

ITAKA

Collaborative Project

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D2.8 Development of UCO specifications

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Executive summary

The objective of the ITAKA project is to support the development of aviation biofuels in an economically, socially and environmental sustainable manner, improving the existing technology and infrastructures. This report investigates the use of used vegetable oil (UCO) as renewable feedstock for the production of drop-in renewable aviation fuels. The development of UCO specifications is crucial to allow the use a lipid waste for commercial hydrotreating process. Raw UCO needs to be filtered and upgraded before its use as feedstock, so the esterification was considered as upgrading treatment: three samples of esterified UCO was analysed and investigated as potential feedstock. High grade filtration reduced contaminants and water content of raw UCO, restoring a large number of properties to initial values of vegetable oils. Then RE-CORD investigated the catalytic pyrolysis of UCO as alternative thermochemical treatment to commercial hydrotreating to produce bio-hydrocarbons suitable for renewable aviation fuels. Best results (35 wt% of bio-hydrocarbons contained into collected bio-oil) was achieved using activated carbons as catalysts, at 500 °C and WHSV of 2.5 h⁻¹. The experience with experimental activities on raw UCO, its upgrading and thermochemical processing, permitted to develop a proposal for UCO specifications.

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Abbreviations

UCO: Used Cooking Oil

GHG: Green House Gas

LCA: Life Cycle Analysis

RED: Renewable Energy Directive

FT: Fisher Tropsch

HEFA: Hydroprocessed Esters and Fatty Acids

HRJ: Hydrotreated Renewable Jet

HVO: Hydrotreated Vegetable Oil

GTL: Gas-To-Liquid

ICAO: International Civil Aviation Organization

FFA: Free Fatty Acid

PFAD: Palm Fatty Acid Distillate

n.a. : not available

Definitions

ASTM International: known until 2001 as the American Society for Testing and Materials (ASTM), is an international standards organization that develops and publishes voluntary consensus technical standards for a wide range of materials, products, systems, and services.

BIO-OIL: the liquid product from pyrolysis process, also called “pyrolysis oil”.

DIN: Deutsches Institut für Normung (German Institute for Standardization) is the German national organization for standardization and is the German ISO member body. DIN is a Registered German Association (e.V.) headquartered in Berlin. There are currently around thirty thousand DIN Standards, covering nearly every field of technology.

DROP-IN FUEL: a fully compatible fuel for blending with traditional hydrocarbon fuels.

HYDROPROCESSING/HYDROTREATMENT: Generic term used to describe a range of refinery processes that use hydrogen, along with an appropriate catalyst, to remove undesired components from refinery streams. The technology is core to a modern petrochemical refinery.

RENEWABLE JET FUEL: a sustainable jet fuel derived from biomass.

UCO: Used Cooking Oil. Also referred to throughout the literature as WVO (waste vegetable oil) and UVO (used vegetable oil), RVO (recycled vegetable oil) and RCO (Recycled Cooking Oil). UCO has been chosen as the standard for this document

1 Introduction

The use of vegetable oils to produce renewable fuels, i.e. biofuels fully composed by hydrocarbons through hydrotreating or FT-synthesis, consists in a real opportunity for greening the aviation sector. Defined ranges of bio-hydrocarbons are requested to substitute the traditional jet fuel into the common commercial mixture, according to ASTM D4054 [1] and D7566 ASTM [2] to approve the renewable jet fuel, and ASTM D1655 [3] for Jet A-1 requirements. While FT-synthesis requires high capital cost to work the process, HEFA cost is largely affected by the high operative cost. From the study of Pearlson et al [4], the cost of feedstock has a relevant impact on the gate price of HEFA (60 – 70%), thus the necessity to find an alternative, lipid-based feedstock, becomes fundamental.

The ITAKA project has the aim of substituting the traditional vegetable oils with camelina and used cooking oil (UCO) as feedstock for commercial hydrotreating, promoting a sustainable chain for commercial aviation transport [5]. Camelina consists in a crop cultivated in marginal lands (i.e. Spain in ITAKA), which can be counted double towards 10% target for biofuels according to RED scheme [6] (as well as for UCO). Its vegetable oil is suitable for commercial process of hydrotreating with no precautions than other traditional vegetable oils. Used cooking oil is a waste that needs to be collected and recycled, and due to its nature, the adoption of this feedstock is not possible without upgrading/cleaning pre-treatment. In order to find a strategy to reduce the HEFA cost, ITAKA scope was focused on the investigation of alternative thermochemical treatments to produce bio-hydrocarbons suitable for aviation fuel.

Despite UCO derives from vegetable oils, cooking process alters some relevant properties of feedstock. An experimental campaign on filtration and centrifugation was performed and reported on D2.3 [7], focusing on macro- and micro-contaminants reduction. The achieved results on UCO showed an important reduction of nitrogen and phosphorous content by high quality filtration (up to 0.8 micron). Despite contaminants and water content were strongly reduced, the still high nitrogen content could be associated to the oil soluble proteins, which were present in the raw UCO. Moreover, acidity and other micro-contaminants such as Ca, Mg, K, Na and other metals need to be monitored before its use as feedstock for next thermochemical processes.

Currently there are no specifications about the use of UCO as feedstock for thermochemical processing: only DIN 51623 [8] can provide an indication about the quality of feedstock, although it is referred to rapeseed oil as fuel. The development of UCO specification for hydrotreating, or generally, for thermochemical processing to produce biofuels, needs an accurate study on feedstock, process and products. In order to develop a proposal for UCO specification, the following issues were considered:

1. the differences between traditional vegetable oils and filtered used cooking oil;
2. the interaction between used cooking oil and catalysts;
3. the presence of hydrogen during the process, as first promoter either of deoxygenation reactions, or other reactions that involve the heteroatoms contained into the oil.

In the case of catalytic pyrolysis, which is the main subject of present document, the reaction pathways do not require hydrogen, thus the quality of feedstock becomes less important. This work investigates the catalytic pyrolysis of UCO, as a process to convert triglycerides in bio-hydrocarbons. The conversion route was divided in two different steps: first the triglycerides are pyrolyzed in a fixed bed reactor; then, the

generated pyrolysis vapours are catalytically cracked in a dedicated reactor. Finally, the pyrolysis vapours are condensed, separated by non-condensable gases, and collected as bio-oil. The main goal is based on the development of a strategy for deoxygenating the carboxylic group of fatty acids molecules, leading the direct production of paraffins and olefins. The investigation on the reaction pathways was carried out experimentally, in terms of quantity and quality of collected bio-oil, by the use of different catalysts. Bio-oils was chemically analysed by both RE-CORD and NESTE laboratories, characterizing the fuel properties and individuating the most significant chemical species. Once the quality of feedstock and bio-oils was assessed, a first proposal of UCO requirements as feedstock for thermochemical processes was carried out.

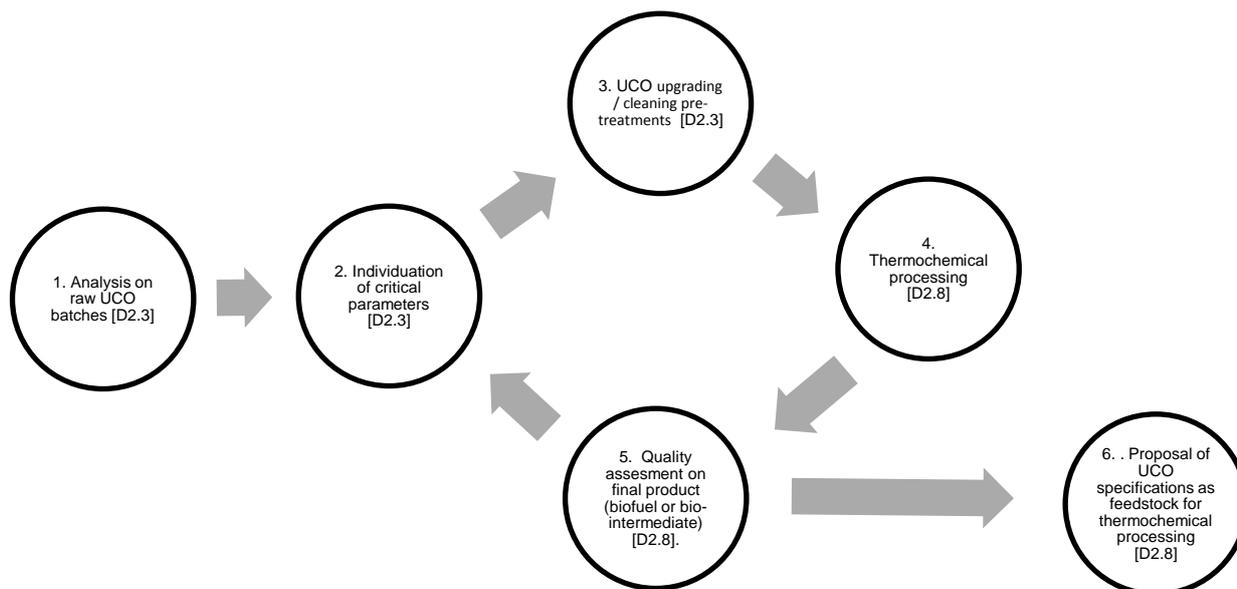


Figure 1: RE-CORD experimental activities on UCO.

2 UCO as feedstock for biofuels production

Used cooking oil (UCO) consists in a mixture of edible vegetable oils, and sometimes animal fats, which derived from the fried food that need large amounts of oil for cooking [9]. In general, if a vegetable oil is heated at high temperatures (140 – 180 °C), an increase in saturation level and FFAs content occur, due to the decomposition of the triglyceride molecules [10]. In the case of the frying process, the interaction between oil and food cause several reaction like: hydrolysis, polymerization, oxidation [11], and in some cases cyclization of the fatty acids [12]. As consequence, the physical and chemical properties of the vegetable oils adopted as frying oil can significantly change; in general UCO has higher acid value, viscosity, moisture and contamination respect to edible vegetable oils. According to literature, UCO can be defined with several synonymous such as WCO (Waste Cooking Oil) or WVO (Waste Vegetable Oil), but in some cases it can include a specific lipid-waste composed by animal fats (e.g. Yellow Grease).

From a legislative point of view, the Waste framework Directive 2008/98/EC1 [13] classifies UCO as “edible oil and fat” and Directive 2004/35/CE2 [14] establishes a framework for environmental liability in order to prevent and remedy the environmental damage, in this case by means of the regulation of UCO chain on production/collection/recovery system. In this optic, EU Member States must control the companies responsible for the collection and handling or treatment of UCO.



Figure 2: On the left side, raw UCO. On the right side, the residual of centrifugation (left) and the separated oil (right).

Animal By-Products Legislation 1774/20023 [15] forbids the use of UCO (originating from restaurants, catering facilities, and kitchens) as ingredient into animal feed (or it is possible only if properly filtered and re-esterified), so its use can only be suitable to produce biofuels and chemicals.

The use of UCO as biofuel was deeply studied, tested and currently adopted for biodiesel production [16–19]. According to the RED scheme, UCO is considered a feedstock for biofuels produced from “wastes, residues, non-food cellulosic material, and lignocellulosic material” which can be counted double against the emissions reduction target of 10% renewable energy goal for transports. Currently the sub-target for the promotion of advanced biofuels is 0.5%, without including UCO, but making its use eligible and double counted for the 10% goal [20]. As a consequence, the market of UCO (despite it is still relatively immature) has changed dramatically over the past few years, passing from being a waste to a product sold up to 250 – 300 €/ton for raw UCO, and up to 880 €/ton for refined oil [21]. Only few data assess the availability of UCO for EU-27 member states: estimations on the available collectable potential range from less than 1 Mtons to above 3.5 Mtons per year was carried out by Tacconi et al. [22]. In regard to extra UE import-export, only a small quantity of Chinese UCO has been found to be imported to the EU. This because all actors involved in UCO supply chain for biodiesel production, starting from UCO collector to end user, have to be certified under one of the existing certification schemes (ISCC EU and ISCC DE) from January 1st, 2013 [23]. This fact is going to limit the import of UCO in EU, in particular for biodiesel production (UCOME), thus the market share from other countries is going through a marked reduction. Currently, approximately 80 - 90% of the UCO collected in the EU-27 is used for biodiesel production, and the other fraction for energy and oleochemicals [24]. Just a small quantity is dedicated to other use, out from fuels and chemical market.

2.1 UCO vs traditional vegetable oils

The properties of UCO as biofuel was deeply investigated in D2.3 “Report describing the main barriers to innovation and recommendations for further research” [7]. Samples of UCO and commercial sunflower oil were analysed to investigate how the cooking process affects the vegetable oils properties as biofuels. From the analysis of several batches of UCO, it emerges higher acidity due to higher free fatty acids content, higher contamination and water content, higher micro-contaminants content (N, P, S, Ca, Mg) than traditional vegetable oils. The adoption of UCO as feedstock in hydrotreating was not possible without upgrading/cleaning pre-treatments. In order to develop a feedstock suitable for the existing infrastructure, an experimental campaign on filtration and centrifugation was performed to remove macro- and micro-contaminants. The achieved results on UCO showed a relevant reduction of contaminations, water content, nitrogen and phosphorous content with a high quality paper filtration (up to 0.7 micron pore size). Despite the achieved improvements, the UCO nitrogen content of still remains a significant amount (80 ppm).

2.2 Industrial esterification of UCO

The main use of UCO as feedstock for biofuels production consist in the conversion in biodiesel. Biodiesel (FAME, Fatty Acid Methyl-Ester) represents the most traditional biofuel in the EU, produced by transesterification of triglycerides. In order to produce 3 moles of biodiesel and 3 of glycerol, 3 moles of alcohol are required to react with one mole of triglyceride [74]. The reaction includes catalysts: in commercial treatment are commonly adopted alkaline solutions, such as sodium or potassium hydroxide, to accelerate the reaction [75]. In contrast, the presence of free fatty acids in UCO inhibits the transesterification reaction [25]. An industrial process to restore the original triglycerides content of UCO consists in the esterification process. A local company of the Florence district, SILO SpA, works on exhausted cooking oil and fats from

several years, collecting the feedstock by means of contracts with private companies. After collection, SILO leaves the UCO to sediment and then filters it at about 50 micron. A part of UCO is then subjected to esterification process, carried out at about 220 - 230 °C, with the addition of glycerol (pure glycerine at 97 – 98 wt%). This process restores the acidity of UCO to comparable values with pure vegetable oils. Three batches of esterified UCO were sampled and analysed. Table 1 shows the properties of esterified UCO, the same as those investigated for raw and filtered UCO in D2.3, and compared to DIN 51623 [8] “Fuels for vegetable oil compatible combustion engines” (a recent German standard for pure plants oil).

Table 1: Esterified UCO analysis (methods of analysis are described in 4.2.3).

Parameter	Unit	Method	DIN 51623	UCO EST 120126	UCO EST 130528	UCO EST 130704
Density	$Kg\ m^{-3}$	UNI EN ISO 3675	900 - 930	938	916	922
Kinematic Viscosity at 40 °C	$mm^2\ s^{-1}$	UNI EN ISO 3104	< 35		34.5	34.08
Acid value	$mgKOH\ g^{-1}$	UNI EN 14104	< 4	0.323	2.4	3.3
Free Fatty Acid	wt%	UNI EN ISO 660	< 2	0.1615	1.2	1.65
Iodine Number	$g\ Iodine\ 100g^{-1}$	UNI EN 14111	< 125	86	96	96
Water content	wt%	UNI EN ISO 8534	< 0.075	0.016	0.944	2.1
Ash	wt%	UNI EN ISO 6245	-	0.01	0.03	0.04
Total contamination	$mg\ kg^{-1}$	UNI EN 12662	< 24		628	1,895
Sulphur	wt%	Internal method	< 0.001	0.136	0.002	0.014
Calcium	$mg\ kg^{-1}$	UNI EN 14538	< 1	15.5	0	0
Magnesium	$mg\ kg^{-1}$	UNI EN 14538	< 1	2.7	0	0
Phosphorus	$mg\ kg^{-1}$	UNI EN 15290	< 3		4.933	7.5
C	wt%	ASTM D5291	-	73.5	76.5	75.8
H	wt%	ASTM D5291	-	11.2	12	11.8
N	wt%	ASTM D5291	-	0	0.029	0.028
O	wt%	calculated	-	15.164	11.439	12.318
Calorific value, higher	$kJ\ kg^{-1}$	DIN 51900-2	> 36,000	37,898	38,729	38,225
Calorific value, lower	$kJ\ kg^{-1}$	calculated	-	35,455	36,183	35,721

Despite the free fatty acids content was fully restored to the acceptable limits of traditional vegetable oils, the esterified UCOs show unacceptable water content, ash content, micro- and macro-contaminants, which were strongly limited by high quality filtration in D2.3. Next chapter investigates alternative lipids-to-biofuels pathways than transesterification, such as hydrotreating and catalytic pyrolysis: these processes can work with the presence of free fatty acids because they are focused on direct de-oxygenation of triglycerides and fatty acids molecules, where the oxygen is located (i.e. carboxyl group). So the esterification process of UCO is useful only to improve the transesterification conversion yield, favouring the production of an ester compound like biodiesel. Considering the direct conversion of triglycerides into bio-hydrocarbons, the presence of free fatty acids in UCO does not affect the conversion process, thus the esterification of UCO as upgrading process was not considered.

3 Lipids to biofuels pathways

One of the main challenge in biofuels production consists in the best grade of deoxygenation from initial biomass to final product. Lipid-based feedstock consist in high quality material for biofuels production due to its low oxygen content compared to other type of biomass (such as lignocellulosic material, which are mainly composed by sugars and polymers). Oxygen content ranges from 39 – 42.5 % [26] for wood, to 10 - 12% of vegetable oils [27] (where these values are in mass, dry and ash free basis). Moreover, the oxygen bonds into chemical structure of lipids are easier to separate than complex polymeric structure of sugars, where the oxygen is located. Lower oxygen content means higher energy density (i.e. higher C-H content), so the challenge consists in the deoxygenation of carboxyl group of triglycerides (i.e. major constituent of lipids). There are three methods to crack long chain of hydrocarbons to short chain of hydrocarbons [28].

1. The first method is known as thermal cracking and occurs with the aid of heat to produce a lighter product.
2. The second process is the catalytic cracking that is conducted in the presence of an acid catalyst without the use of hydrogen and needs less thermal energy than thermal cracking.
3. The third method is known as catalytic hydrocracking (or hydrotreating) and occurs in the presence of a bifunctional catalyst and a high hydrogen pressure. The catalytic hydrocracking process consumes less thermal energy and the presence of hydrogen minimizes coke formation and therefore reduces catalyst deactivation by pore blockage. However the cost of hydrogen have a relevant impact on the economic costs.

A scheme with inputs (lipid-based feedstock), processes, and products (biofuels) were reported in Figure 3. The main technology able to remove the heteroatoms of oxygen from biomass is the derived technology from oil refineries named “hydrotreating”. The product from lipids hydroprocessing, HVO (Hydrotreated Vegetable Oil), consists in a renewable fuel with the same characteristics of fossil fuel (i.e. full aliphatic hydrocarbons fuel). Despite its high fuel quality, the process requires relevant operative and maintenance costs, thus in recent years the research looked towards novel processes based on thermochemical conversion, mainly catalytic pyrolysis (based on catalytic cracking). In this section a commercial and an experimental pathway to produce renewable hydrocarbons are evaluated.

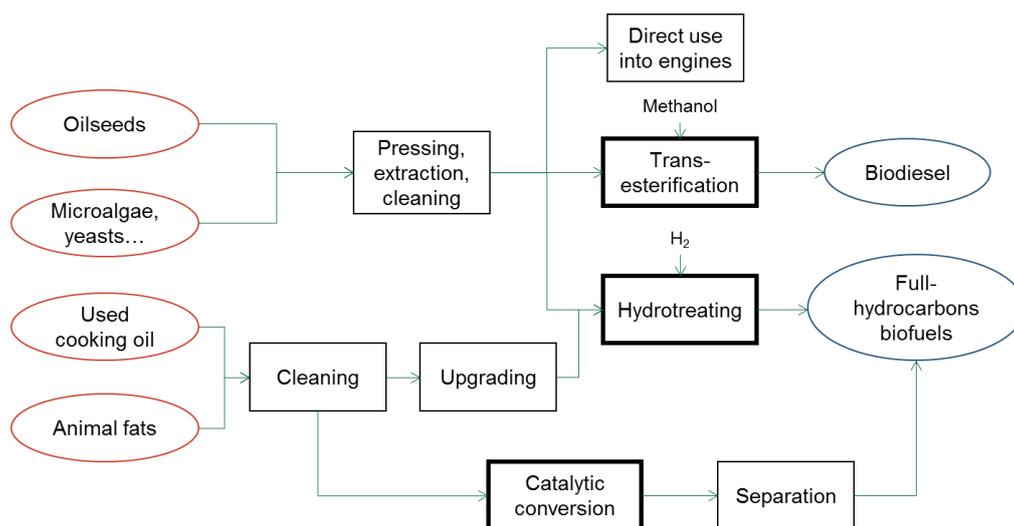


Figure 3: Thermochemical conversion routes from lipids to biofuels [29].

3.1 Hydroprocessing of vegetable oils

Hydroprocessing is used in the petroleum refinery to remove S, N and metals from petroleum-derived feedstock, including heavy gas–oil or vacuum gas–oil. These processes, even into existing refineries, can be used for lipids hydroprocessing, introducing the biorefinery concept. These treatments can be sometimes called “hydrotreating” when applied to oxygenated paraffin chains, such as triglycerides or FFAs, as they lead to the removal of oxygen by hydrogenation, decarboxylation and decarbonylation [30]. A scheme of the ideal reactions pathway was carried out by Huber et al. [31] and reported in Figure 4, showing the production of iso-paraffins in the range of diesel fuel. The reaction conditions, together with catalyst nature, are crucial to define the performance and yield of conversion. Sotelo-Boyás et al. [28] reported a detailed review on type of oil, reactor, reaction conditions, catalyst, and main products obtained during hydroprocessing of pure oil and oil plus gas oil mixture.

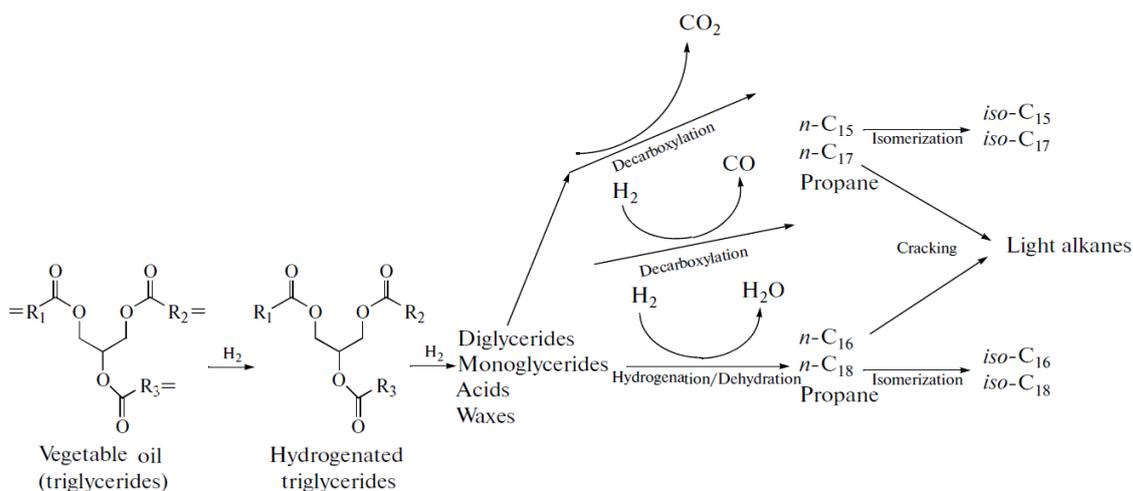


Figure 4: Scheme of the main reactions in the hydrotreatment of generic vegetable oils and fatty acids [31].

Since few years, several companies such as Neste Oil, Petrobras and ENI/UOP started the commercial production of HVO, both for road and air transport fuels [32]. A recent study found that the baseline cost for

HEFA fuel production ranges between 1.01 - 1.16 \$/liter, where the cost of process impact for 30 – 40 % of total cost per litre [4]. Considering the all operating and under commissioning World plants, currently the global HVO/co-processing production reaches 4.9 Mtoe/yr, where 2.8 from EU sites only [6].



Figure 5: Neste Oil's renewable diesel plant in Singapore, with a capacity of 800,000 tons per year. Source: neste.com

3.2 Experimental pathways

While biodiesel is a traditional biofuel with defined blend walls (up to 20% in diesel engines without requiring any modification [33]), currently the fuel demand is going towards the production of renewable hydrocarbons due to their ability to be drop-in fuels. In addition to hydrotreating, a possible alternative pathway consists in the adoption of the current technology of petroleum refineries, mixing lipids with petroleum fractions such as straight run gas oil and/or vacuum gas oil, in order to be processed on conventional hydrotreating reactors [28]. Another alternative consists in the hydrothermal conversion of vegetable oil by means of batch reactors in severe reaction conditions [34], but also this way implies high operative energy costs. The next paragraph explores the catalytic pyrolysis of lipid-based feedstock: the simplicity of process and the promising experimental results from literature make of this process a promising alternative for the production of renewable hydrocarbons.

3.2.1 Catalytic pyrolysis of lipids

Thermal and catalytic pyrolysis of lipid-based feedstock represents a pathway for the production of renewable bio-based products such as fuels and chemicals, with a final products composition similar to diesel fuel [35]. Several works on lipids reaction schemes were proposed [36–40]. The cleavage of the triglycerides molecules originates a mixture of hydrocarbons of smaller chains and oxygenated compounds, such as alkanes, alkenes, alkadienes, aromatics, aldehydes, ketones, and carboxylic acids. Teixeira and Sousa [41] proposed a mechanism based on two step of cracking that occur simultaneously: first (i.e. primary cracking), acid species (mainly carboxylic acids) are formed during the thermal decomposition of triglycerides by means of the breakdown of C-O bonds of carboxylic group, then (i.e. secondary cracking) the products from the first reaction lead the formation of organic compounds with shorter chain lengths, including saturated and/or unsaturated hydrocarbons. The effect of catalysts affects the selectivity of secondary reactions, e.g. in the case of zeolite cracking favours the formation of aromatics compounds by means of complex reaction mechanisms. Given the difficulties to understand a defined reaction mechanism, Zhenyi et al. [42] studied pyrolysis mechanism of triglycerides focused on triolein thermal degradation (selected as reference structure for vegetable oils). Calculation results gave that the cleavage of C–O bond takes place at the temperature of about 288 °C while the C-C bond at β position occurs at about 388 – 426 °C. However,

the initial pyrolysis (at temperature above 400°C) may begin with the contemporary cleavage of C–O bonds and β bonds of double carbon bonds (C=C). In general the presence of unsaturation favours the cracking in proximity of the C=C bonds [43], and the energy of the C–C bonds in n-alkanes decreases by moving towards the centre of the molecule. Currently the exact reaction mechanism of thermal decomposition of lipids remains a challenge due to the multiple cracking reactions and re-polymerization that occur during pyrolysis. A true indication of the nature of reaction products is given by experimental tests investigated in next chapter.

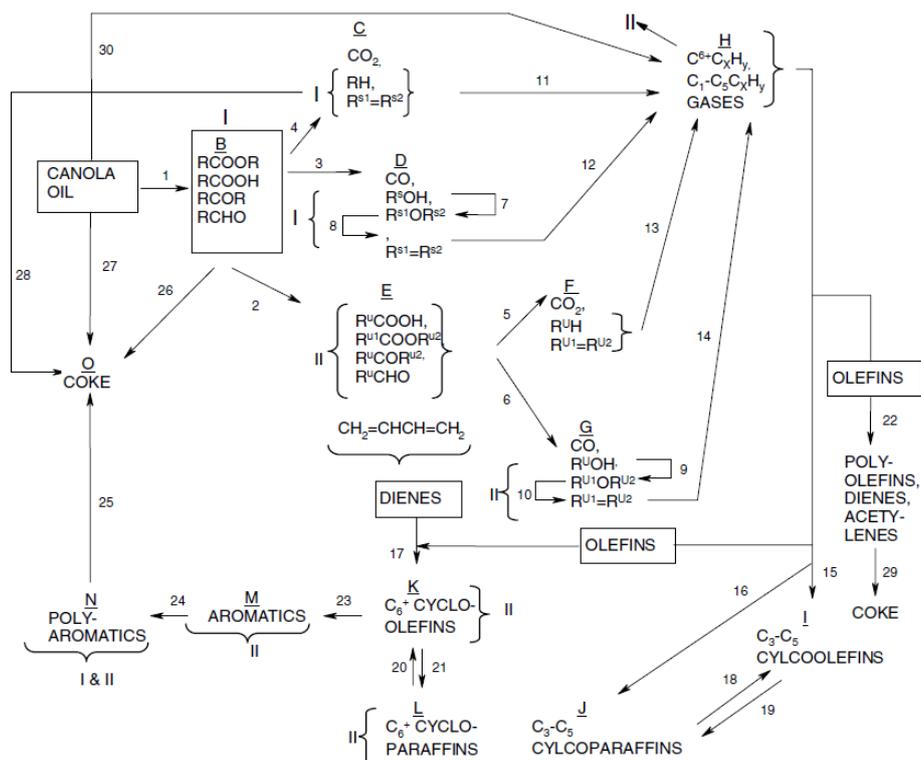


Figure 6: Reaction scheme for the pyrolysis of saturated and unsaturated triglycerides proposed by Idem et al [39].

4 Experimental campaign on catalytic pyrolysis of UCO

4.1 Goal and Scope

Catalytic pyrolysis could be effectively applied to lipids and fatty acids to remove the oxygen and generate hydrocarbons. The potential benefit of pyrolysis versus hydroprocessing relies in the fact that the process does not require hydrogen and noble catalysts, or alternatively can operate with low-cost catalysts, thus more tolerant to irregularly contaminated feeding as UCO. Moreover, pyrolysis can be better downscaled than hydroprocessing, and thus it – especially targeting road transport fuels - could be implemented at smaller scale in decentralised unit, placed close to the collection points of residual oils and well integrated in a local circular economy scheme. Finally, catalytic pyrolysis can be evaluate as first step of UCO conversion before hydrotreating, to save hydrogen demand.

The present process of catalytic pyrolysis of used cooking oil is based on two separate thermochemical steps of conversion: a first primary thermal cracking of UCO; a secondary catalytic upgrading (selective cracking) of generated pyrolysis vapours from first step of process. The main goal is based on the development of a strategy for deoxygenating the carboxylic group of fatty acids molecules (i.e. principal constituents of triglycerides), leading the direct production of bio-hydrocarbons (in the range of aviation fuels). The target bio-hydrocarbons suitable for aviation fuel, as well as the characteristics of commercial and renewable aviation fuels, were investigated in D2.3. The investigation on the pyrolysis products was carried out experimentally, in terms of quantity and quality of collected bio-oil. Four catalysts were tested at different process conditions. In order to evaluate the effect of pyrolysis on an alternative lipid-based feedstock, a final test on pure unsaturated fatty acids was carried out, and the liquid product was compared to UCO pyrolysis oil.

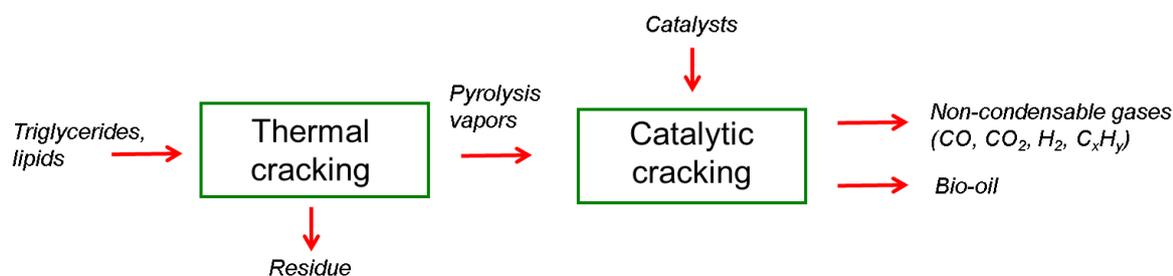


Figure 7: A scheme for RE-CORD catalytic pyrolysis of triglycerides-based materials.

4.2 Materials and methods

4.2.1 Pyrolysis unit

A dedicated continuous catalytic pyrolysis unit was designed, assembled and adopted in the framework of ITAKA. The unit can process 1.5 kg h^{-1} of bioliquids. The experimental rig is composed by a first pyrolysis fixed bed reactor, able to convert the lipids into pyrolysis vapours, that are subsequently upgraded by a second dedicated catalytic reactor, and finally condensed into a bio-oil (pyrolysis oil). The feeding system consists in a pressurized injection system, electrically heated, to reduce the oil viscosity and improve atomization in the reactor. The pyrolysis chamber is heated by 12 kW_e electrical resistors, able to maintain

the operative temperature up to 550 °C: the reactor temperature is measured and controlled by means of a K type thermocouple placed in the middle of the reactor. The catalytic reactor, properly heated by a dedicated resistor (3 kW_e), up to 550 °C, allows the catalytic upgrading of pyrolysis vapours. During operation, a nitrogen flow is heated and flushed into the thermal reactor at a constant flow rate of 4 L min⁻¹ in order to maintain the inert atmosphere. The condensation system consists of two water-cooled condensers (water at 15-20 °C) connected in series and a water bubbler to remove the aerosol from non-condensable gases. Pyrolysis gases enter the first condensation section at 400°C, leave this first condenser at ≈80 °C, and exit at ≈20°C from the second condenser. Pyrolysis oil from the two condensers is mixed and collected in a bottle placed at the bottom of the two condensers. The water bubbler temperature is kept at 15-20 °C. Permanent gases are sucked through the whole plant and discharged by a blower. A schematic representation of the process is given in Figure 4. Char is batch-wise discharged at the outlet of the pyrolysis chamber. Liquid yield was calculated as the ratio of the mass of the collected pyrolysis oil to the mass of processed feedstock.

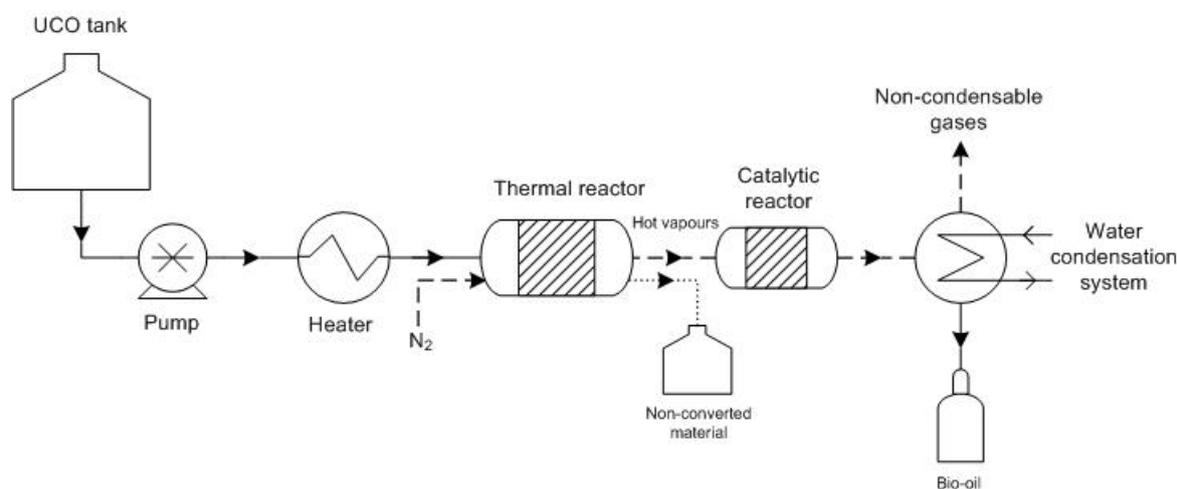


Figure 8: A representative scheme of the catalytic pyrolysis unit for UCO conversion.

4.2.2 Feedstock

UCO was supplied by SILO: the company acquires raw UCO from restaurants and eating-places in the metropolitan area of Florence. The oil is then stored in dedicated stainless steel tanks at SILO premises. The collecting of samples from these UCO tanks requires the use of a special tool, named “sonda Marsigliese”, which is also used as sampling methods for the acceptance of each UCO batch. This instrument allows taking UCO samples at the same time from different heights in the tanks, so to ensure that the collected liquid is representative of the whole liquid stored in the tank. UCO is then pumped through 1 µm mesh cardboard filters, that reduce contamination as well as water content (MP Filtri GRF015 portable off line oil transfer/filtration unit). This filtered UCO was adopted as feedstock for the present work. The Fatty Acid (FA) mixture was instead supplied by InnovHub (Milan, Italy), formerly known as Experimental Station for Oil and Fats.

4.2.3 Methods of analysis

Bio-liquids were characterized before and after the catalytic pyrolysis process, according to the following procedures.

i. Elemental analysis

The elemental analysis was performed by LECO-Truespec according to ASTM D5291 [44]. A 50-100 mg sample was used to perform the determination of C, H, N, while oxygen content was obtained by difference. The TruSpec Add-On Module was used for the determination of Sulphur content according to an internal method. The more accurate nitrogen content was measured by Thermo Finnigan FlashEA 1112 NC analyzer, according to ASTM D4629 [45].

ii. LHV and HHV determination

HHV was determined by a LECO-AC500 calorimeter following DIN51900-2 [46]. LHV was calculated from HHV taking into account moisture and Hydrogen contents as specified in DIN51900-1 [47].

iii. Acid value and free fatty acid content

The acid value, used to assess the free fatty acid concentration in the feedstock, was evaluated as the amount (milligrams) of potassium hydroxide necessary to neutralize a mixture of the sample blended with a proper solvent (Ethanol: Diethyl ether 1:1). According to the ISO 660 [48], a manual titration is used as reference method for this analysis. The determination of free fatty acid content was verified according to EN 14104 [49]. The acid value is expressed as a mass fraction, the free fatty acid content is expressed as a percentage mass fraction.

iv. Kinematic Viscosity

Kinematic viscosity of feedstock and pyrolysis products was determined at 40°C by a LAUDA Proline PV15 viscometer, according to the reference norm UNI-EN ISO 3104 [50].

v. Water content

The water content was measured by Karl Fisher's titration according with the UNI 8534 [51] for the feedstocks. For the pyrolysis products, the water content is determined with the modified procedure proposed by Oasmaa and Peacocke [52]

vi. Macro and microelement determination

Macroelements (such as Ca, Mg and P) were measured according to UNI EN 14538 [53] and UNI EN 15290 [54] by means of ICP, IRIS Intrepid II Thermo Fisher.

vii. Total contamination

Total contamination was measured according to UNI 12662 [55], adopting a high retention glass-fibre filter of 0.7 µm (mean pore size), solubilizing the sample in n-heptane.

viii. Density

Density of liquids was measured at 15°C by a calibrated glass hydrometer according to UNI 3675 [56].

ix. Ash

Ash was determined with a Leco TGA 701 according to EN ISO 6245 by heating up to 750 °C and holding there for at least 1h 30min.

x. Insoluble impurities

Insoluble impurities was measured according to EN ISO 663 [57], adopting a Glass-fibre filtre (Whatman GF/D type, i.e. 2.7 µm mean pore size), solubizing the sample in n-hexane.

xi. Iodine number

Iodine number was measured according to procedures, reagents and calculations indicated in EN 14111 [58].

xii. Determination of fatty acid composition by GC-FID technique

The fatty acid composition of feedstock was determined by GC-FID GC 2010 Plus (Shimadzu) equipped with a HP88 column (Agilent) (length 60 m, internal diameter 0.250 mm, film diameter 0.20 µm). Transesterification was performed according to EN ISO 5509 [59]. The analysis was carried out with a column flow of 0.46 cm³ min⁻¹ at initial temperature of 120°C (holding time: 1 min) increased to 175°C (heating rate 10 min, holding time 10 min), 210°C (heating rate 5 min, holding time 28 min) and finally 230°C (heating rate 5 min, holding time 28 min). The identification of different methyl ester peaks was carried out by comparison with the retention time of the pure compounds (FAME Sigma Aldrich mix standard).

xiii. Chemical class composition by gas chromatography techniques

The composition of hydrocarbons, fatty acids and other compounds in the pyrolysis oils was measured using GC-MS and GC-FID (GC 2010 Plus-Shimadzu). Both analyses were performed using 500 mgr of sample, dissolved in 25 cm³ of isopropanol and then injected (1 mm³) in split mode; the used column was a Zebron ZB-5HT INFERNO (Phenomenex) (length 30 m, internal diameter 0.250 mm, film diameter 0.25 µm). The analysis was performed with a column flow of 2.02 cm³ min⁻¹ for GC- MS and 3.17 cm³ min⁻¹ in GC- FID with an initial temperature of 40°C (holding time 10 min) increased to 200°C (heating rate 8 min, holding time 10 min) and then to 280°C (heating rate 10 min, holding time 30 min). For GC-MS the mass to charge ratio (m/z) ranged from 35 to 550. Compounds were first identified in GC-MS by the comparison of their mass spectra with the NIST library. For quantification of specific chemical compounds in GC-FID, their response factors, relative to the internal standards o-terphenyl or D-6 benzene, were determined by using standard compounds injected in a range of concentrations that reflects those found in the samples. All standards are provided by Sigma Aldrich. Regarding the hydrocarbons standards the compound considered were n-paraffins, n-olefins, aromatics (BTEX and PAHs), As chromatograms of catalytic intermediate pyrolysis of lipid-based materials show a hump at the

central zone (at about 15-30 min), similar to diesel/gasoline chromatograms, even if less accentuated, in order to maintain a conservative approach as regards quantitative assessments of hydrocarbons in the pyrolysis oil mixture, a “valley-to-valley” integration has been performed, thus not considering the bottom area. This approach, while probably underestimating the actual amount of hydrocarbons, avoids possible interferences of unidentified chemicals with the pure peaks in the chromatogram and therefore overestimation of results.

xiv. Distillation procedure

Two samples of pyrolysis oil were analysed for a detailed investigation by separating their boiling fractions. The distillation was carried out at atmospheric pressure by a distillation rig heated with a diathermic oil bath, using a 1 kW heating plate. Distillation temperatures were selected on the basis of the most representative boiling ranges of paraffinic hydrocarbons fuels, and three different fractions were separated: A (< 150 °C); B (150 – 200 °C); C (200 – 250 °C).

4.2.4 Catalysts

Four catalysts were selected for present experimental campaign. Catalysts were bought by commercial companies, in form of pellets or spheres. The selection criteria on catalysts type was based on a review reported in precedent works [60–62]. In order to screen the best catalyst performance, a neutral, a moderate and strong acid, and a strong basic catalyst was selected. Catalysts features are shown in Table 2. Before thermochemical processing, each catalyst was maintained into the thermal reactor at 500 °C for 2 hours, under a nitrogen flow to maintain the inert atmosphere.

Table 2: Evaluation of properties of the adopted catalysts.

Product name	Catalyst	Shape	Dimensions	Acidity	Si/Al ratio	Surface area	Bulk density
-	-	-	Diameter x Length [mm]	-	-	[m ² g ⁻¹]	[kg dm ⁻³]
Gale Galicarb ESO 4	Activated carbon	pellet	4 x 2-10	Neutral			0.45
Gale GAL 501	Alumina	spheres	6-8 (diameter only)	Moderate acid		300	0.80
ACS Material H-ZSM-5	Zeolite	pellet	2 x 2-10	Strong acid	38 - 50	> 300	0.72
Tritrust MgO 99%	Magnesium oxide	pellet	3 x 6	Strong basic			

4.2.5 Experimental runs

A summary of the experimental tests is reported in Table 3. First tests were initially carried out without catalyst in order to evaluate the best conversion temperature in terms of bio-oil yield at 500 °C temperature. The first catalytic run of experiments investigated the effect of four selected catalysts on pyrolysis products, at two different catalytic reactor temperatures (i.e. 500 and 550 °C) and fixed WHSV (mass feed-to-catalyst

weight ratio) equal to 4 h^{-1} . The catalyst mass was then increased to 2.5 h^{-1} WHSV in following tests with the best performing catalyst (i.e. activated carbons). A final test was carried out with pure fatty acids and with the same configuration.

Table 3: Description of experimental activities.

Activity	Description	Feedstock	Test N.	Catalyst	Thermal reactor temperature	Catalytic reactor temperature	WHSV
n	-	-	n	-		$^{\circ}\text{C}$	h^{-1}
1	First experimental campaign	UCO	1	none	500	500	-
1.1.1.		UCO	2	Activated carbons	500	500, 550	4
1.1.2.		UCO	3	Alumina	500	500, 550	4
1.1.3.		UCO	4	H-ZSM-5	500	500, 550	4
1.1.4.		UCO	5	Magnesium Oxyde	500	500, 550	4
2	Second experimental campaign	UCO	6	Activated carbons	500	500	2.5
1.1.5.		FAs	7	Activated carbons	500	500	2.5

4.3 Results

This section reports the experimental results from the catalytic pyrolysis campaign and feedstock and products characterization.

4.3.1 Oil-based feedstock

Filtered UCO and pure FAs have been characterized in most of relevant biofuel properties. After high grade filtration (up to 1 micron), the UCO presents similar characteristics of a traditional vegetable oil (in this case a commercial sunflower oil, reported in Table 4). A batch of commercial sunflower oil was compared to filtered UCO and pure FAs. UCO viscosity is slightly higher than sunflower oil, while the water content and the contaminations are strongly reduced (by high grade filtration) from the original feedstock (analysed in D2.3) to comparable values of traditional vegetable oils. Ca, Mg and P content are even under DIN 51623, and there are no other significant changes compared to traditional sunflower oil. A relevant difference is observed on the acid values: while UCO and vegetable oils may contain a small fraction of free fatty acids, pure fatty acids are in the range of about $200 \text{ mg}_{\text{KOH}} \text{ g}^{-1}$ (for vegetable oils the fatty acid content can be estimated equal to half than the acid value, according to Knothe and Steidley [10]).

Table 4: Analytical analysis on feedstock .

Parameter	Unit	Method	Sunflower oil	UCO filtered at 1 μm	Pure FAs
Density	kg m^{-3}	UNI EN ISO 3675	920	911	
Kinematic Viscosity at 40 °C	$\text{mm}^2 \text{s}^{-1}$	UNI EN ISO 3104	27.84	38.15	18.03
Acid value	$\text{mg}_{\text{KOH}} \text{g}^{-1}$	UNI EN 14104	7.2	2.63	201.7
Free Fatty Acid	wt%	ISO 660	3.6	1.31	100.85
Iodine Number	$\text{g}_{\text{Iodine}} 100\text{g}^{-1}$	UNI EN 14111	118	93	
Water content	wt%	UNI EN ISO 8534	0.125	0.080	0.08
Ash	wt%	UNI EN ISO 6245	0	0.01	
Total contamination	mg kg^{-1}	UNI EN 12662	206.3	256	68
Insoluble impurities	wt%	ISO 663	0.01	0.05	
Sulphur	mg kg^{-1}	Internal method	52	0	
Calcium	mg kg^{-1}	UNI EN 14538	39.51	0	
Magnesium	mg kg^{-1}	UNI EN 14538	3.17	0.22	
Phosphorus	mg kg^{-1}	UNI EN 15290	8.075	10.1	
C	wt%	ASTM D 5291	76.5	76.3	76.3
H	wt%	ASTM D 5291	11.3	11.7	12.2
N	wt%	ASTM D 5291	0.33	0.02	0.02
N	mg kg^{-1}	ASTM D 4629	116	137	
O	wt%	Calculated	11.87	11.98	11.48
Calorific value, higher	MJ kg^{-1}	DIN 51900-2	39.32	38.91	39.4
Calorific value, lower	MJ kg^{-1}	Calculated	36.92	36.43	36.8

Fatty acids profile of both feedstock were investigated by GC techniques. While for UCO the analysis represents a traditional fatty acid profiles as well as vegetable oils, for pure fatty acids it consists on a full-composition analysis due to absence of glycerol. As regards Table 5, UCO is mainly composed by palmitic, oleic and linoleic acid (15, 43 and 34 wt% respectively), while pure fatty acid are mainly composed by oleic acid (i.e. about 62 wt%) and small fractions of other fatty acids, due to its olive oil original nature.

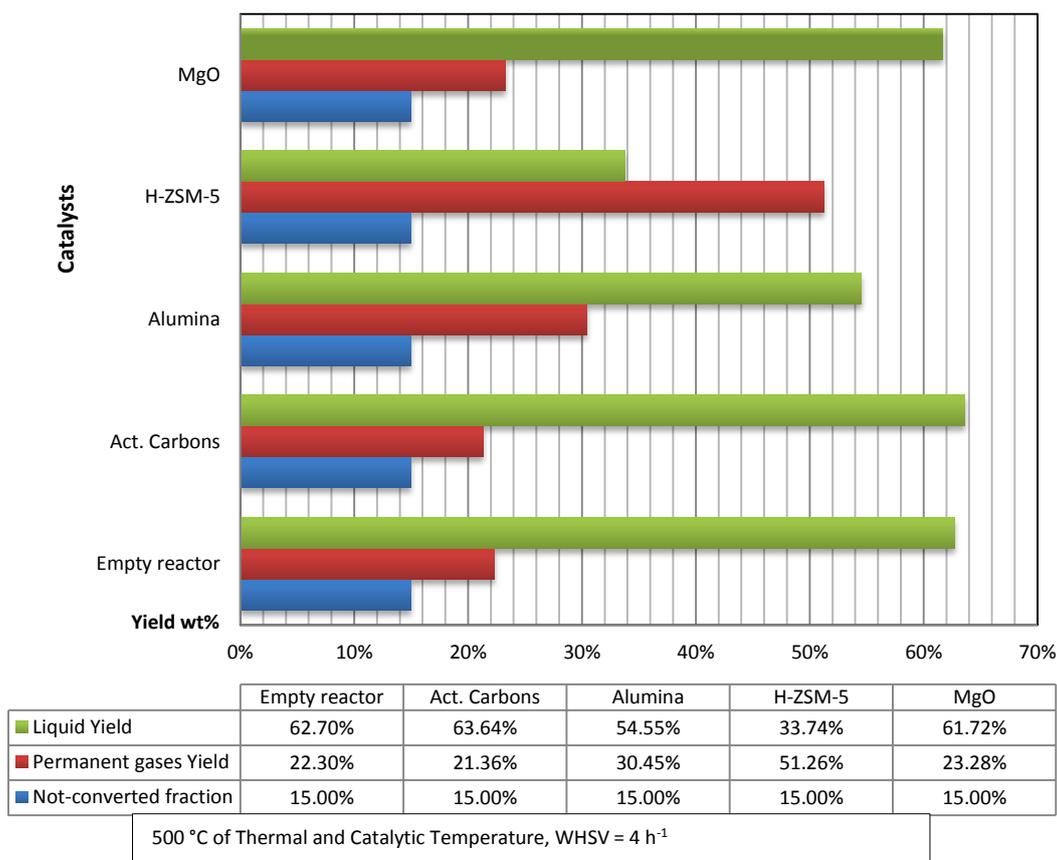
Table 5: Fatty acids profile of adopted feedstock.

Fatty acids	Chemical structure	UCO	Pure FAs
-	-	wt%	wt%
Lauric	C12:0	0.09	2.83
Mystiric	C14:0	0.40	1.43
Palmitic	C16:0	15.11	4.03
Stearic	C18:0	3.96	1.17
Oleic	C18:1	43.43	61.81
Linoleic	C18:2	33.93	13.47
Linolenic	C18:3	0.34	0.38
Erucic	C22:1	0.00	6.41
Others	-	2.75	8.47

4.3.2 Results from first experimental campaign

The process temperature for the first step of pyrolysis was selected by precedent tests. The temperature of 500 °C was selected as the most performant in terms of bio-oil yield (i.e. empty reactor test). Once the thermal reactor temperature was fixed, eight tests (four catalysts, tested at 500 and 550 °C into catalytic reactor) were performed. Tests conducted at 550 °C led to the formation of higher fractions of non-condensable gases against lower fraction of bio-oil, thus the following investigation of products was carried out at constant 500 °C in both pyrolysis steps.

Table 6: First run yields of catalytic campaign at 500 °C.



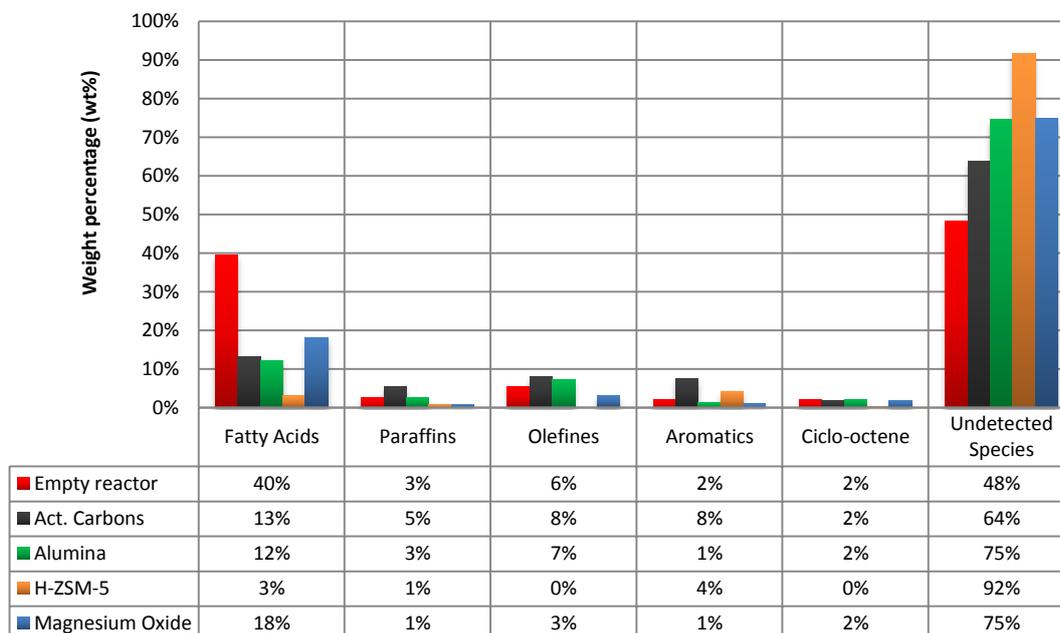
Depending on the catalyst type, products present different characteristics, in terms of products yields (Table 6) as well as in chemical and physical properties of bio-oils. Bio-oils are collected in the range from 33.74 to 63.64 wt%, depending on catalyst, and the unconverted fraction collected at the end of each test is about 15 wt% of total feed (because catalysts aging on pyrolysis vapours). This leads to estimate the permanent gas yield by difference, that is minimized in test with activated carbons (21.36 wt%), favouring the maximization of bio-oil collected. The characteristics of bio-oils are shown in Table 7. From elemental analysis emerges that the overall deoxygenation grade is lower than expected, but significant changes are observed in the chemical composition as shown in GC analysis. Water content is higher in test with zeolite, where the produced reaction water is probably caused by the higher grade of cracking, which led the production of larger amount of permanent gases. Density is reduced up to 0.85 kg l⁻¹ in all tests, and more significantly the viscosity values were reduced in the range of 5.68 - 1.19 cSt, close to fossil fuel parameters (e.g. 0.845 kg l⁻¹ and 4.5 cSt as density and viscosity limits for road Diesel fuel according to UNI EN 590:2010). Acid value is strongly increased due to FFAs content and other acidic compounds derived from catalytic cracking of triglycerides molecules (probably carboxylic acids). The catalytic effect produced high values of acidity in bio-oils, ranging from 117.73 (test without catalyst) to 20.45 (test with H-ZSM-5). Finally the measured heating value is slightly higher than original feedstock despite the CHNO content was approximately maintained constant.

Table 7: Analysis on bio-oil quality for each catalytic test.

Parameter	Unit	Norm	Empty reactor	Act. Carbons	Alumina	H-ZSM-5	MgO
C	wt%	UNI 15104	76.75	76.10	76.03	77.90	78.17
H	wt%	UNI 15104	11.45	11.10	11.65	10.10	11.48
N	wt%	UNI 15104	0.02	0.03	0.08	0.07	0.03
O	wt%	calculated	11.98	12.77	12.25	11.93	10.33
Water content	wt%	UNI 8534	0.89	0.77	1.18	8.36	1.61
Acid value	mg _{KOH} g ⁻¹	UNI 14104	117.73	74.10	61.97	20.45	80.07
Density	Kg dm ⁻³	UNI 3675	0.87	0.85	0.85	0.90	0.86
Kinematic viscosity (40°C)	cSt	UNI 3104	4.47	2.24	3.36	1.19	5.68
LHV	MJ kg ⁻¹	calculated	36.82	37.79	39.57	36.48	37.46
HHV	MJ kg ⁻¹	DIN 51900-2	39.25	40.14	42.02	38.55	39.95

A detailed identification and quantification of the chemical species contained into bio-oil has been carried out following the procedure in Paragraph 4.2.3 and reported in Table 8. Essentially, this table shows the most significant chemical species for biofuels contained into bio-oil, in particular the hydrocarbons fraction and FFAs produced for each test.

Table 8: Composition of bio-oil fractions on first run tests analyzed by GC MS/FID.



In this case, the GC-MS analysis is adopted to identify the chemical species and then, the GC-FID is aimed to quantify the fraction of detected compounds (mainly hydrocarbons and FFAs) which are identified by means of internal standards of the instrument (Shimadzu GC 2010 plus). A large amount of unidentified classes such as oxygenated compounds (e.g. ketones, aldehydes, carboxylic acids and esters [35]), other free radicals from cracking reactions and polymerized products are not detectable by this method. The

interest mainly goes towards hydrocarbons classes such as paraffins, olefins and aromatics, and their distribution into each sample of bio-oil. Moreover, the FFAs content indicates the conversion grade obtained by the catalytic upgrading of vapours due to the effect of catalysts, that favours secondary reactions (e.g., decarboxylation, decarbonylation, aromatization, cyclization, hydrogenation) according to scheme proposed by Idem at al. [39] for the catalytic conversion of canola oil. From non-catalytic reference test, the FFAs content into bio-oil is 40 wt%, which has been strongly reduced after each catalytic tests. The test with H-ZSM-5 (i.e. 3 wt%) as catalyst the 92 wt% as the sum of undetected species, maybe due to high grade of cracking that leads the production of a large amount of undetectable species. Other catalytic tests show promising results in terms of hydrocarbon content, in particular the bio-oil from activated carbons test contains the 23 wt% as the sum of detected hydrocarbons, which is the highest. Except the test with zeolite, all tests indicate the presence of 2 wt% of ciclo-octene. From these results, activated carbons test was selected for a following run at $WHSV = 2.5 \text{ h}^{-1}$, i.e. increasing the catalyst mass and maintaining the other process parameters unchanged.

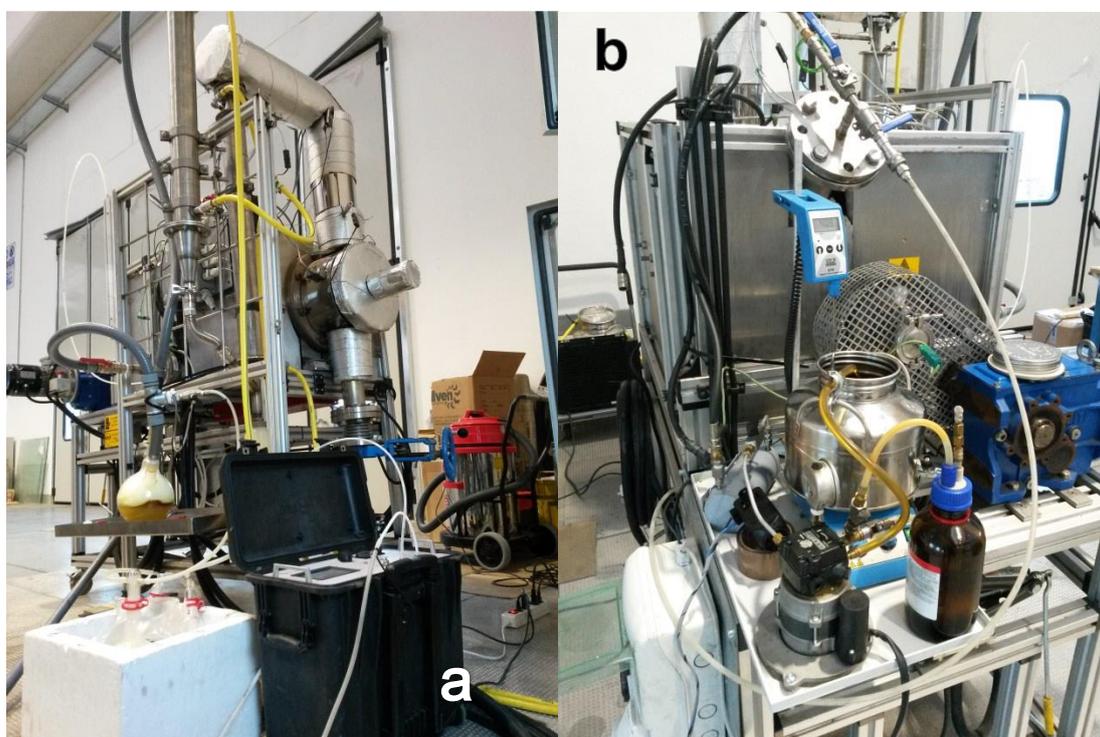


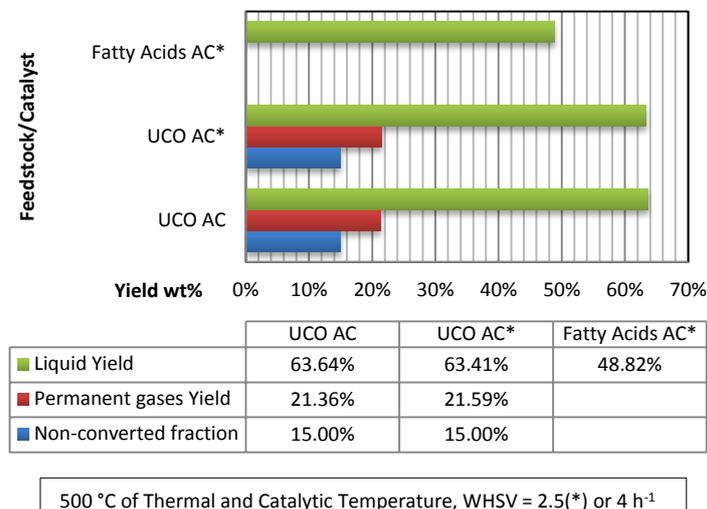
Figure 9: (a) back view of the reactor and condensation system during experimental campaign; (b) bioliquid feeding system during operation.

4.3.3 Results from second experimental campaign

The identification of the best catalyst performance was deeply investigated by increasing the catalyst mass up to $WHSV = 2.5 \text{ h}^{-1}$ (i.e. test with activated carbons, AC*), maintaining the same temperature and the other parameters of last experiments. Two tests were carried out: first maintaining the filtered used cooking oil as feedstock, and then testing the most performant catalytic effect on pure fatty acids. In terms of products yields, used cooking oil test with increased activated carbons mass (UCO AC*, Table 9) achieved the same

products quantities as the previous test, while pure fatty acids processing converts about 50 wt% into bio-oil fraction (non-converted fraction and permanent gases yields were not measured).

Table 9: Second run yields of catalytic campaign. UCO AC test consists in precedent test reported in Table 6. Asterisk (*) means tests carried out with increased catalysts mass.



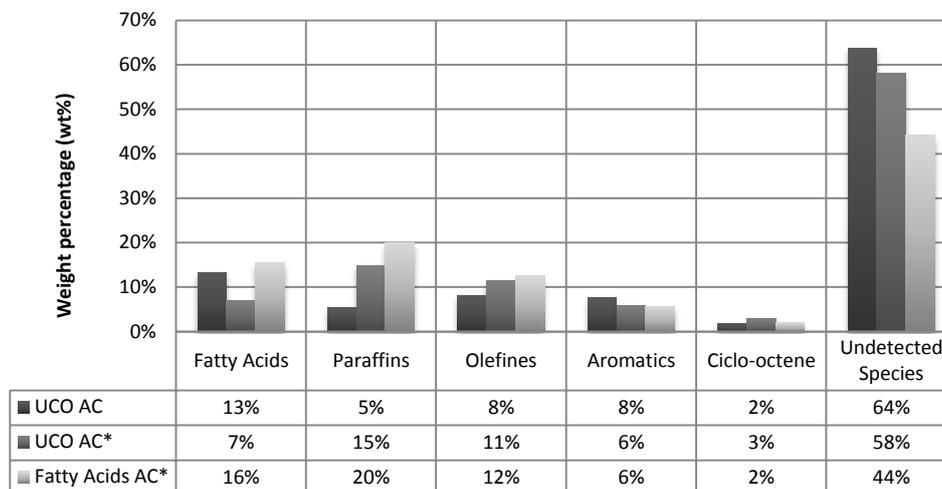
Significant results were obtained by elemental analysis as shown in Table 10. Despite the oxygen content of UCO AC run is approximately maintained constant, compared to previous tests, relevant differences are observed in terms of produced hydrocarbon fractions. No other significant changes are observed except a reduced acid value. Relevant results are obtained in pure fatty acid test: from the original feedstock to bio-oil, the deoxygenation grade reached the 67.5 wt% (from 11.48 to 3.73 wt% of oxygen content) and consequently, viscosity is reduced and heating value considerably increased. The importance of oxygen reduction corresponds to higher hydrocarbons fractions detected by GC analysis.

Table 10: Analysis on bio-oil quality for catalytic tests at reduced WHSV. UCO AC test consists in precedent test reported in Table 6. Star (*) means tests carried out with increased catalysts mass.

Parameter	Unit	Norm	UCO AC	UCO AC*	FAs AC*
C	wt%	UNI 15104	76.1	76.3	83.53
H	wt%	UNI 15104	11.1	11.50	12.7
N	wt%	UNI 15104	0.03	0.04	0.04
O	wt%	calculated	12.77	12.17	3.73
Water content	wt%	UNI 8534	0.77	0.54	0.17
Acid value	mg _{KOH} g ⁻¹	UNI 14104	74.1	51.45	44.4
Density	Kg dm ⁻³	UNI 3675	0.85	0.84	
Kinematic viscosity (40°C)	cSt	UNI 3104	2.24	2.48	1.5
LHV	MJ kg ⁻¹	calculated	37.79	38.9	40.1
HHV	MJ kg ⁻¹	DIN 51900-2	40.14	41.34	42.79

The following table shows the results of GC analysis, which also compared with previous test corresponding results.

Table 11: Composition of bio-oil fractions on second run tests analyzed by GC MS/FID. UCO AC test consists in precedent test reported in Table 6. Asterisk (*) means tests carried out with increased catalysts mass.



Increasing the catalyst mass on UCO test, the FFAs content is reduced in favour of higher paraffinic and olefinic hydrocarbons fraction, respectively from 5 to 15 wt% and from 8 to 11 wt%. However, the aromatic fraction is reduced from 11 to 8 wt%, while the ciclo-octene content is slightly increased up to 3 wt%. It appears that larger paraffins and olefins content into bio-oil is favoured by decarboxylation and decarbonylation reactions occurred by longer residence times of the hot vapours into the catalyst reactor. Despite the lower liquid yield, pure fatty acid test results in higher paraffins and olefins fractions, with a higher overall detected hydrocarbons content (from 35 wt% for UCO AC* to 40 wt% for FAs AC*). In this case their higher fraction of total hydrocarbons is probably caused by the easier removal of carboxylic group from fatty acids molecules, due to absence of glycerol into feedstock.

Figure 10 shows the UCO AC* spectrum from GC FID analysis, that identifies the nature of hydrocarbon classes. In particular, higher peaks consist in paraffinic hydrocarbons and the last lower intensity peaks consist in higher molecular weight compounds (in this case FFAs), that are strongly reduced by increasing catalysts mass. The detected higher peaks consist in paraffinic hydrocarbons in the range of C7 - C11 and C15, which are probably formed by the deoxygenation reaction of palmitic and oleic acid (respectively C16:0 and C18:1). In this case, the desired cracking reactions (i.e. decarboxylation) occurred in the proximity of the carboxyl group (C17 and C15) or where the double bond is located along the chain of the fatty acid (from C7 to C10).

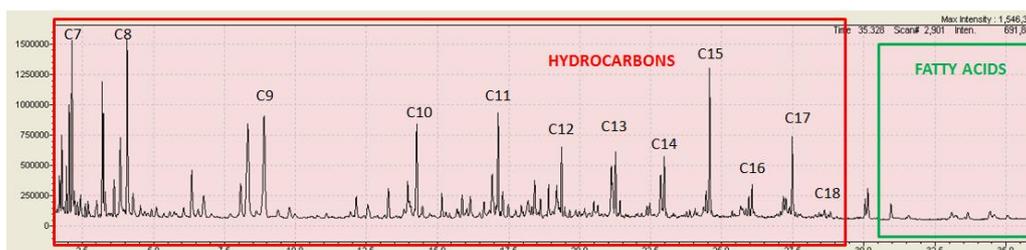


Figure 10: GC-FID spectrum from UCO AC* test.

Comparing the range of detected hydrocarbons with traditional fossil fuels, the fraction between C8 and C12 takes interest in the production of renewable jet fuel, while the heavier and lighter fractions can be evaluated as gasoline and diesel-range fuel. However, a large fraction of undetected oxygenated compounds were detected into bio-oil, thus the separation of hydrocarbons from the other chemical classes represents the next challenge.

4.3.4 Investigation of unidentified fraction of bio-oil

After the experimental campaign, RE-CORD and NESTE worked together to a more detailed characterization of bio-oil samples. In particular, the bio-oil sample from UCO, produced at 500 °C of pyrolysis temperature and 2.5 h⁻¹ of WHSV, was selected as the most representative for further investigation. NESTE received 0.5 litre sample of bio-oil from RE-CORD laboratory and focused the analysis to identify the unidentified fraction from GC MS/FID. Here following the analysis performed by NESTE: GPC (UNI EN ISO 16931 (CEN. Animal and vegetable fats and oils - Determination of polymerized triacylglycerols by high-performance size-exclusion chromatography HPSEC) and ESI MSMS techniques were performed to investigate the presence of glycerides-based compounds: TriAcylGlycerides (TAG), DiAcylGlycerides (DAG), MonoAcylGlycerides (MAG), oligomers. GPC detect also free fatty acids (FFA).

The results GPC analysis (Table 12) show the overall size distribution of these molecules in the sample as area% including also compounds with similar molecular weight to those investigated, such as oxidized or oligomerized lipids.

Table 12: GPC results.

Compound	Area%
TAG	4.7
DAG	16.3
MAG	8.7
FFA	69.6
OLIGOMERS (larger then TAG)	0.7

GPC analysis shows that there are only 0.72 % (area-% of the chromatogram) oligomers, which are identified in the range of C22:0-C50:0. In addition, quite a large number of the components identified as being the size of TAG, DAG or MAG could be actually something else: other lipid species, oxidized lipids or oligomerized lipids. The ESI-MSMS analysis (Table 13) gives the actual amounts of MAG, DAG and TAG, which are in total less than 0.7 wt%.

Table 13: ESI-MSMS results.

Compound	wt%
TAG	≤ 0.4
DAG	≤ 0.3
MAG	0.0

In order to determine an approximate content of hydrocarbons, another set of GPC analyses was performed after two solid phase extraction (SPE-GPC).

Two different SPE cartridges (NH₂ and Si) were adopted to characterize the “neutral lipids” and FFA fraction (including all acidic components classified as “polar lipids”). Neutral lipids was then fractionated to separate the pure hydrocarbons. The three fractions were then analysed by GPC giving the results shown in Table 14, which are semi-quantitative, derived from analytical standards, and affect by a relevant error of 15-20%. The estimation of the polar components is calculated by difference.

Table 14: SPE-GPC results.

Fractions	%
Hydrocarbons	≈20
Neutral fraction	≈20
Free fatty acids	≈15-20
Polar fraction by difference	≈40

According to these data only a small amount of glycerides was detected in the sample, even if GPC suggest the presence of glyceride sized components, probably other oxygenated lipid species, which are not detected by ESI MSMS. The SPE-GPC identified different fractions of the sample, hydrocarbons, neutral lipids and polar lipids and give an estimation of their distribution in the sample.

GPC or the ESI-MSMS are not able to detect hydrocarbons: they only measure the lipid-type components, so the size distribution is only for the lipid part of the sample. GPC analysis is also used in NESTE labs to measure the total lipid content of samples. It is not as accurate as GC-MS analysis, because length of the fatty acids has a limited effect on the results. So the total oil content of bio-oil sample is 64 wt%, according to the GPC measurement. The remaining part, approximately 36 wt%, is close to 35 wt% of total hydrocarbons content, detected by GC MS-FID at RE-CORD lab, and reported in the precedent paragraph.

A final GC-simulated distillation [63], was performed to define the boiling point distribution of the total sample. According to 76 wt% of bio-oil sample, this fraction has carbon number less than C24-C26, while 90 wt% fraction, less than C40-C42. It seems that GPC/ESI-MSMS analysis gives too low figure for these heavier components, because they are not anymore fatty material, but hydrocarbons.

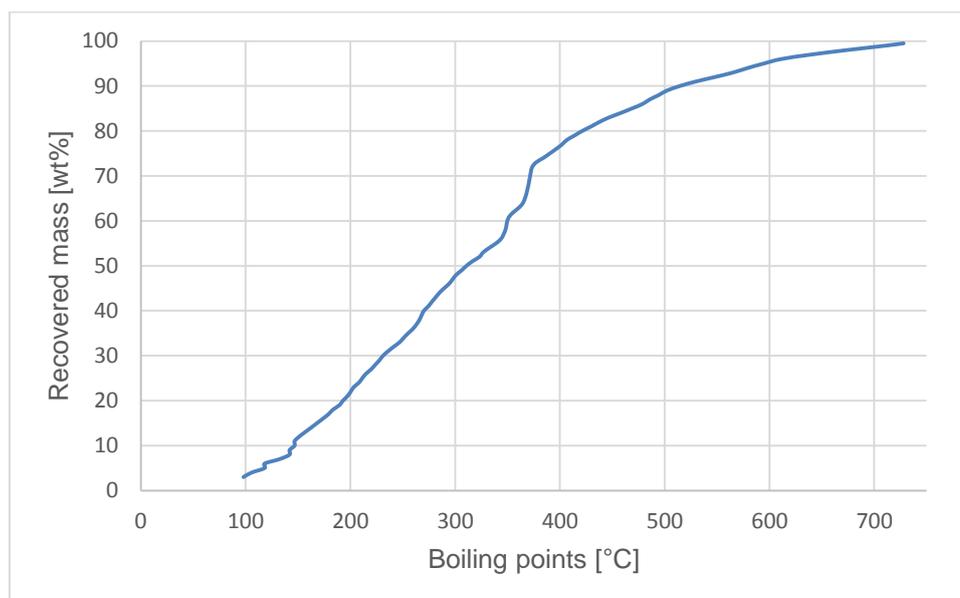


Figure 11: GC-simulated distillation.

4.3.5 Discussion

Bio-hydrocarbons fractions were produced and detected. However, a relevant oxygenated lipid-derived fraction was generated during catalytic cracking of pyrolysis. The best results, achieved with activated carbons as catalyst, suggest a detailed investigation on other process parameters, such as temperatures and WHSVs, to improve the bio-oil quality in terms of hydrocarbons and reduce the lipid-derived fraction. Moreover, the small scale of experiments generates lower yields which can be improved by scaling up the process.

The author studied the energy requirements for pyrolysis process of triglycerides [60]: assuming the industrial scale of the process, it can be theoretically self-sustained adopting the 72% of the heat generated from the combustion of the non-condensable gases.

Moreover, the evaluation of commercial process of hydrotreating could be an opportunity to upgrade the bio-oil in order to deoxygenate the lipid-derived species, The implementation of catalytic pyrolysis into an existing biorefinery could be considered an opportunity in terms of reduced hydrogen demand than the current HEFA process. Moreover, once assessed the true nature of the bio-oil, some fraction could be also evaluated for chemicals production.

5 Development of UCO specifications

On the basis of the acquired experience during the experimental campaign of catalytic pyrolysis, a preliminary filtration of UCO before processing does not affect the process functioning. However, the small scale of experiments and their short duration, suggest further investigation to understand the true nature of bio-oil and the effect of UCO on catalysts. Hydrotreating requires high quality catalysts due to presence of noble metals [64], less tolerant to irregularly contaminated feed as UCO. In addition, the same catalysts adopted for vegetable oil conversion, could be not effective changing some properties of feedstock, Next paragraph investigates on the effect of catalysts deactivation and HVO properties when used cooking oils or fatty acids are processed. The investigation of the constraints and barriers for their use will give further detail to investigate the required quality of feedstock. Finally, a proposal of UCO specification is carried out.

5.1 Hydrotreating barriers and constraints

The role of catalysts is crucial in the production of high grade jet fuels from vegetable oils [65]. Catalysts based on Ni and Mo supported on oxides are considered very active for the hydrotreating process whereas Pd and Pt supported on zeolites are the most adopted hydro-isomerization catalysts. The mechanisms of catalysts deactivation are numerous and complex [66], but their understanding permit to have fundamental information on the quality of feedstock.

The impact of hydrotreating products originating from heteroatoms (mainly H₂S, NH₃ and water from S, N and O initial content of feedstock) on the catalyst activity and selectivity was deeply studied [67]. It has been shown that ammonia strongly inhibits both hydrodeoxygenation and (hydro)decarboxylation reactions. Water has less effect on this side. In contrast, hydrogen sulphide promoted deoxygenation of esters over both NiMo and CoMo catalysts [67].

Kubicka and Horáček [68] investigated the catalytic deoxygenation of different rapeseed-oil-derived feedstocks (i.e. used cooking oil) over sulfided CoMo catalyst, at 310 °C of process temperature and 3.5MPa (H₂ pressure), in a fixed-bed reactor, aiming at description of parameters affecting the catalyst deactivation. Presence of alkalis promoted catalyst deactivation due to their deposition on catalyst surface leading to blockage/poisoning of active sites. The effect of phosphorus content was two-fold: when charge-compensating alkalis were present, corresponding phosphates were deposited above and at the beginning of catalyst bed leading to gradual build-up of deposits. On the other hand, in absence of alkalis decomposition of phospholipids yielded phosphoric acid that catalysed oligomerization reactions leading to rapid catalyst deactivation by carbonaceous deposits. Presence of sulphur compounds, here demonstrated by addition of dimethyldisulfide (DMDS), was shown to be beneficial for the catalyst deoxygenation performance. While in absence of DMDS gradual deactivation was observed, addition of DMDS resulted in a stable catalyst performance. The changes in active sites structure caused by their desulfurization under hydrogen atmosphere were shown to be partially reversible. Nonetheless, part of the active sites was irreversibly lost. In addition to modifying catalyst activity, H₂S formed by DMDS decomposition, influenced significantly the selectivity of deoxygenation reactions. The presence of H₂S resulted in an augmented (hydro)decarboxylation catalyst selectivity plausibly owing to the increased catalyst acidity.

Bezergianni et al [69] studied the effect on HDT catalysts for waste cooking oil, conducting the process in a temperature range of 330–390 °C, under constant LHSV (1 h^{-1}) and a range of pressure 8.27–13.79 MPa. As typical hydrotreating catalyst, HDT showed a drastic activity on heteroatoms removal: sulphur from 27,200 to 71.8 ppm, and nitrogen from 219.8 to 0.59 ppm (starting values were high due to presence of additives, such as DMDS, to regulate the catalyst activity).

The effect of feedstock acidity in hydrotreating was also tested: Simakova et al [70] investigated the catalytic deoxygenation of palmitic and stearic acids mixture over four synthesized Pd catalysts supported on synthetic carbon (Sibunit) in a semi-batch reactor and dodecane as a solvent at 260–300 °C. The main liquid phase products were heptadecane and pentadecane, and an optimum Pd dispersion was found. The same authors [71] tested five different fatty acids, C17–C20 and C22, as in a semibatch reactor over 1 wt% Pd/C (Sibunit) catalyst. The same decarboxylation rates were obtained for pure fatty acids, whereas extensive catalyst poisoning and/or sintering and coking occurred with low purity fatty acids as reactants. One reason for catalyst poisoning using behenic acid (C22) as a feedstock was its high phosphorus content (266 mg kg^{-1}). The decarboxylation rate of fatty acids decreased also with increasing fatty acid to metal ratio. The catalytic hydroconversion of C18 fatty acids was also tested for the production of iso/n-paraffins at different temperature, WHSV, pressure and H_2 /oil ratio [72] and evaluating the performance of different hydrogen donors (H-donors) [73] than pure hydrogen. Hengst et al [74] tested the gas phase deoxygenation of oleic acid over palladium containing acidic catalysts under solvent-free condition, with a selectivity of diesel fraction up to 90% using 1wt% Pd/Siral70 as catalyst, at 350 °C, WHSV of 1.85 s^{-1} and a H_2 pressure of 15 bar.

So the use of hydrogen is fundamental to promote the deoxygenation of fatty acids, but selecting the most effective catalyst at the optimum reaction conditions, a high quality product can be obtained. Na et al [75] tested the decarboxylation of oleic acid without hydrogen using hydrotalcites, where the effect of MgO content in hydrotalcites and reaction temperatures on the decarboxylation performance in terms of oleic acid conversion and product distribution were investigated. However, in this case, the absence of hydrogen does not favour the removal of other heteroatoms contained into initial feedstock. Oleic acid conversions were more than 98% and the oxygen content in the reaction product was less than 1wt% in the case of decarboxylation with catalysts at MgO content of 63 and 70 wt%, at 673 K.

A possible pathway to

5.2 A proposal for UCO specifications

On the basis of the feedstock requirements for catalytic pyrolysis, but more in detail, for the use of alternative lipid-based feedstock in hydrotreating (such as UCO), a proposal of UCO specification was carried out. This list includes limits and barriers related to filtered UCO its thermochemical processing. DIN 51623 [8] was adopted as guideline for some parameters. The following table shows the proposal of UCO specifications.

Table 15: Esterified UCO analysis (methods of analysis are described in 4.2.3).

Parameter	Unit	Method	ITAKA UCO specifications	UCO filtered at 1 μm
Density	kg m^{-3}	UNI EN ISO 3675	900 - 930	911
Flashpoint	°C	DIN EN ISO 2719	> 220	

Cetane Number	-	DIN EN 15195	> 39	
Kinematic Viscosity at 40 °C	mm ² s ⁻¹	UNI EN ISO 3104	< 40	38.15
Acid value	mgKOH g ⁻¹	UNI EN 14104	0 - 200	2.63
Free Fatty Acid	wt%	UNI EN ISO 660	0 - 100	1.31
Iodine Number	g Iodine 100g ⁻¹	UNI EN 14111	< 125	93
Water content	wt%	UNI EN ISO 8534	< 0.2	0.080
Ash	wt%	UNI EN ISO 6245	< 0.01	0.01
Total contamination	mg kg ⁻¹	UNI EN 12662	< 180	256
Sulphur	wt%	Internal method	< 0.001	0
Calcium	mg kg ⁻¹	UNI EN 14538	< 1	0
Magnesium	mg kg ⁻¹	UNI EN 14538	< 1	0.22
Phosphorus	mg kg ⁻¹	UNI EN 15290	< 3	10.1
C	wt%	ASTM D5291		76.3
H	wt%	ASTM D5291		11.7
N	mg kg ⁻¹	ASTM D 4629	< 100	137
O	wt%	calculated		11.98
Calorific value, higher	kJ kg ⁻¹	DIN 51900-2	> 36,000	38.91

- Density, Iodine number, Ca and Mg content, calorific value: no significant difference were measured in UCOs compared to vegetable oils, once it was filtered and water content removed. The UCO specifications maintained the same limits of vegetable oils as fuel (DIN 51623).
- Flash point and Cetane number: despite the UCO samples was not investigated in flash point and Cetane number, the limits are maintained the same as DIN 51605, a less severe limits than DIN 51623.
- Kinematic viscosity at 40 °C: 40 cSt was selected as limit for kinematic viscosity. The measured value in filtered UCO (about 38 cSt) was sufficient to process the UCO in catalytic pyrolysis and probably, in hydrotreating.
- Acid value and free fatty acid: as investigated in precedent paragraph, a large number of experiments were performed with pure fatty acids as feedstock for hydrotreating. Moreover, the catalytic pyrolysis tests showed an improved deoxygenation than the tests with UCO. No limits of FFAs content were assumed for UCO specifications (and the correlated acid value).
- Water content: a more tolerant 0.2 than 0.075 wt% (DIN 51623) was selected as limit for moisture content into filtered UCO. This value can be easily carried out by paper filtration.
- Ash: despite ash content is not present in traditional vegetable oils, the contamination of UCO can increase its content. A conservative limit of 0.01 wt% was adopted to preserve catalysts selectivity.
- Total contaminations: during D2.3 experimental activities, an high grade filtration reduced the solid impurities (up to 0.8 micron, according to UNI EN 12662) under 180 ppm. For this reason, a limit of 180 ppm was selected as suitable before UCO thermochemical processing.
- S, P, O, N content: the removal of heteroatoms content by means of the use of hydrogen is possible during hydrotreating. However, as reported in precedent paragraph, their presence could affect the process. DIN 51623 limits were assumed also for UCO specifications. Despite N and P content of filtered UCO was above these limits, the catalytic pyrolysis process was not affected by their

contaminations. Considering the hydrotreating process, depending of catalysts adopted, further study to assess these limits are necessary.

- Metals: the presence of metals content has to be reduced to avoid catalysts deactivation due to poisoning. DIN 51623 limits were also assumed for these specifications (even for K and Na content, above 1 ppm).

6 Conclusions

The chance to recycle a waste, such as used cooking oils, for aviation renewable fuel production represents a promising opportunity for greening the sector. Several samples of raw UCO were collected, analysed and evaluated in their relevant properties as feedstock for commercial hydrotreating process of vegetable oils (D2.3). Raw UCO needs to be filtered and upgraded before its use as feedstock for thermochemical processing. Esterification of UCO was considered as upgrading treatment: three samples of esterified UCO were analysed and investigated as potential feedstock. However, thermochemical bio-hydrocarbons production can be also carried out from pure fatty acids, thus esterification of UCO was not considered. High grade filtration reduced contaminants and water content of raw UCO, restoring a large number of properties to initial values of vegetable oils.

An experimental investigation on catalytic and non-catalytic pyrolysis of filtered used cooking oil (UCO) and pure fatty acids (FAs) was necessary to investigate on UCO requirements as feedstock. It aimed also at developing a preliminary screening and understanding of the process and catalysts, focusing on lipid conversion to hydrocarbon. Representative batches of UCOs and FAs were opportunely filtered and characterized. Four catalysts were selected and tested at 500 °C of process temperature and 4 h⁻¹ of WHSV in a 1.5 kg h⁻¹ pilot catalytic pyrolysis unit. The evaluation of bio-oils properties and gas chromatographic investigation on produced hydrocarbons indicated that, by selecting the most appropriate catalyst (activated carbons) and process parameters, deoxygenation (decarboxylation) can be performed through catalytic pyrolysis without hydrogen addition.

An improved experimental campaign by increasing catalyst mass (at 2.5 h⁻¹ of WHSV) produced about 63 wt% of bio-oil (from UCO) containing the 35 wt% of hydrocarbons, and 49 wt% of bio-oil (from FAs) containing 40 wt% of hydrocarbons. A large fraction of undetected species was found into bio-oils samples, thus RE-CORD, in close collaboration with NESTE, selected the most suitable blend for the production of bio-kerosene. Numerous analysis were performed on the best selected samples to identify the contained chemical species: a mixture of lipid-derived species.

The developed process, which was demonstrated that is theoretically self-sustained, integrates the concept of biorefinery including the commercial process of the hydrotreating of vegetable oils (HEFA) to upgrade the bio-oil, with an overall reduction in terms of hydrogen demand. The experience on the analysis of UCOs and bio-oil samples, together with NESTE and literature data on hydrotreating process, permitted to identify the critical parameters of UCO as feedstock for thermochemical processing. A proposal of UCO specification was finally carried out.

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