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Advanced Sustainable BIOfuels for Aviation

Deliverable D2.9:
R&D tests and product characterization report

Consortium:

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CCE	CAMELINA COMPANY ESPANA S.L.	BEN
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PRO	Technical/economic progress report (internal work package reports indicating work status)	**X**
DEL	Technical reports identified as deliverables in the Description of Work	
MoM	Minutes of Meeting	
MAN	Procedures and user manuals	
WOR	Working document, issued as preparatory documents to a Technical report	
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Dissemination Level		
PU	Public	**X**
PP	Restricted to other programme participants (including the Commission Services)	
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CO	Confidential, only for members of the consortium (including the Commission Services)	
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1 Summary

A hydrothermal liquefaction and pyrolysis test campaign was performed on three UCO samples from restaurants, fast food restaurants and domestic collection. Pyrolysis was the only thermal treatment that exhibited a significant effect on the feedstocks, as the HTL products were essentially identical to the initial UCO samples.

A higher yield was observed from the pyrolysis of fast food UCO (88.6 wt.%). Indeed domestic UCO pyrolysis exhibited a lower yield (63.3 wt.%), but the corresponding product possessed an improved quality, being its carbon content increased from 76.6 to 82.2 wt.% and its oxygen content decreased from 11.3 to 5.1 wt%.

2 Introduction

Used cooking oil (UCO) is a sustainable waste feedstock and, being not in competition with food, it represents a possible alternative to vegetable oils for greening of air transport. However, being composed of several vegetable oils, it is characterized by a variable quality and it is often contaminated with animal fats and solids. Pyrolysis and hydrothermal liquefaction represents two thermochemical conversion processes which can be adopted to convert this material with extremely variable contamination/quality.

3 Materials and Methods

3.1 Used cooking oil samples

Used cooking oil (UCO) samples were collected from SILO S.P.A. (Florence, Italy). In particular three samples from different origin were provided: UCO from restaurants, UCO from fast food restaurants and UCO from domestic collection (Figure 1).

Figure 1: UCO samples used for the HTL and pyrolysis experiments; left: UCO from domestic collection, centre: UCO from restaurants, right: UCO from fast food restaurants.

3.2 Micro-Reactor Test Bench (MRTB)

The hydrothermal liquefaction experiments as well as pyrolysis experiments were carried out in RE-CORD's custom-made micro-reactor test bench (MRTB, Figure 2). The MRTB allows performing batch experiments of biomass conversion (pressurized pyrolysis, HTC, HTL, etc.) under a wide range of operating conditions. Its fully modular architecture and small scale permits to rapidly screen the effect of distinct process parameters, allowing the systematic investigation of their effect on products relative distribution, quality or properties. Leveraging its flexibility, moderate operating cost and high availability, the bench is particularly suited for research, from preliminary screening to process optimization. The Micro-Reactor Test Bench consists in a lab-

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scale plant on a five-wheeled modular aluminium structure (Robotunits). Its main components are:

- Reactor(s)
- Air-fluidized sand bed
- Water bath
- Gas cylinder
- Temperature and pressure sensors
- Data acquisition system

The reactor was designed to withstand up to 300 bar at 400 °C. It consists of a ¾" AISI 316 Sandvik tube (0.109" thickness), which is connected to the bench by means of Swagelok stainless steel fittings. Because it is composed of commercially available items, it is modular and the length, thickness and number of the reactors can be varied according to the specific needs of the experiment. The capacity of each reactor can be up to approx. 40 ml. The data acquisition system consists in a NI cDAQ-9178 (National Instruments), with digital and analog I/O modules; the control logic and the user interface (UI) were in-house developed (Figure 3).
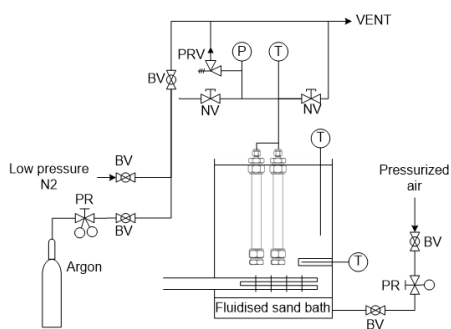
BV: ball valve; NV: needle valve;
PR: pressure regulator; PRV: pressure relief valve

Figure 2: Simplified scheme (left) and photo (center) of the MRTB test bench in a double-reactor configuration (right).
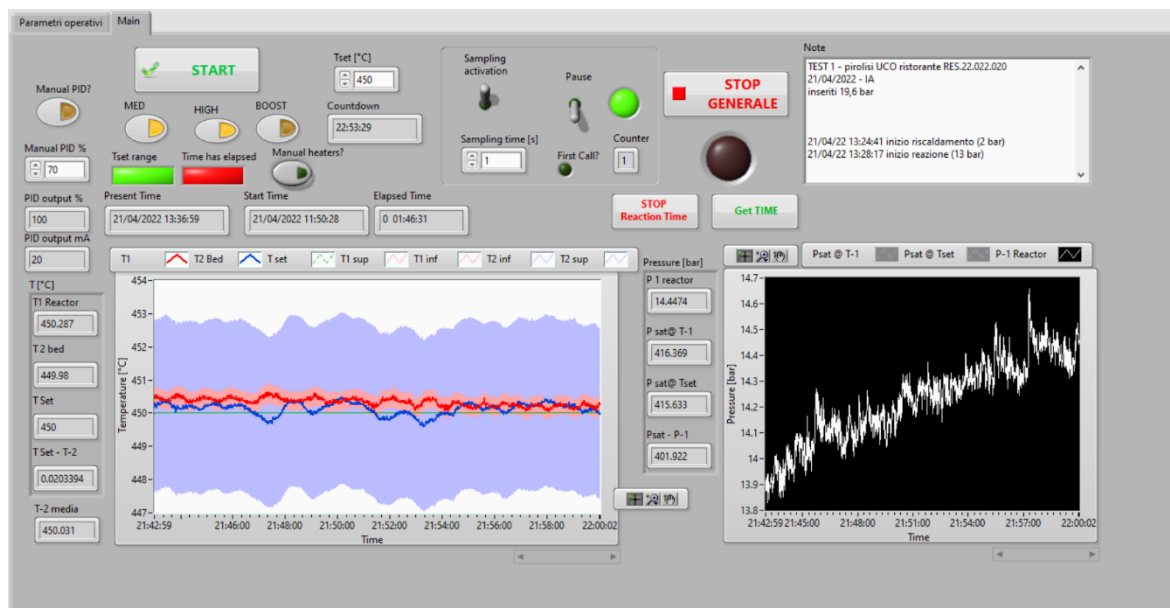

Figure 3: Screenshot of the user interface of the data acquisition software during a pyrolysis experiment.

The reactor is equipped with two needle valves for initial pressurization and final depressurization, a high-pressure relief valve, a pressure transducer and a temperature sensor (class 1/10 3-wires Pt100), which measures the inner slurry temperature. The high-pressure relief valve (HPRV) was conveniently calibrated with a dedicated hydraulic pressure comparator (Huaxin Instrument, Figure 4).

Figure 4: Pressure comparator used for HPRV setting.

The air-fluidized sand bed (FSB-4, Omega Engineering, Figure 5) is equipped with four 1 kW electric heaters and is able to reach a maximum temperature of 600 °C. Due to the high amount of sand (F0885 Alundum, brown aluminium oxide), the inertia of the system is relevant and the higher the desired set temperature the longer the heating time. The advantage of using a fluidized bed is that a fast heating rate and a high homogeneity of temperature can be achieved. The pressure sensor is a 0-400 bar strain gauge pressure transducer (Trafag); its sensitive membrane is made of stainless steel, making it able to tolerate harsh conditions. The reaction temperature is measured inside the reactor by means of an immersed 3-wire RTD sensor (100 Ohm, 1/10 DIN accuracy class), while the sand temperature is monitored by two 3-wire RTD sensors (B accuracy class).
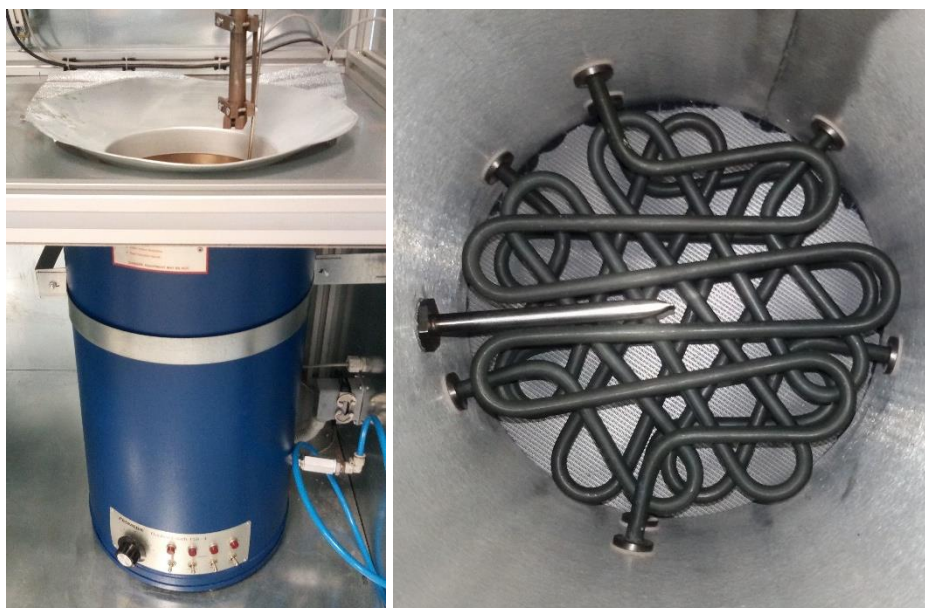
Figure 5: Fluidized sand bed (left) and inner view with heating elements and well of the temperature sensor (right).

3.3 Methodology of a typical experiment

In order to prepare hydrothermal liquefaction experiments, the feedstock was mixed with ultrapure water (0.055 µS cm^{-1}) to attain the desired UCO:water mass ratio of 1:3. Specifically, 6 g of UCO sample was mixed with 20 g of water. Prior to each experiment, a leakage test was performed with argon pressurized at 8 MPa. Then, three purging cycles with nitrogen (0.5 MPa) were carried out in order to remove air and ensure an inert atmosphere in the reactor. An initial pressure of 1.8 MPa was set using argon, then the reactor was immersed into the fluidized sand bath. Counting of residence time started when the inner reactor temperature reached 2 °C below the set reaction temperature (350°C): after the selected residence time of 15 min expired, the reactor was rapidly cooled by immersion in a water bath. After nearly 20 min, the pressure was gradually released, the reactor opened and disconnected from the test bench. The content of the reactor was then subjected to centrifuge at 3000 rpm for 10 min and the oil phase separated from the water phase. In order to recover an additional amount of oil phase the reactor was washed with hexane.

A similar procedure was followed for the pyrolysis experiments. In particular, 5 g of UCO feedstock were inserted in the reactor, reaction temperature and residence time were 450°C and 40 min, respectively, while initial pressure was atmospheric.

3.4 Analytical methods

3.4.1 CHN
The total carbon (C), hydrogen(H) and nitrogen(N) content of UCO feedstocks and HTL/pyrolysis products were measured in a Leco TruSpec CHN analyzer according to UNI EN 16948. Oxygen content was evaluated by difference.

3.4.2 Water content
The water content of UCO feedstocks and HTL/pyrolysis products was performed by Karl Fisher method according to UNI EN ISO 8534 in an automatic titration system Metrohm 848 Titrino Plus.

3.4.3 GC MS
Qualitative analysis of the organic compounds of UCO feedstocks and HTL/pyrolysis products were performed by GC-MS. The samples were solved in acetone (0.1 g:10 ml) and 2 µl were injected in a Shimadzu GC 2010 with a GCMS-QP2010 mass spectrometer equipped with a ZB-5 MS Phenomenex column (30 m length, internal diameter 0.25 mm, film diameter 0.25 µm). Temperature was held at 40 °C for 10 min and then increased to 200 °C (heating rate 8 °C min$^-$

[1], holding time 10 min) and 280 °C (heating rate 10 °C min^{-1}, holding time 30 min). The qualitative analysis was performed comparing the mass spectra to the NIST 17 library.

4   Results

4.1   UCO feedstocks characterization

Table 1 reports the results from the characterization of the UCO samples. Similar amount of carbon and hydrogen content were observed between the fast food and the domestic UCO; the latter was characterized by a slightly higher amount of nitrogen, possibly coming from food contamination, and a lower amount of oxygen. On the other hand, the used cooking oil from fast food had a higher amount of water (6.1 VS 0.2 wt.%). Surprisingly, the restaurant UCO sample we received was almost completely composed by water (93.7 wt.%) and therefore its properties were not comparable with the other two samples.

Table 1: Properties of the UCO samples; absolute standard deviation is reported in brackets.

Parameter	Unit of measure	Method	Fast food	Restaurant	Domestic
C	wt.%	UNI EN 16948	74.8 (0.21)	3.8 (0.05)	76.6 (0.42)
H	wt.%	UNI EN 16948	11.9 (0.10)	10.8 (0.17)	12.0 (0.05)
N	wt.%	UNI EN 16948	0.05 (0.01)	0.11 (0.03	0.14 (0.02)
O	wt.%	Calculated	13.3	85.3	11.3
Water content	wt.%	UNI EN ISO 8534	6.1 (0.29)	93.7 (0.35)	0.2 (0.01)

4.2 Hydrothermal liquefaction experiments

Table 2 reports the results from the HTL experiments in terms yield of oil fraction obtained after the process and pressure and temperature values. Specifically, P_0 represents the pressure by which the reactor was charged before immersion in the sand bed, P_{max} is the maximum recorded pressure during the reaction, while P_{fin} is the pressure value in the reactor after 20 min of cooling. T_{mean} represents the average temperature during the residence time and T_{max} and T_{fin} have the same meaning of their equivalent pressure values. Pressure is relative to the atmospheric value. Unfortunately, due to an error of the control and data acquisition system, it was not possible to acquire the data from the HTL experiment of domestic UCO and, therefore, only the yield of the oil fraction was determined.

During the experiments high values of pressure were observed, due to the presence of water, but the difference between the final and initial value was below 1 bar, indicating that a little amount of gas has been produced during the conversion process. The fast food UCO was the one that yielded the highest amount of oil phase (78.5 wt.%), while the yield of oil from the domestic one was 69.0 wt.%. As the UCO from restaurant was almost completely made by water, no oil phase was detected even after centrifugation (Figure 6).

Table 2: Main operative results from the HTL experiments.

Sample	P_0 [bar]	T_{mean} [°C]	T_{max} [°C]	P_{max} [bar]	P_{fin} [bar]	T_{fin} [°C]	P_{fin}-P_0 [bar]	Yield [wt.%]
Fast food	18	342.7	345.2	137.9	18.9	23.3	0.92	78.5
Restaurant	18	344.2	345.8	137.8	18.9	24.3	0.89	n.d.
Domestic	18	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	69.0

The following figures depicts the HTL products before and after centrifugation. The UCO from restaurant produced mainly a single aqueous phase product (except for a negligible fraction of solids), while a clear distinction between a water and an oil phase was observed for the other two samples.
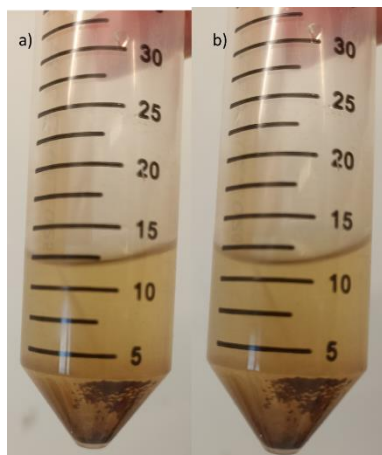
Figure 6: Sample of the products from the HTL conversion of the UCO from restaurants; a) before centrifugation, b) after centrifugation.
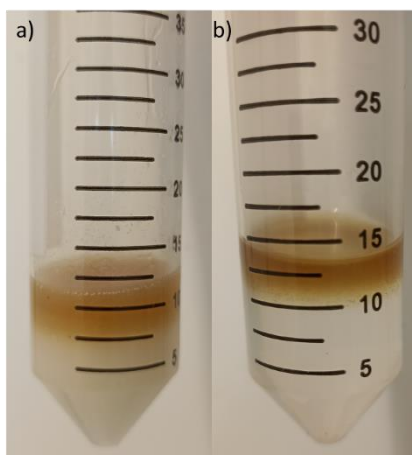

Figure 7: Sample of the products from the HTL conversion of the UCO from fast food; a) before centrifugation, b) after centrifugation.
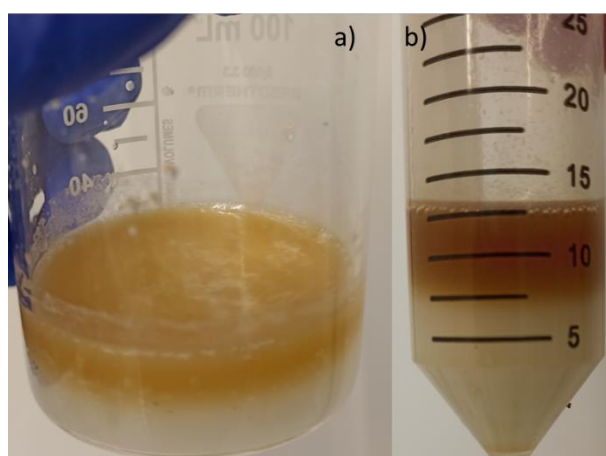

Figure 8: Sample of the products from the HTL conversion of the UCO from domestic collection; a) before centrifugation, b) after centrifugation.

Figure 9 and Figure 10 depict the operating diagram of the HTL experiments of fast food UCO and restaurant UCO, respectively.
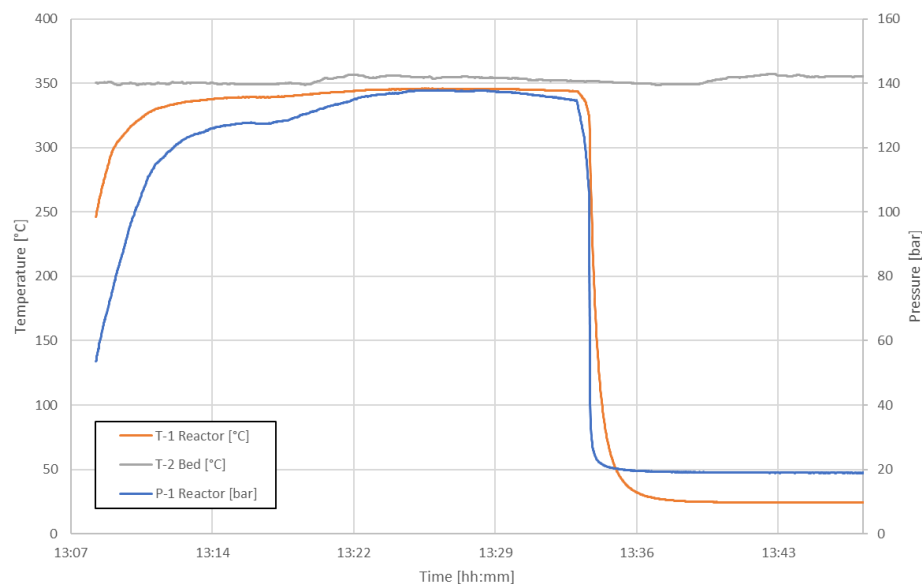

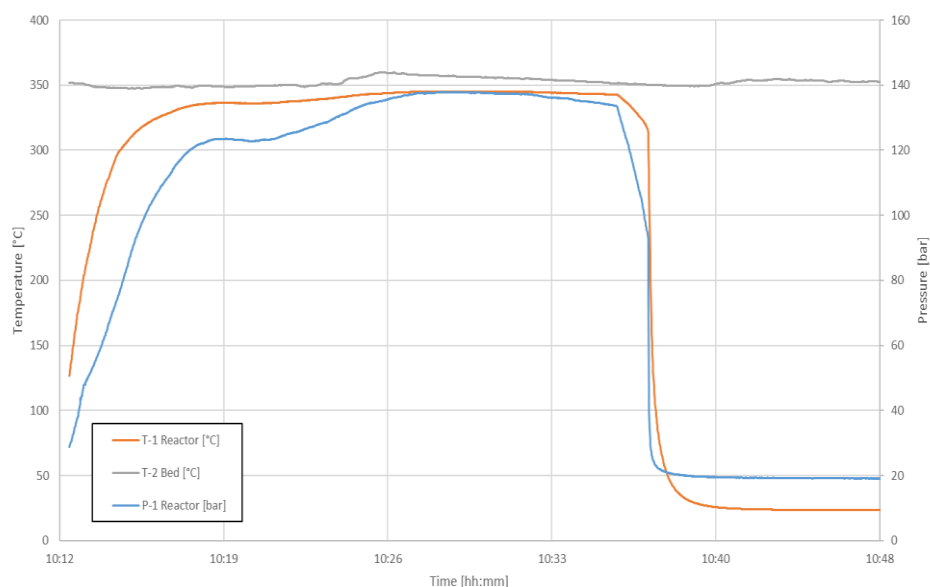**Figure 9: Pressure-temperature diagram of fast food UCO HTL experiment.**

Figure 10: Pressure-temperature diagram of restaurant UCO HTL experiment.

4.2.1 Characterization of hydrothermal liquefaction products

From the results shown in Table 3, it is clear that the oil samples obtained from the HTL experiments were almost identical to the initial UCO samples, at least in terms elemental analysis, only slight differences were observed in the nitrogen content. A relevant decrease in the water content in the UCO from fast food was detected.

Table 3: Properties of the HTL products; absolute standard deviation is reported in brackets.

Parameter	Unit of measure	Method	Fast food	Restaurant	Domestic
C	wt.%	UNI EN 16948	75.7 (0.16)	0.90 (0.02)	75.5 (1.20)
H	wt.%	UNI EN 16948	12.2 (0.13)	10.8 (0.52)	12.1 (0.07)
N	wt.%	UNI EN 16948	0.11 (0.03)	0.06 (0.04)	0.08 (0.08)
O	wt.%	Calculated	11.9	88.2	12.4
Water content	wt.%	UNI EN ISO 8534	1.0 (0.07)	99.3 (0.05)	0.80 (0.10)

4.3 Pyrolysis experiments

Likewise to what have been reported for the hydrothermal liquefaction experiments, Table 4 shows the main operative results of the pyrolysis experiments; HR represents the heating rate and was evaluated by considering the difference between the temperature values inside the reactor at the starting of the reaction and at immersion in the sand bed. The highest HR value was observed with the restaurant UCO, followed by fast food and domestic UCO, this differences can be explained by the different value of water content of the samples. The maximum values of the pressure inside the reactor were lower than those measured in the HTL experiments, due to the fact that the a lower amount of volume was occupied by the reacting medium. The highest value of residual pressure was found in the fast food UCO experiment (10.9 bar), while the lowest in the experiment where UCO from restaurant was adopted as feedstock (1.3 bar).

Table 4: Main operative results from the pyrolysis experiments.

Sample	HR [°C min^{-1}]	P$_0$ [bar]	T$_{mean}$ [°C]	T$_{max}$ [°C]	P$_{max}$ [bar]	P$_{fin}$ [bar]	T$_{fin}$ [°C]	P$_{fin}$-P$_0$ [bar]	Yield [wt.%]
Fast food	77.1	0	450.2	451.5	41.0	10.9	25.2	10.9	88.6
Restaurant	125.9	0	450.5	452.4	17.8	1.3	24.3	1.3	72.2
Domestic	56.5	0	449.3	450.1	35.6	8.8	22.9	8.8	63.3

Figure 11 shows a picture of the pyrolysis products: the product from the pyrolysis of the UCO from restaurant, as expected, is really similar to the untreated sample as it is almost composed of water; the other two products, however, exhibited a darker colour and a small amount of water was observed in the product from fast food UCO conversion, probably deriving from the starting material.
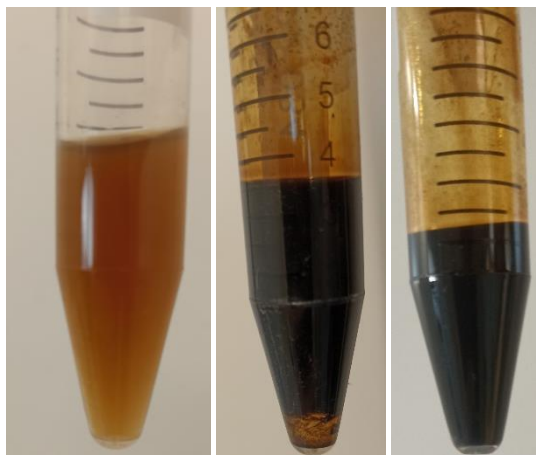
Figure 11: Sample of the products from the HTL conversion of the UCO from restaurant (left), fast food (centre), domestic collection (right).

Figure 12, Figure 13 and Figure 14 depict the operating diagram of the pyrolysis experiments of restaurant, fast food and domestic UCO, respectively.
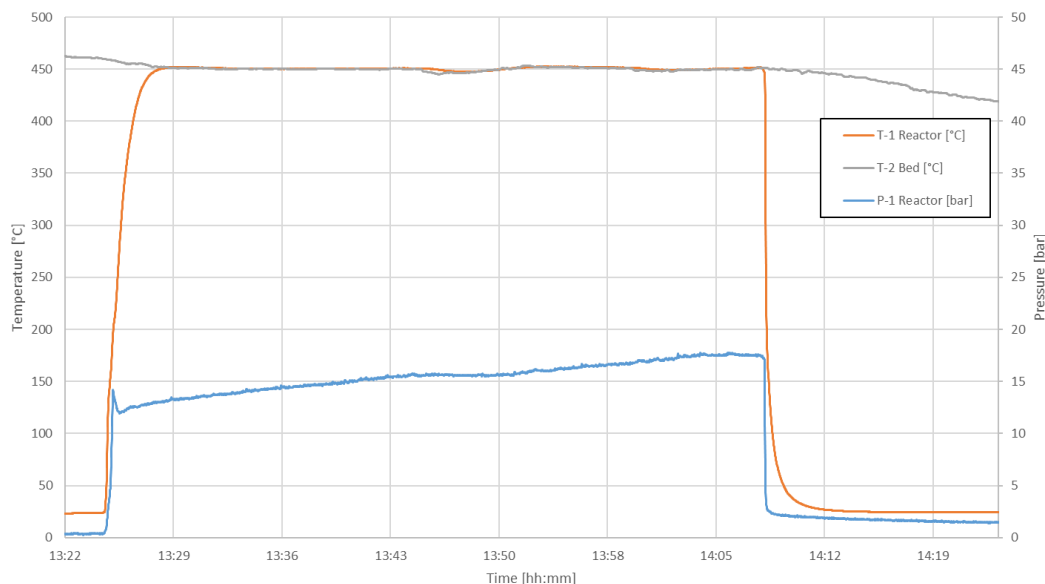

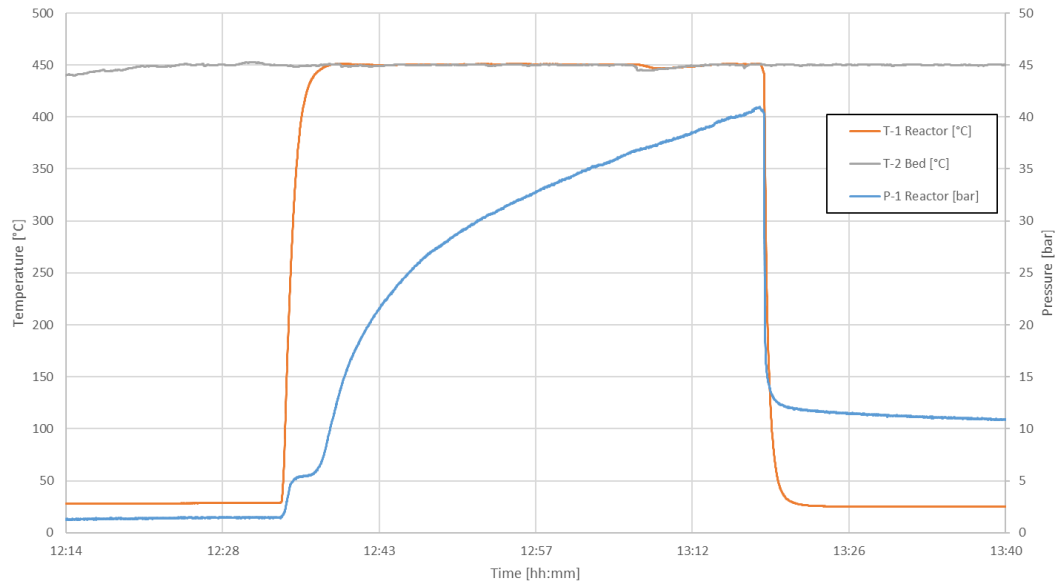**Figure 12: Pressure-temperature diagram of restaurant UCO pyrolysis experiment.**

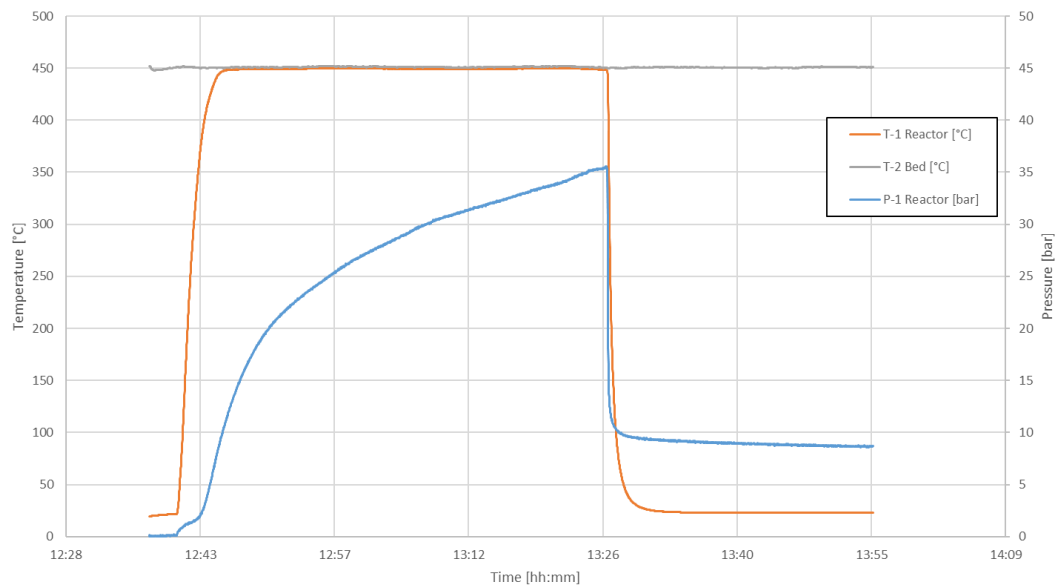**Figure 13: Pressure-temperature diagram of fast food UCO pyrolysis experiment.**

Figure 14: Pressure-temperature diagram of domestic UCO pyrolysis experiment.

4.3.1   Characterization of pyrolysis products

Differently from HTL, the effect of pyrolysis was more significant as a greater variation in the elemental and water content of the pyrolysis products was observed (

Table 5). Domestic UCO yielded an oil with improved quality, being its carbon content increased from 76.6 to 82.2 wt.%, while oxygen content decreased from 11.3 to 5.1 wt%.

Table 5: Properties of the pyrolysis products; absolute standard deviation is reported in brackets.

Parameter	Unit of measure	Method	Fast food	Restaurant	Domestic
C	wt.%	UNI EN 16948	63.2 (3.14)	3.0 (0.01)	82.2 (1.05)
H	wt.%	UNI EN 16948	10.5 (1.36)	11.06 (0.09)	12.6 (0.18)
N	wt.%	UNI EN 16948	0.11 (0.03)	0.04 (0.01)	0.12 (0.04)
O	wt.%	Calculated	11.9	85.9	5.1
Water content	wt.%	UNI EN ISO 8534	0.42 (0.30)	90.8 (3.8)	0.13 (0.01)

4.4 GC-MS analysis

Qualitative analysis of the organic compounds in the UCO, HTL and pyrolysis products was performed by GC-MS. A comparison between the chromatograms of the starting UCO materials and the respective pyrolysis and HTL products is reported.

The restaurant UCO feedstock, Figure 15 black chromatogram, presents glycerol (around 15-16 min) and short-chain fatty acids (C3-C6) as the main identified compounds (the first 10 minutes of the chromatogram) followed by long-chain fatty acid (C16-C18) as Palmitic, Oleic, Linoleic and Stearic acid (around 30-35 minutes),their area % is shown in Table 6.

Table 6: GC MS main identified compounds of restaurant UCO.

Compound	Area %
C2-C6 fatty acids	15
C16-C18 fatty acids	10
Glycerol	40

In the product derived from the HTL process, Figure 15 red chromatogram, are present most of the UCO peaks but with lower intensity as the restaurant UCO was soluble in water resulting in a probable dilution of the feedstock compounds in the HTL product. Peaks corresponding to short-chain fatty acid as Propanoic (around 3 min) and Butanoic acid (5 min) are visible. The peak of glycerol (large peak around15-16 minute) is still present in the HTL product. Unlike the UCO starting material, long-chain fatty acids are not visible in the product, probably due to the dilution effect.
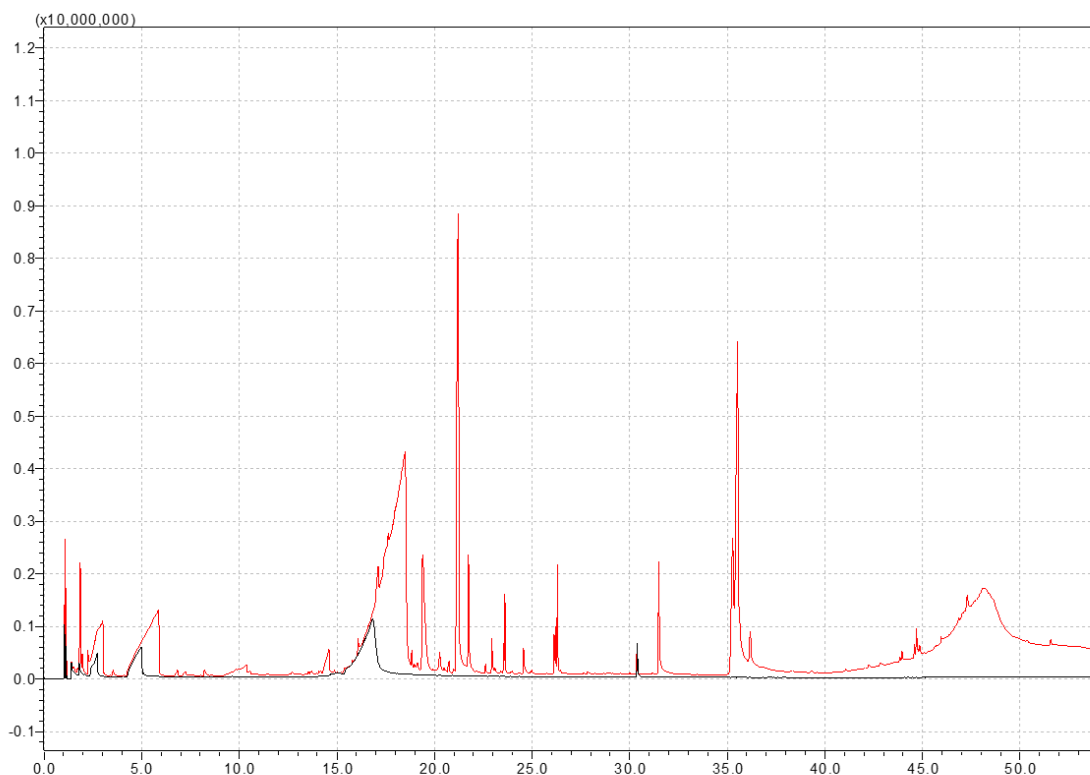
Figure 15: GC MS chromatograms comparison of the restaurant UCO feedstock (red line) and of its HTL product (black line).

A comparison between the chromatograms of the same UCO starting material and its pyrolysis product is also reported in Figure 16. Both chromatograms are very similar and the same peaks are present even if there is an intensity decrease of the Glycerol peak. This molecule could be involved in condensation reaction with other compounds such as fatty acids to originate higher molecular weight products, or in hydrolysis reactions by giving gaseous products or volatile compounds (i.e. methanol).
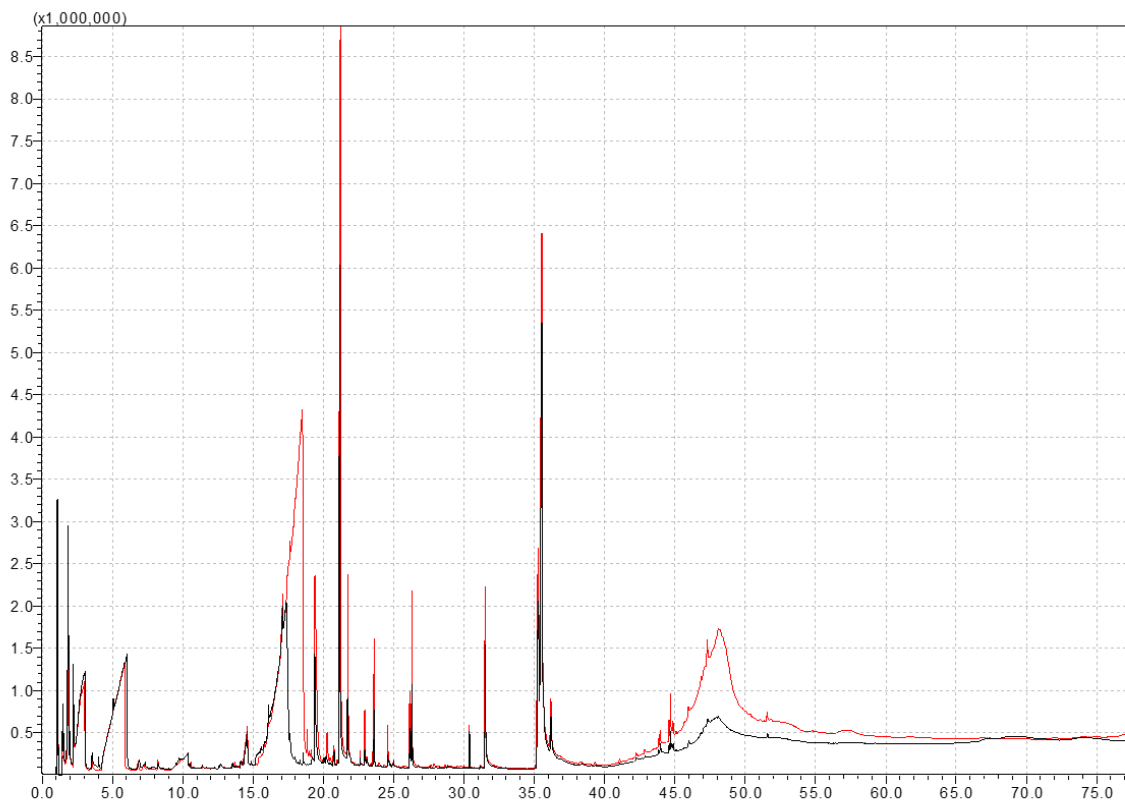
Figure 16: GC MS chromatograms comparison of the restaurant UCO feedstock (black line) and of its pyrolysis product (red line).

In the fast-food UCO, whose identified compounds are reported in Table 7 in terms of A%, long-chain fatty acids (C16-C18) are the main compounds (i.e. Palmitic, Oleic, Linoleic and Stearic acid) while no Glycerol or short chain fatty acid were detected; higher molecular weight molecules such as sterols (i.e. Cholesterol, Sitosterol) or compounds derived from fatty acid condensation (Butyryl triglyceride) are instead present in the chromatogram (Figure 17).

Table 7: GC MS main identified compounds of fast food UCO.

Compound	Area %
C16-C18 fatty acids	74
Heavier compounds	26

In the chromatogram of the fast-food UCO HTL product, Figure 17 black chromatogram, the same long-chain fatty acids are still present. The peaks have a lesser intensity probably due to the dilution effect. The peak of Butyryl triglyceride, around 29 minutes, however disappeared, probably this molecule broke into smaller volatile compounds.
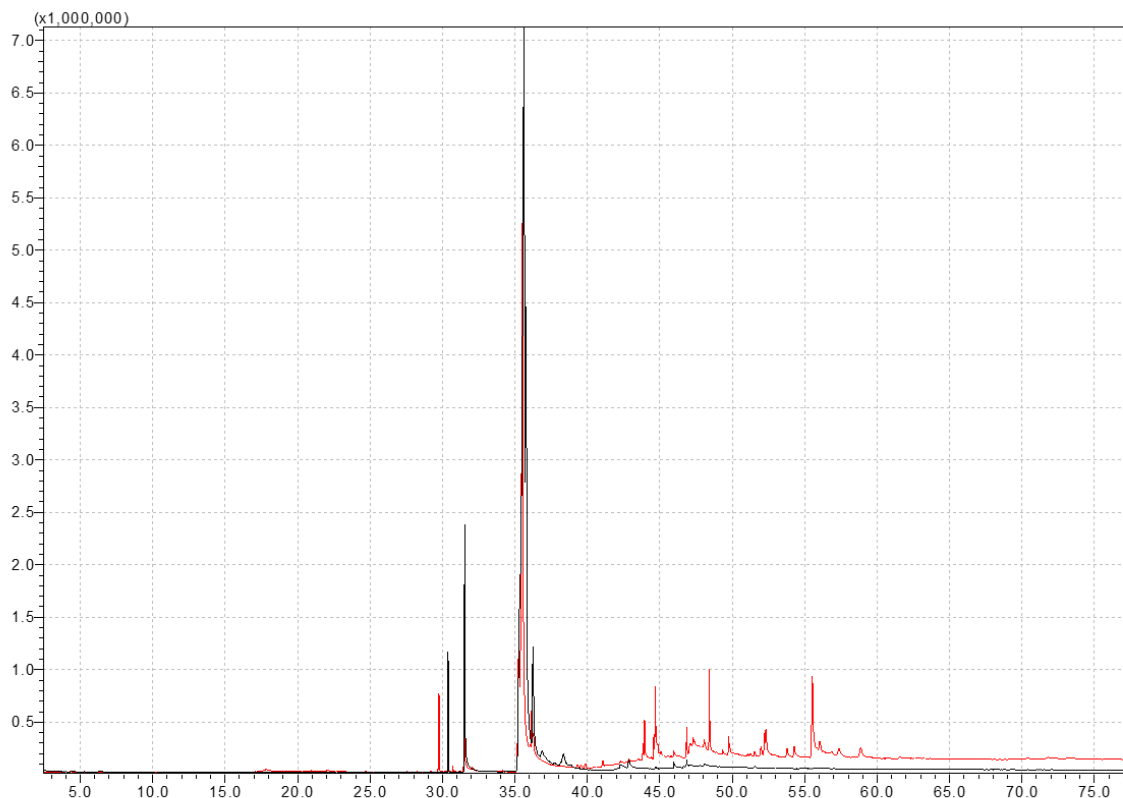
Figure 17: GC MS chromatograms comparison of the fast food UCO feedstock (red line) and its HTL product (black line).

The chromatogram of the product obtained by pyrolysis, Figure 18 black chromatogram, shows several peaks with high intensity. Different compounds classes were identified and their A% is reported in Table 8.

Table 8 : GC MS identified compounds classes of fast food UCO pyrolysis product.

Compound Class	Area %
Linear Alkanes	20.3
Cyclic compounds	16.3
Fatty acids	11.6
Aromatics	10.8
Alkenes	7.4
Ketones	4.6
Unidentified	29.1

Linear Alkanes are the main compound class with a number of carbon atoms in the range C6-C20. These compounds most probably originate from thermal-cracking reactions that are involved during fatty acid pyrolysis leading to the breaking of fatty-acid chains into shorter ones. Alkanes of the same carbon length are also present and probably share the same origin from the cracking of unsaturated fatty-acid chains.
Long-chain fatty acids are still visible in the chromatogram of the pyrolysis product with a number of carbon atoms in the range C7-C20. Among them, compounds such as Heptanoic, Octanoic, Oleic, Stearic, Eicosanoic acid have been identified which are the same present in the feedstock and probably where not converted during the pyrolysis treatment. Compounds formed by one or two aromatic rings with different substituents, such as Toluene, Ethylbenzene, p-Xylene, Naphthalene, and other benzene and naphthalene derivates have been identified in the

chromatogram of the pyrolysis product. These may originate from polycondensation and isomerization reactions that occur during the process.

Cyclic compounds with a number of carbon atoms in the range of C3-C6 such as Cyclopropane, Cyclobutane, Cyclopentene and Cyclohexene with different substituents has been identified. This class of compounds may originate from fatty acid chain cyclization and isomerization.

Long chain ketones were also present such as Heptadecanone and Nonadecanone, probably originating from long chain fatty acids.
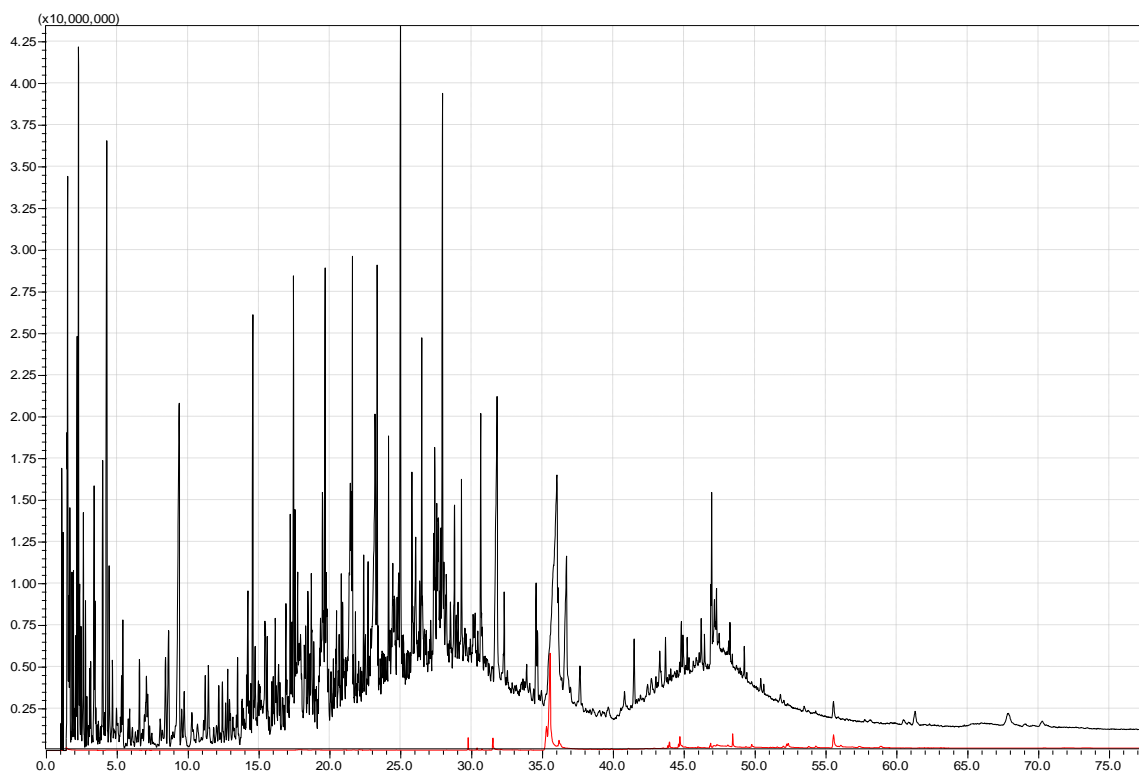

Figure 18: GC MS chromatograms comparison of the fast food UCO feedstock (red line) and its pyrolysis product (black line).

The domestic UCO feedstock main GC detectable constituents were the long-chain fatty acids (C16-C18) as Palmitic, Oleic, Linoleic and Stearic acid (Table 9).

Table 9 : GC MS main identified compounds of domestic UCO

Compound		Area %
C16-C18	fatty	97
acids		

The domestic UCO HTL product, Figure 19, presents the same fatty acid compounds suggesting that no reaction occurred during the HTL treatment.
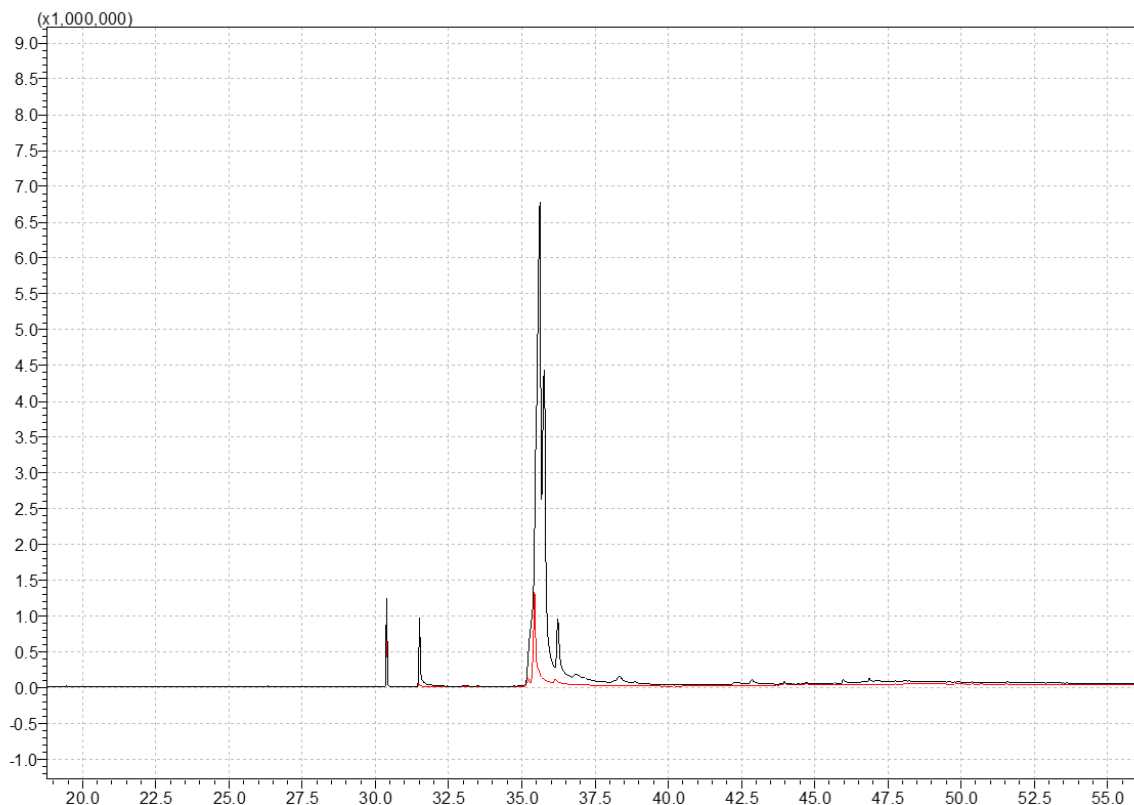
Figure 19: GC MS chromatograms comparison of the domestic UCO feedstock (red line) and its HTL product (black line).

The chromatogram of the product obtained by pyrolysis, Figure 20 black chromatogram, results very similar to the domestic UCO pyrolysis product. GC MS compounds classes are shown in Table 10.

Table 10: GC MS identified compounds classes of fast food UCO pyrolysis product.

Compound Class	Area %
Linear Alkanes	23.1
Cyclic compounds	12.0
Fatty acids	21.8
Aromatics	7.4
Alkenes	7.8
Ketones	1.7
Unidentified	26.1

Linear Alkanes are also for this product the main compound class with the same number of carbon atoms in the range C6-C20 as the alkenes. Aromatics, cyclic and long chain ketones were also present as in the domestic UCO pyrolysis product. Long-chain fatty acids with a number of carbon atoms in the range C7-C18 remain in the product as unreacted materials.
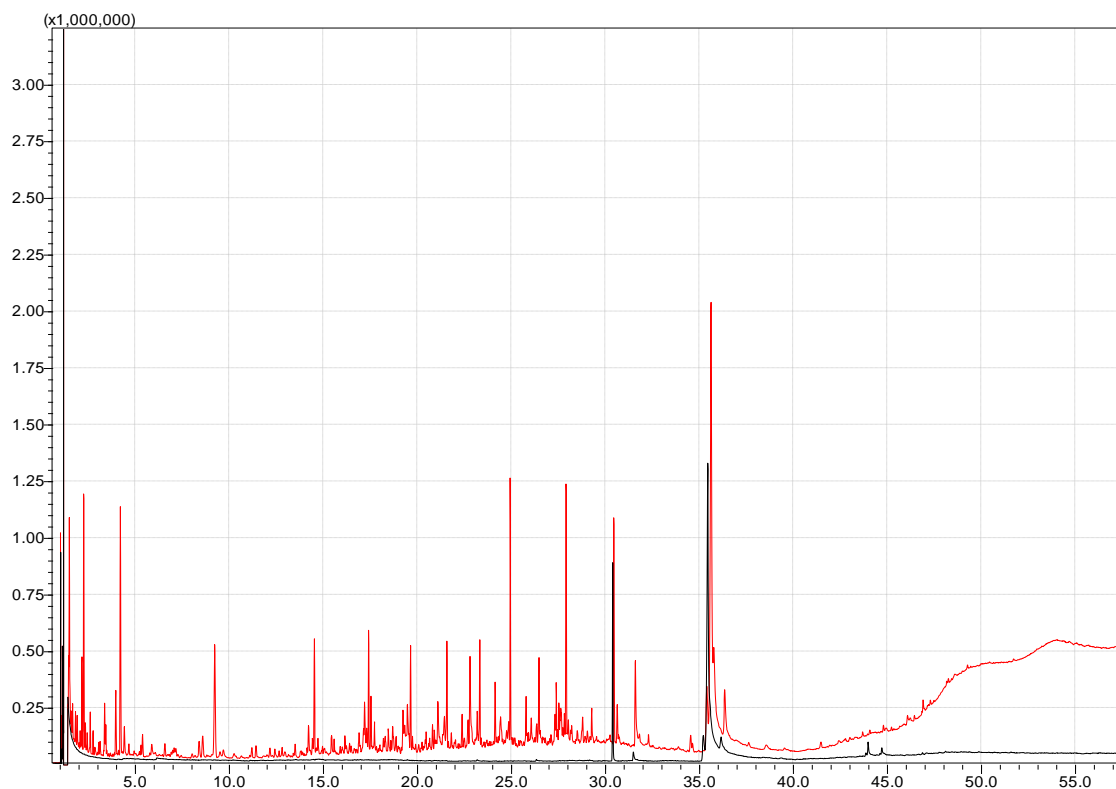
Figure 20: GC MS chromatograms comparison of the domestic UCO feedstock (red line) and its pyrolysis product (black line).

5 Conclusions

Three UCO samples of different origin were converted via hydrothermal liquefaction and pyrolysis. As confirmed by the elemental and GC-MS analysis, pyrolysis resulted as the most performing thermal treatment. In particular, the domestic and fast-food UCO pyrolysis yielded an oil with a large varieties of compounds, mainly hydrocarbons, such as linear alkanes or aromatics derived from the fatty acid conversion. The HTL tests, on the other hand, showed no significant differences from the feedstock regarding the GC detectable compounds, suggesting that the UCO did not react in these investigated reaction conditions.

A higher yield was observed from the pyrolysis of fast food UCO (88.6 wt.%). Indeed domestic UCO pyrolysis exhibited a lower yield (63.3 wt.%), but the corresponding product possessed an improved quality, being its carbon content increased from 76.6 to 82.2 wt.% and its oxygen content decreased from 11.3 to 5.1 wt%.