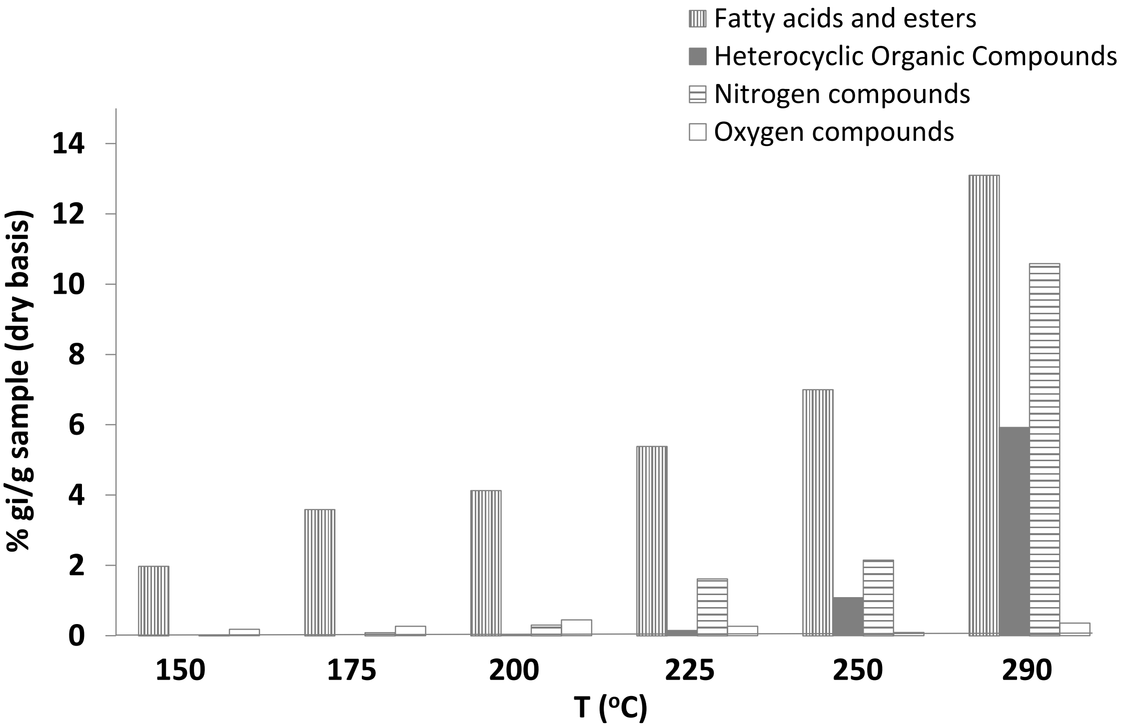

Figure 5. Clusters of compounds of biocrude at different temperatures.

Karagöz et al. (2004) carried out HTL experiments in an autoclave at 180, 250 and 280°C using sawdust as raw material. Although the biocrude composition obtained cannot be compared with that of the present paper, due to the differences in the composition of both raw materials, the influence of temperature on the product composition is also reported, distinguishing between 180°C and the highest temperatures. Gai et al. (2015a) performed an HTL study with two low-lipid content microalgae at 200-320°C. Similarly to the results shown in this paper, fatty acid derivatives are almost exclusively found in the biofuel at low temperature. By increasing operating temperature, more compounds (amides, heterocyclic compounds, cyclic oxygenates, hydrocarbons) appear. According to the total relative peak area, fatty acids derivative and amides are the major compounds.

As commented on previously, the study of the pathways and conditions for the decomposition of lipids, proteins and carbohydrates allows finding the source of the compounds detected.

Thus, for example, lipids hydrolyse easily in hot compressed water, producing glycerine and free fatty acids, which are quite stable under these conditions (Toor et al., 2011). The high percentage of free fatty acids found in this paper shows that the decarboxylation mechanism is limited. No hydrocarbons were detected in the biocrude, although low percentage of paraffins and olefins (C1-C7) together with carbon oxides can be found in the gas fraction. As in the previous runs, the percentage of gas in this series was lower than 3%. At low temperatures gas fraction was formed almost exclusively by carbon oxides (CO_2 mainly), while the percentage of light hydrocarbon increased by increasing process temperature. This distribution of compounds is a consequence of the general mechanisms of decomposition of biomass, and particularly of those of triglycerides and amino acids, which include decarboxylation reactions in the early decomposition stages, producing CO_2, before other type of scissions that lead to light hydrocarbons (Castro Vega et al., 2007; Collard and Blin, 2014; Maher and Bressler, 2007; Sato et al., 2004).

Protein hydrolysis produces amino acids that can suffer decarboxylation (producing CO_2 and amines) or deamination (generating organic acids and ammonia). Percentage of NH_3 was measured in the run carried out at 250^oC resulting in a value of $1.64\ 10^{-2}$ mg compound/g dry raw material. The amount of NH_3 produced can react with the fatty acids formed in the lipid hydrolysis producing amides (Gai et al., 2015a). In the present paper, this type of compounds has been mainly found at high temperatures. Heterocyclic compounds (pyrrolidine and piperidine derivatives) have been also found at high temperatures, probably as a consequence of reactions between amino acids and reduced sugars from carbohydrates hydrolysis.

3.3. Comparison of biocrude with other fuels

The biocrude obtained has been compared with other different liquid fuels. Thus, for example, the biocrude obtained in this paper shows a HHV in the range 30-39 MJ/kg. This value is high comparing with those obtained from other biomasses and techniques such as pyrolytic oil or wood-tar (around 25 MJ/kg), it is similar to the oil from digested sludge (around 34 MJ/kg) and it is around 75-85% of the HHV of the petroleum-derived fuel oils (41-46 MJ/kg). These differences in the HHV result from the differences in the elemental analysis. For example the C content in diesel or heavy fuel oil is around 85%, while in pyrolytic oils from lignocellulosic materials is around 55% and in the biocrude obtained in this paper is around 70%. In the case of O content, the value of the commercial petroleum-derived fuel oils is very low (lower than 0.2%) while in the case of using any type of biomass the results will depend on the O content in the raw sample (around 50% in the pyrolytic oil taking into account the water content of the biooil obtained with this technology) or 12% in the biocrude of this paper. The N content of this biocrude is high due to the N content of the sample (around 0.4-5%, depending on the raw material and conditions) but the values of N percentage in the oil from digested sludge, for example, are close to 6%. In the case of high-nitrogen content oils (bitumen, heavy crude oil, medium oil) the N value is in the range 0.3-1.2% (Channiwala et al., 2002; Prado et al., 2016; Bridgwater et al., 1999). According to these data, the potential of the biocrude obtained from ABPs and HTL technology is high and the biocrude obtained can be used as fuel and chemical source studying the necessary upgrading steps. Obviously, as fuel, the potential NO_x emissions are a disadvantage. In order to reduce them, there are two ways of acting: a) nitrogen removal from oil and b) NO_x removal from gas effluent. Prado et al. (2016) prepared a wide review compiling different methods belonging to the first case. Although methods such as hydrotreating, adsorption, liquid-liquid phase partitioning or chemical conversion+separation appear as viable, nowadays hydrodenitrogenation appears to be the only industrially viable process for nitrogen removal from oils with high nitrogen content. In the second case, selective and non-selective catalytic reduction technologies (SCR and NSCR) are commonly used. In these techniques, the flue gas passes through catalyst layers and NO_x is reduced to N_2 by adding NH_3 (SCR) or by reacting with unburnt hydrocarbons (NSCR). The selective non-catalytic reduction technology (SNCR) involves the reduction of NO_x to N_2 by reaction with amine-based reagents at high temperatures (Mahmoudi et al., 2010). Other methods to reduce the NO_x in the gas stream involve the use of adsorbents or absorbents (EPA, 1999).

3.4. Aqueous phase recycling in HTL process.

Thinking in the scale-up of this type of processes, a continuous system including the recycling of aqueous phase instead of adding fresh water appears as an interesting alternative. Actually, this aspect is vital for the process to be economically competitive (Marcilla et al., 2017). In order to simulate the conditions of this continuous process, four experiments were performed using, each time, the aqueous phase obtained in the previous run. The results obtained under these conditions are presented in Appendix 8 and they would be close to those obtained in a continuous process. By considering the moisture of the ABP used as well as the organics in the aqueous phase recycled, the water content in these experiments was 60-65%. Obviously, the water content can be modified by modifying the amount of aqueous phase recycled.

3.4.1. Product distribution

According to the results obtained, when the aqueous phase is reused in consecutive runs, the main differences were observed in the first round, with a significant reduction of the biocrude yield, from 73% (fresh water) to 45.1%, and an increase in the organics of the aqueous phase, from 13.2% (fresh water) to 26.4%. This fact could be related to the pH of the aqueous phase. As was observed previously, a basic reaction media leads to a reduction of the biocrude yield and an increase of organics in the aqueous phase. Basic nitrogen-containing compounds in the aqueous phase recycled could increase the pH of the reaction media causing the effect observed. Subsequent reusing of the aqueous phase led to lower changes in the results obtained (biocrude yield about 51% in second and third round) and organics in aqueous phase (26% in second and third round) seemed to have reached a saturation degree.

This saturation degree was also detected in the TG analysis. The great similarity between curves corresponding to the second and third cycles shows that the composition of each phase reached a plateau in a short number of cycles.

The similarity among the chromatograms of the biocrudes obtained in the first run, where fresh water was added, and the two last recycling rounds is evident, showing that the use of recycled aqueous phase does not influence on the compounds and their ratios obtained.

Li et al. (2013) studied the recycling of aqueous phase in the HTL process of a lignocellulosic material. According to their results, the recycling improves the biocrude yield due to the presence of acetic acid in the aqueous phase formed in the process, which can promote the hydrolysis of lignin. Therefore, the benefits of reusing the aqueous phase, beyond economic and environmental benefits, should be studied for each specific raw material since, as can be deduced, they depend strongly on their composition.

3.4.2. COD and BOD analysis of aqueous phases

COD and BOD parameters have been measured for the aqueous phases of different runs. The influence of the variables studied on these values is not significant, except the recycling of water and the number of cycles, since a significant increase in the value of these two parameters is obtained, as a consequence of the build up of organic compounds in that phase.

Thus, values of 50000-74000 mg O_2/l for COD increase up to 208000 by increasing the number of cycles. The BOD_5 values moves from 35700-52800 to 149000 mg O_2/l.

All the results, and especially those from the experiment with recycled aqueous phase, are larger than typical wastewaters COD from the rendering, wine industry or slaughterhouses (10000-25000 mg O_2/l), in some manner, related processes (Seoanez, 2002). Nevertheless, the recycling of the aqueous phase appears as very convenient, since that water is not actually a residue but participates in many cycles, thus reducing water and energy requirements of the process.

Ecotoxicity results reveal that one cycle aqueous phase is below the allowed limit for disposal (<333 UT), whereas recycled aqueous phase is well above (485 UT). In a recycled aqueous phase HTL process, the liquid effluent would be the aqueous phase purged, which is necessary as a consequence of the moisture of the sample fed. As any other industrial effluent, the aqueous phase purged must undergo a pretreatment before its discharge and a wider study of this phase would be required to assure its possible use as a source of chemical products (such as glycerine), its use as fertilizer or other useful alternatives.

4. CONCLUSIONS

Hydrothermal liquefaction experiments of animal by-products were carried out under different conditions (initial pressure, residence time, total mass in the reactor, headspace, water content, pH and temperature) in order to deduce their influence on the fractions obtained, especially on the biocrude, yield and composition.

In general terms, under the conditions studied, the biocrude yield was in the range 55-70% (in dry-basis). Its high heating value was around 30-38 MJ/kg. Protein content of the raw material mainly generated pyrrole derivatives and amides, while the fat content generated triglycerides and fatty acids. In the aqueous phase it is worthy to remark the high percentage of glycerine obtained.

The process temperature affects the biocrude composition very significantly since free fatty acids and amides increase with temperature whereas triglycerides decrease, causing the spectrum of compounds to change significantly in a narrow range of temperatures. This aspect is of paramount importance when considering the optimal strategy for the final use of the biocrude for energy, fuels or chemicals.

Besides temperature, water content and pH show a significant influence on the HTL process. It has been observed that higher water content favours the separation between aqueous and organic phases, which must be had into account for the scale-up of the process. The minimum percentage of water content required for this type of materials was 60%.

About the pH of the reaction medium, an acidic value led to a similar yield of biocrude, comparing with neutral medium, but affected significantly its composition, increasing fatty acids and esters and reducing the heterocyclic organic compounds. A basic reaction medium reduces by half the amount of biocrude, increasing the organics dissolved in the aqueous phase.

The selection of preferred operating conditions depends on the process objective, especially if the goal is to maximise the production of a particular family of compounds. In the case of the generation of biocrude with high HHV being the particular objective, minimising water and energy requirements, the optima conditions selected would be: temperature 225^{o}C, initial pressure 28 bar, water content 60% and neutral pH. The use of the aqueous phase for subsequent experiments reduces the biocrude yield and increases the organic contents in the aqueous phase up to a saturation degree, approximately double percentage than that of the first cycle, although no significant changes in the composition of the biocrude obtained were observed. The recycling of aqueous phase is a vital aspect for the competitive economy of the process.

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