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## ACRONYMS AND ABBREVIATIONS

Acronym/Abbreviation	Description
ABP	Animal by-products
HTL	Hydrothermal liquefaction
UA	University of Alicante
EU	European Union
OP	Organic phase
AP	Aqueous phase
TG/FTIR	Thermogravimetric analyzer (TG) coupled with a Fourier-transform infrared (FTIR) spectrometer
DTG	Differential Thermal analysis
GC/MS	Gas Chromatography / Mass Spectroscopy



## 1. Publishable summary

The HTL pilot plant has been built, set up and operated by GreenE. Samples obtained in the experiments have been sent to University of Alicante for analysis by TG/FTIR and GC/MS. The results have been compared with those obtained at lab scale.

Three preliminary experiments have been carried out in the HTL pilot plant. Operating conditions have been in the range 120-170 bar for pressure and around 200°C for temperature. The bio crude obtained is mainly formed by fatty acids, amides and amines. The results show that, although the composition of the bio crude obtained is similar to that of the previous experiments at lab scale, higher temperature in the reactor would be needed to improve the yield.

Real wastes must be fed to test the limits of the system. Particle size must be reduced to below 0.5 mm to be processed in this reactor.

The results obtained are very encouraging since they have proven the feasibility of the system to obtain bio crude from ABP residues, as well as to dispose them. In addition, the possibility of treating other type of residues and materials by this new continuous HTL screw reactor is being considered for future projects.

## 2. Introduction

The main aim of this deliverable is to describe the preliminary results obtained in a pilot plant with the optimum parameters at a lab-scale and to evaluate possible changes in the process due to scaling.

In the deliverable D2.1, page 68, the University of Alicante proposed a co-rotating twin screw with a constant channel depth and constant lead design. GreenE, decided to build a single variable depth and lead screw HTL pilot plant with a channel depth at the entry of 10 mm and 2.5 mm at the exit. This design differs significantly from that proposed by the UA. These changes have important consequences on the operating conditions, since the reaction volume of the system is much lower than that suggested and the particle size that the system can process, that is also much lower, since the channel depth is lower than that suggested, especially at the exit of the reactor.

In addition, the pump chosen for the plant is capable of pressurizing the system. The UA suggested using a pump capable of feeding the material at the pressure of the system that would be attained by the water vapor pressure at the operating temperature (typical in HTL processes). This selection will provide more operating flexibility to the system since it may allow certain degree of independence between the operating temperature and pressure.

Consequently, the operating conditions of the pilot plant will differ from those suggested by the UA in the deliverable D2.1.

As described throughout the project, one of the main problems of this process are related to the complexity of the flow of the raw material depending on its nature and composition. In order to get more insight on these aspects, different mixtures of ABP and additives have been studied to enable and improve the fluidity of the raw material through the reactor and its pump ability.



### 3. Pre-treatment of samples

#### 3.1. Raw material

During the first tests, the following materials were used: bacon, pork fat, entrails, skin, small bones, lean pork and additives (extensan-540 and a surfactant agent). Extensan-540 is an additive very used in the meat industry because it increases the water absorption capacity of meat.

#### 3.2. Grinding

For the initial experiments the raw material has been grinded and the fraction with a particle size below 1 mm has been selected.

Only meat was used since skin and bones were very difficult to grind below 2 mm in a pilot plant scale mill. This size was considered excessively large for the preliminary experiments.

Entrails were not used in order to avoid possible bacterial infections in these preliminary tests.

#### 3.3. Viscosity

The materials were mixed with water to obtain the desired percentage of water content (i.e.: 80%).

The viscosity was measured with a PCE instruments viscometer model PCE RVI-1, spindle 3 and 12 rpm. An emulsion of pork fat, water and 10 g of emulsifier was measured. The results are shown in table 1.

	<b>Viscosity (mPa·s)</b>
<b>Bacon and water</b>	5.000
<b>Pork fat</b>	7.000
<b>Emulsion</b>	1.000

Table 1. Viscosity of the mixtures used.

### 4. Characteristics of the equipment

As GreenE described in the deliverable 3.1, the individual components of the plant were tested. Figure 1 shows the flowchart of the pilot plant.

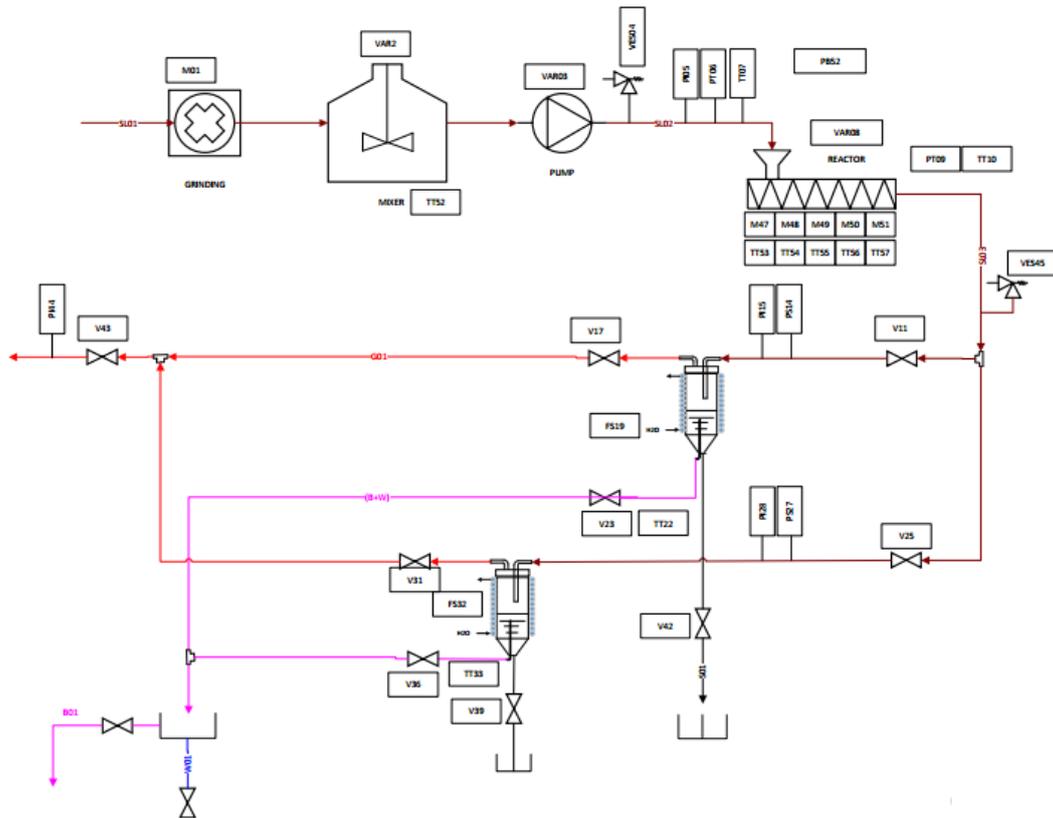


Figure 1. Diagram of the pilot plant operation.

The technical characteristics of the pump are described in table 2.

<b>Fluid</b>	Sewage sludge
<b>Fluid Temperature</b>	250 °C
<b>Emulsion Density</b>	1 g/cm <sup>3</sup>
<b>Viscosity</b>	20000 mPa·s
<b>Vapor pressure</b>	0.03 bar
<b>% solids/size</b>	20%/1 mm
<b>Total flow</b>	6.25 l/h
<b>Output pressure</b>	170 bar
<b>Inlet pressure</b>	1 bar

Table 2. Characteristics of the pump.

## 5. Verification of the operation conditions

The operation conditions checked were pump flow rate , reactor internal volume, fluid maximum pressure, maximum temperature, water tightness and automatic control.



### 5.1. Pump flow rate

Flow was measured at different pump opening and different initial pressure. The results are in table 3.

Opening (0-30)	Pressure (bar)	Flow (mL/h)
5	5	2100
5	10	1800
5	20	1140
30	140	8100
30	100	9900

Table 3. Flow obtained under different conditions.

Opening 30 and pressure 140 bar were selected for subsequent tests.

### 5.2. Reactor internal volume

The internal volume of the reactor was determined by GreenE, by weighing the water required to fill the reactor. The result obtained 1350 mL was very close to the volume determined from the equipment dimensions.

With this volume and the continuous conditions selected in the previous point, the initial retention time for the tests was 10 minutes.

The residence time established by the University of Alicante from lab scale runs was 5 min at the maximum reaction temperature, showing that times in the range 5-15 min do not show significant differences. A residence time of 10 min in the pilot plant reactor satisfies the established requirements.

### 5.3. Maximum working pressure and tightness

Another of the preliminary tests needed to tune up the process is the checking of the maximum working pressure and tightness of the systems. Two tests were performed. In the first test all the pipes and valves were closed for five minutes, except valve V11. In the second one only valve V25 was left open (see valves in figure 1). In cold conditions no leaking was detected.

When the system was operated at 200°C and the initial pressure was 140 bar, the pressure of the system decreased at a rate of 1 bar/min. When operating at 90 bar as initial pressure, the pressure loss was at a rate of 1/3 bar/min. No pressure decrease was observed when working at 50 bar.

The leaks observed during the process were localized at the exit of the reactor, just where the thermocouple is located as well as in the union of the outlet pipe. These leaks were reduced to the half when replacing the viton join by a viton-teflon join and sealing the unions of the thermocouple and the outlet pipe.



#### 5.4. Maximum temperature reached by the fluid

In order to measure the maximum temperature reached by the fluid, the reactor was filled with water and kept it in static condition, all resistances were turned on and the ventilation of the system was off. In these conditions, the temperature of the reactor reached 324°C.

Then a water flow of 8100 mL/h was fed into the reactor, reaching in this case the system a temperature of 263°C.

If the water flow is reduced to 2100 mL/h, the temperature reached 307°C.

These values define the operating temperature range with this system.

#### 5.5. Automatic control

The maximum and minimum for the working pump values and reference temperatures of the resistances in the heating sections were programmed in the SCADA.

The correct performance was checked in this way.

### 6. Experiments performed

After checking all the parameters of the HTL process in the pilot plant, three experiments were carried out with different mixtures. In the first run an emulsion of pig fat, emulsifier and water was used. In the other two experiments, mixtures of meat and water were used. The conditions of the experiments were selected by considering the results obtained in the previous runs.

#### 6.1. Raw material

The raw material used in the first experiment was pork fat mixed with distilled water. The total amount of water was 80%. With the aim of obtaining a homogeneous mixture, a surfactant agent was added.

The other two experiments were carried out with a grinded pig meat (size particle < 1 mm) mixed with water.

In table 4 the proportions and principal characteristics of the mixtures used are shown.

Figure 2 shows the aspect of each one of the feeding mixtures.

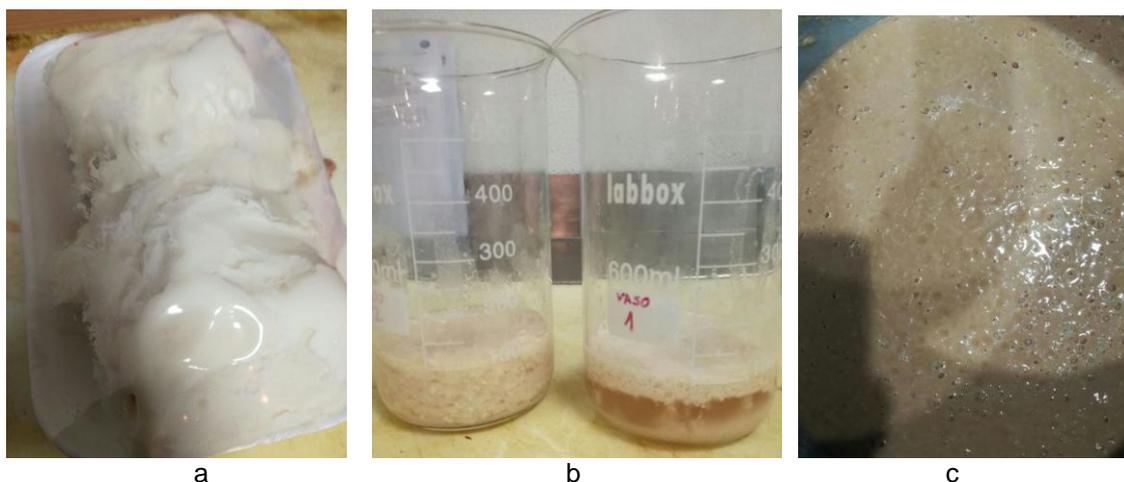


Figure 2. Raw material. Fat mixture (a); Meat mixture of run 2 (b); Meat mixture of run 3 (c)

Run	Raw material	Amount of raw material	Amount of water	Surfactant agent	Density (kg/m <sup>3</sup> )
1	FAT	1000 g	4000 g	25 g	---
2	Meat	5170 g	5170 g	---	989
3	Meat	4300 g	5300 g	---	991

Table 4. Mixtures used in preliminary HTL pilot plant experiments.

## 6.2. Run conditions

All experiments began with a water flow rate of 8100 mL/h. Once the stationary regime had been reached, the material was fed into the reactor. Table 5 shows the principal conditions of experiments.

Run	Raw material	Pressure (bar)	Final Temperature (°C)
1	FAT mixture	140	182
2	Meat mixture	170	220
3	Meat mixture	120-130	200

Table 5. Principal conditions of preliminary runs

- Run 1.

In the first run, 1 kg of pork fat, 4 L of water and 25 g of surfactant agent were mixed and the mixture was introduced into the reactor. 4.5 L of liquid product was obtained. The presence of the surfactant yielded in an apparently single phase product, not decanting after 24 h. The product was dried at 65°C until



constant mass. 3.9 L of final product was obtained. According to these results, it seems that the emulsion retained the water.

- Run 2.

The second run was started by feeding water continuously until steady conditions were reached. Then the feed was shifted into the meat mixture. The mixture used was 5170 g of minced meat (particle size < 1mm and 50% of humidity) and 5170 g of water. The density of the material used in the experiment 2 was 989 kg/m<sup>3</sup>. In this experiment the pressure dropped at rate of 2 bar/s through a leak in the join until it remained at 120 bars. After 30 minutes, the pump failed and the experiment ended. A strange piece of 4 mm size was found inside the pump perhaps because the deposit of raw material was opened in the experiment. Hereinafter, the deposit was closed during the experiment. Furthermore, the raw material was grinded instead of minced.

It was observed that the viton joint is not suitable for this system, it was coated with teflon while a graphite joint is manufactured.

It is decided not to work the flow control for V11 and V25, since the depressurisation and vaporization of the material produces fluctuations in the pressure of the circuit.

It is also decided to work with zone 5 (last part in the reactor) limited to 220°C and to remove the heat insulation from the area of the joint in order to keep it cool.

- Run 3.

With the results obtained in the first runs, a new experiment was carried out with a mixture of grinded meat and water.

The meat was grinded and humidity of the sample was measured (50% moisture). In the literature, the water contain of this kind of meat was about 70%, it is supposed that the loss of moisture was due to the friction of the blades. Once the optimum particle size was obtained, the material was mixed with water to obtain 72% of moisture.

To obtain the continuous conditions required, the system was filled with water at 4.4 bar pressure and flow rate of 8800 ml/h. The temperature used in the first four heating sections of the reactor was 450 °C, and in the last section the fixed temperature was 220°C. The expected temperature inside the reactor with this heating is 200°C. The working pressure was set up at 120-130 bar. All the system, including the coolers, was pressurized. For this operation conditions, the valve V11 was open, V23 closed and valve V17 slightly open until equilibrium pressure (see valves in figure 1).

The stationary regime was achieved after 4 hours of operation. In these conditions, the mixture was added into the filling tank. The run lasted 2 hours and 5 minutes and the material introduced was 9600 g.

Figure 3 shows the stationary conditions before introducing the meat mixture. The reached temperature shown in the figure was lower than the expected 200°C. After inspection and measuring the temperature of the material it was detected that the temperature reading display was not correct, since the actual temperature was around 100 °C higher that that displayed. This system was replaced.

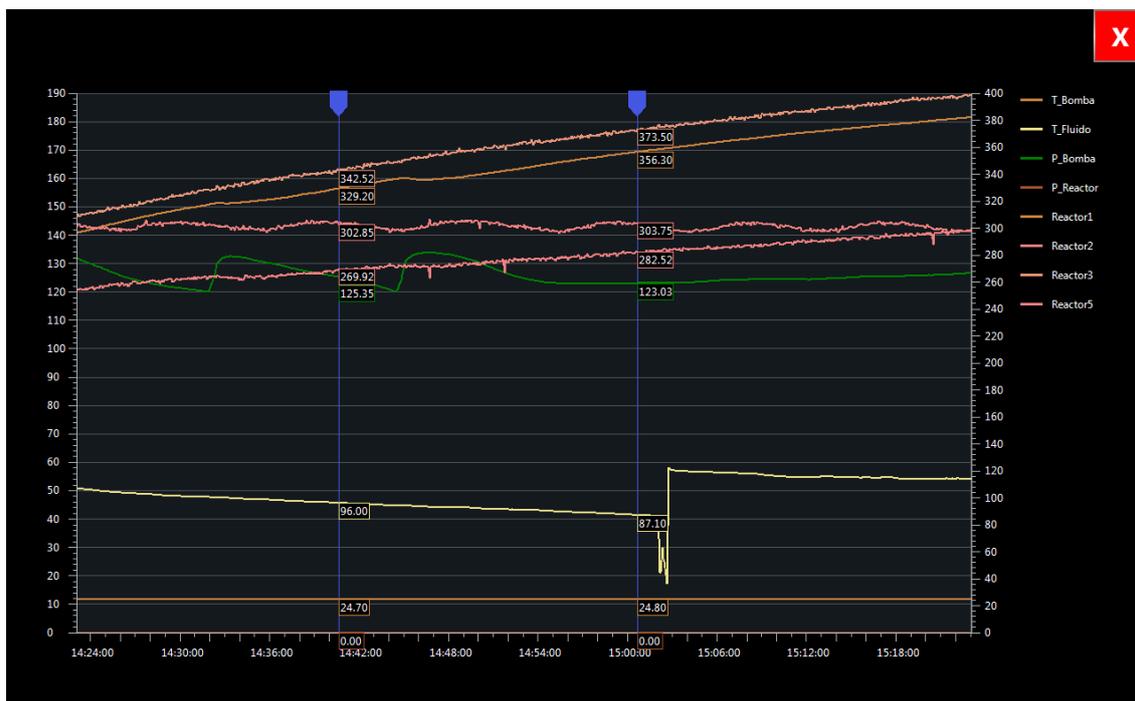


Figure 3. Stationary conditions before introducing the raw material in run 3.

### 6.3. Analysis of products

The analysis of the liquid products obtained was carried out for runs 1 and 3. Run 2 was useful to set up the process and detect operational problems, but the products obtained were not analysed.

In case of run 1, only a fat emulsion was obtained.

From run 3 two fractions were separated: biocrude and aqueous phase. However three more samples, not only those picked up from the outlet vessel, were collected at different points along the system: in the pipes, inside the reactor and the water used to cool down the outlet vessel (water is in contact with the liquid product).

TGA analyses were performed using a thermobalance METTLER TOLEDO, model TGA/SDTA851e/SF/1100 coupled to FTIR detector. Approximately 6 mg of each sample were heated from 25 to 850°C under nitrogen atmosphere (50 ml/min) with a heating rate of 35°C/min. The temperature of the sample was measured with an R type thermocouple located under the crucible.

As explained in the deliverable D2.1, TGA/FTIR allows us to obtain an idea of what type of functional groups and chemical products are formed during the process. The FTIR 3D-spectra show the absorbance corresponding to the vibrational modes of bonds and functional groups. In D2.1 the assignment of the bands (wavenumber) was determined.

Figure 4 shows the TG/DTG curves for the product obtained in run 1 as well as the 3D-FTIR spectrum for the volatiles evolved in the TG analysis. The liquid product presents two phases: a clear yellowish liquid and a fatty supernatant. Figure 4 shows the analysis of both phases separately. As can be seen, both techniques, TG and FTIR, indicate that the clear liquid obtained was mainly



water (sharp loss weight at temperatures lower than 100°C related to wavenumbers of 1500 and 3640-3550 cm<sup>-1</sup>). In the case of the supernatant the presence of carbonyl groups and C-H and C-N bonds were observed.

Figure 5 shows the TG/DTG curves for the organic samples collected in run 3: biocrude phase, sample in the pipe and sample in the reactor. Curves of three samples show significant similarities, although some differences are also detected.

By analyzing the curves corresponding to the biocrude collected from the outlet vessel, at least 4 processes can be distinguished. A first weight loss that takes place at around 80°C followed by a second one at 117°C. Both processes can be related to the removing of the water present in the sample. The first one is probably caused by the loss of free water while the second one can be related to the water loosely bound to biomolecules. The main weight loss takes place in the range 200-500°C, the DTG showing two defined peaks at 300 and 400°C.

In the case of the sample picked up from the pipe, instead of four peaks, two are mainly distinguished: the one at 117°C and that at 300°C.

The percentage of residue in both samples is around 10%.

Sample collected in the reactor seems to be heavier than the others. Thus, this sample shows the highest percentage of residue (around 20%), the lowest percentage of decomposition under 200°C and the main decomposition peak centred at around 350°C with some shoulders.

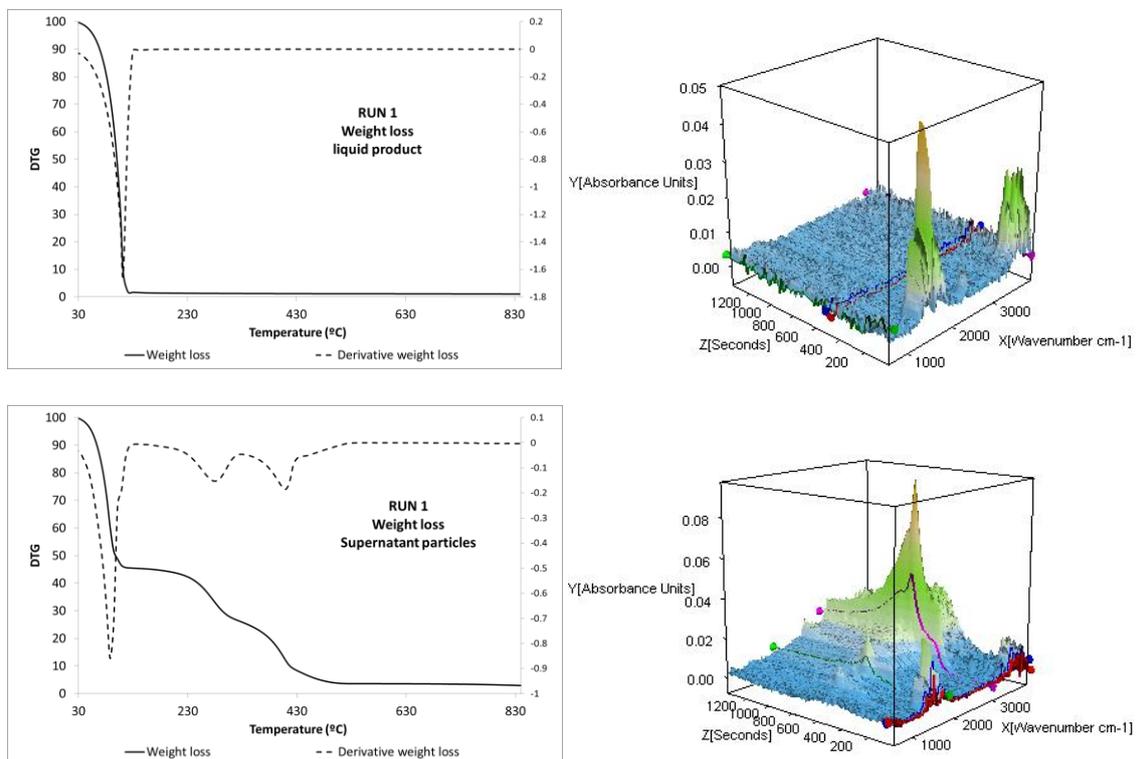


Figure 4. TGA-IR results of the liquid phase and fatty supernatant obtained in run 1.

According to these results, it is necessary to increase temperature and pressure in the reactor to improve the extension of the process and to get a more



homogeneous product, since the three samples analyzed would have to present more similar composition.

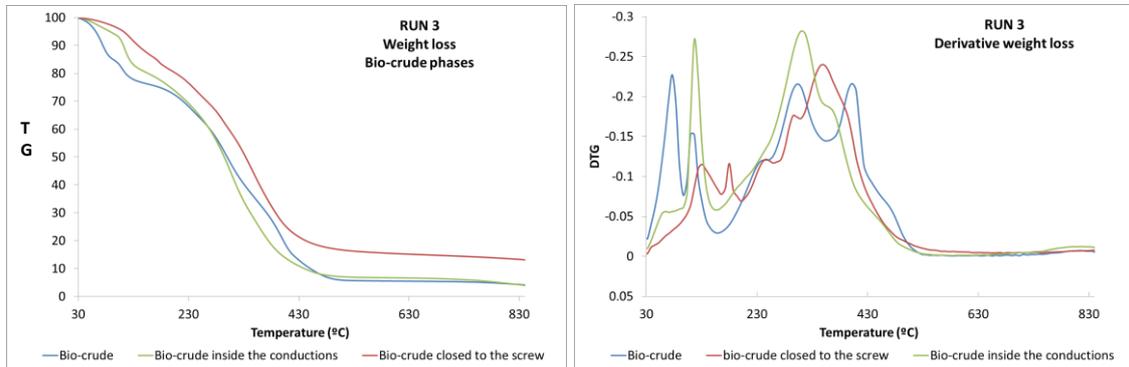


Figure 5. TGA and DTG curves of the organic samples collected in run 3.

The FTIR spectra of the volatiles evolved from the biocrude phase obtained (Figure 6) shows, at 350°C, mainly the presence of alkanes or alkyl substituents ( $2970-2950\text{ cm}^{-1}$ ), carbonyl groups ( $1800-1700\text{ cm}^{-1}$ ), C-N stretch ( $1100-1360\text{ cm}^{-1}$ ) and  $\text{CO}_2$  ( $2400-2224\text{ cm}^{-1}$ ). This spectra generated from the biocrude obtained in pilot plant is very similar to that obtained at lab scale (see deliverable D2.1 page 47) which shows the viability of the process and the closeness between lab scale reactor and the pilot plant system. At 117°C, only signals related to water loss are detected.

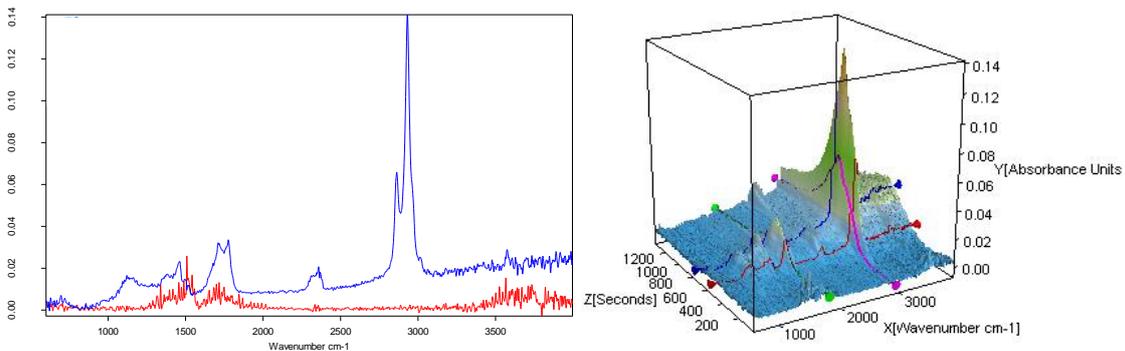


Figure 6. FTIR spectra of the volatiles evolved from the pyrolysis of the bio-crude phase at 117°C (red line) and 350°C (blue line) and 3D-IR spectrum.

In the case of the aqueous phases obtained, one from the outlet vessel and a second one from the refrigerator, TG/DTG curves as well as the FTIR analysis show that organic content in those samples is almost nil and they are mainly composed of water (Figure 7)

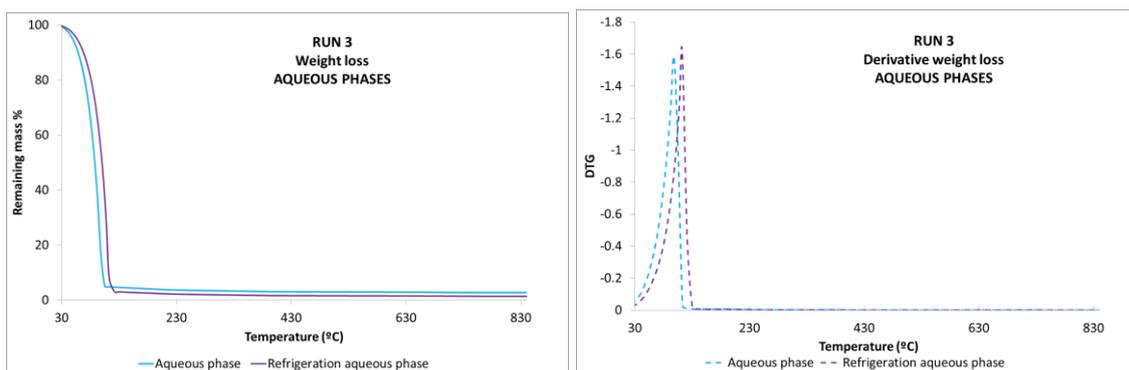


Figure 7. TGA and DTG of the aqueous phases obtained in run 3.

In order to identify the specific components of the biocrude obtained, this phase was dissolved in n-hexane and analysed by GC/MS. The chromatogram obtained is shown in figure 8 together with chromatograms obtained in HTL lab scale experiments at different temperatures. The major compounds obtained are listed in table 7, which includes the components with area higher than 1% of the total area in the chromatograms. As can be seen, most of the compounds identified in this phase are fatty acids, amides and amines, which were also the main components in the biocrude produced at lab scale (see D2.1 page 56). The major component, at both lab and pilot plant scale, has been 9-octadecenoic acid. Other compounds, with a low match quality index, that did not have been detected at lab scale runs are also found in these preliminary results.

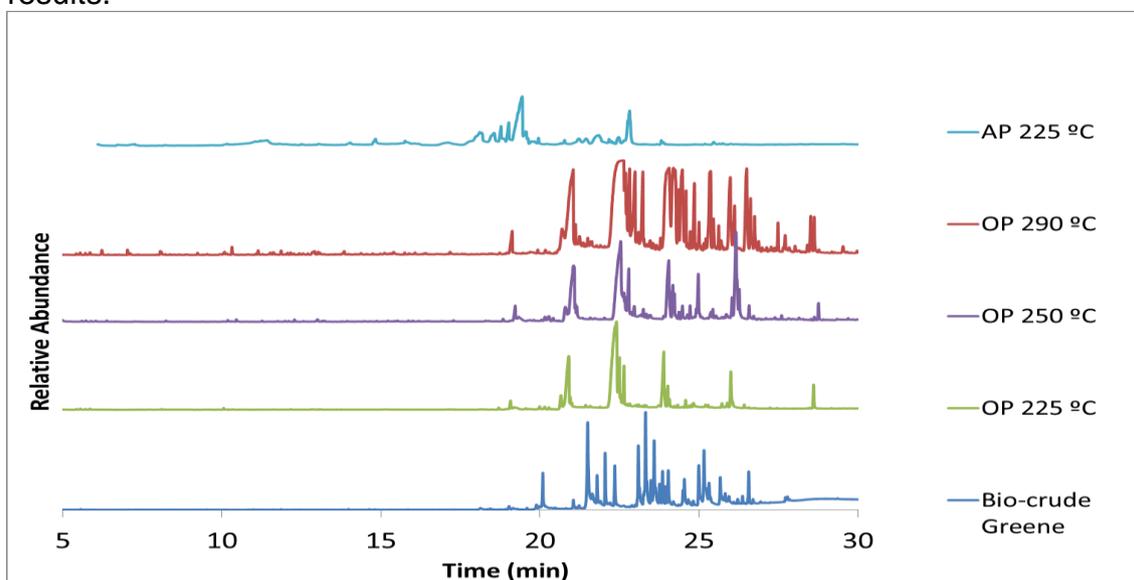


Figure 8. Chromatograms of some biocrude phases (OP) and aqueous phase (AP) obtained at lab scale HTL experiments and biocrude phase obtained at pilot plant.



RT	Match Quality	Library/ID	% Area
20.09	99	Hexadecanoic acid	3.26
21.50	99	9-Octadecenoic acid	12.67
21.65	89	Octadecanoic acid	1.25
21.80	95	Hexadecanamide	2.18
22.05	40	Decanal-O-methyloxime	4.06
22.35	87	N,N-DIMETYLPALMITAMIDE	3.61
23.10	96	9-Octadecenamide	6.67
23.32		Unknown (m/z=73, 86, 115,58)	9.81
23.49	50	1,12-Dodecanadiazine	1.77
23.59	93	9-Octadecenamide,N,N-dimethyl	7.95
23.76	81	N,N-Dimethyldodecanamide	1.80
23.86	50	Naphthalene, 1,2,3,4-tetrahydro-1-methoxy	2.48
23.96	49	1,5-Cyclodecadiyne	1.21
24.04	52	1-[1'-phenylethenyl]-2-trifluoromethyl-2-hydroxycyclopentane	3.09
24.50	90	9-Octadecenamide,n-butyl	1.20
24.54	97	Pyrrolidine, 1-(1-oxooctadecyl)-	2.51
24.99	59	3-(2,2-dideuterobutyl)-thiophene-1,1-dioxide / 2H-Isoindole-2-a	4.52
25.16	81	2-Oxazoline, 4,4-dimethyl-2-(1-hydroxy-heptadec-8-enyl)-	5.38
25.22	43	Oleic diethanolamide	2.15
25.32	49	Boric acid, (2-cyclohexylidene-1,1-diethylpropyl ethyl-, trimeth	1.54
25.40	99	Pyrrolidine, 1-(1-oxo-9-octadecenyl)-	2.73
26.37	99	Cholest-5-en-3-ol	2.93

Table 6. Major compounds in the biocrude phase obtained in run 3.

## 7. Conclusions

The preliminary experiments show the viability of the process and the pilot plant operation.

The results obtained show a significant similarity between the compositions of the bio crude obtained in the pilot plant runs and those of the lab scale.

An increase in temperature and pressure would be needed to reach optimum HTL conditions and improve the yield of the bio crude obtained.

Working with real animal-by products, of the adequate particle size, instead of meat and water mixtures, would be very interesting in order to test the limits of the pilot plant.