

# ITAKA

Collaborative Project

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## D2.3 Report describing the main barriers to innovation and recommendations for further research

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## **Executive summary (it can be used for dissemination purposes)**

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 describes, in the context of the use of used vegetable oil (UCO) as renewable feedstock for the development of drop-in renewable aviation fuels, the main barriers to innovation and recommendations for further research. UCO has been collected (with the support of an Italian company), and analysed. The typical parameters normally examined in vegetable oils (according to DIN 51605) were evaluated and compared with commercial vegetable oils. Main critical parameters are Nitrogen and Phosphorous content, total contamination, acidity and moisture content. Strategies to upgrade the UCO as feedstock for biofuel production were examined. An investigation on the Nitrogen source of commercial vegetable oil suggest that N is located into the solid residual from oilseed squeezing, confirmed by filtration. The results achieved on UCO show an important reduction of Nitrogen and Phosphorous content with a high quality filtration. Despite the achieved improvements, the Nitrogen content of UCO still remains higher than commercial vegetable oils.

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## Abbreviations

UCO: Used Cooking Oil

WCO: Waste Cooking Oil

ILUC: indirect Land Use Change

GHG: Green House Gas

LCA: Life Cycle Analysis

RED: Renewable Energy Directive

Bio-SPK: Bio-Derived Synthetic Paraffinic Kerosene

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

RENEWABLE JET FUEL: a jet fuel derived from biomass.

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

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.

HYDROPROCESSING: 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.

LCA: Life Cycle Assessment accounts the inflows and outflows “from cradle to grave”: this is from the extraction, manufacturing, consumption, recycling to the finale disposal.

EU ETS: European Union Emission Trading Scheme.

ILUC: The Indirect Land Use Change impacts of biofuels, relates to the unintended consequence of releasing more carbon emissions due to land-use changes around the world induced by the expansion of croplands for ethanol or biodiesel production in response to the increased global demand for biofuels.

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.

## 1 Introduction

The role of used vegetable oil (UCO) as renewable feedstock was investigated in order to identify the main barriers that could limit its use as feedstock in aviation, and make recommendations for future innovation and research to solve them. UCO is used vegetable oil where the cooking process significantly modifies some properties, thus its adoption as feedstock for thermochemical upgrading or even as biofuel is not as simple as for the pure vegetable oils. Chemical and physical parameters must be monitored before using this feedstock in existing infrastructures. In the framework of the ITAKA project, RE-CORD focused its activity on the investigation of the UCO properties and its conversion through an experimental thermochemical process, where the main product would be an intermediate biofuel component suitable for further refining (e.g. hydrotreating).

An investigation on the quality of the aviation fuels and the commercial and experimental pathways to reach a drop-in fuel was carried in chapter 2. In the following chapters the study focused on UCO properties and its main characteristics versus the DIN 51605 norm, i.e. the current standard of pure vegetable oils for road transport. In general, hydrotreating requires an accurate monitoring of the feedstock composition to control the interactions between catalysts and feedstock. The adoption of UCO as feedstock instead of vegetable oils could be crucial, thus key parameters such as density, acidity, iodine value, contaminants, Phosphorus, Nitrogen and moisture content were investigated and compared with norms.

Table 1: Comparison of norms adopted in UCO analysis.

Density	EN ISO 12185 (at 50°C)
Density	UNI EN ISO 3675
Free Fatty Acids	ISO 660
Acid value	UNI EN 14104
Iodine value	UNI EN 14111
Iodine value	UNI EN ISO 3961
Total contamination	UNI EN 12662
Insoluble impurities	UNI EN ISO 663
Phosphorus	ASTM 5185
Phosphorus	UNI EN 15290
Water content	ISO 8534
Moisture & Volatile	ISO 662 (method B)
Nitrogen	ASTM D5291
Nitrogen	ASTM D4629

UCO samples were collected in collaboration with the Italian company SILO SpA. A significant variability of the chemical parameters due to changes in composition of used frying oil samples was found, as expected. Considering the characteristics of the cooking process, several parameters such as Nitrogen, Phosphorous, impurities, acidity and moisture need to be monitored. An investigation on pure vegetable oil composition was considered for searching the Nitrogen source. An experimental campaign based on preliminary centrifugation and filtration of the raw UCO was carried out in order to evaluate the solid residuals, and in view of achieving a minimum quality feedstock suitable for subsequent processing.

## 2 Renewable jet fuel

### 2.1 The context

Aviation, as other ways of transport, is going through a challenge based on greening the sector as well as even numerous and significant financial issues. The emission reduction goal of 2 Mt aviation alternative, drop-in fuels by 2020 extend, on a voluntary basis, the EU RED, that is enforced only in road transportation. A study on the current aviation market has been carried out in D2.6 “Information related to economic, social and environmental parameters 2<sup>nd</sup>”, investigating on the environmental and social issue related to the aviation renewable fuels, together with an analysis of the pathways and the regulatory framework [1].

The relevant data are:

- In 2010, air transport consumed 10% of global transportation energy and this is projected to increase to 13% by 2030.
- About 25-40% of the operating costs of an airline are on fuel expenditure: jet fuel cost for the aviation industry was \$216 billion in 2013, increased by 60% compared to 2010.
- The extension of the European Union Emission Trading Scheme (ETS) to the air transport sector since January 2013 will add another component to the overall cost of jet fuel.

### 2.2 Aviation renewable jet fuel standards

In commercial aviation the JET-A-1 (i.e. the conventional fossil aviation fuel) is regulated by DEFSTAN 91/91 (UK) and ASTM D1655 (USA) specifications. The adoption of renewable fuels needs to meet strict quality specifications, which include e.g. detailed requirements for hydrocarbon composition. New renewable fuels must be certified and approved by the ASTM International aviation fuels subcommittee, by means of two main standards:

- ASTM D4054 - “Standard Practice for Qualification and Approval of New Aviation Turbine Fuel and Fuel Additives”;
- ASTM D7566 - “Standard Specification for Aviation Turbine Fuel Containing Synthesized Hydrocarbons”.

ASTM D7566 is the standard that defines the composition and properties of renewable aviation fuels. The ASTM D4054 standard is a guidance for a new fuel or additive approval process that includes the prerequisite testing and required interactions with the engine and airframe manufacturers, standards organizations and airworthiness agencies such as the FAA and EASA. In particular the ASTM D7566 norm allows for blending up to 50% v/v of Fischer-Tropsch (FT) and hydroprocessed esters and fatty acids (HEFA) with conventional petroleum-derived jet fuel, and for the inclusion of up to 10% (by volume) of synthesized iso-paraffinic fuel (SIP), i.e. farnesane. Other new pathways of renewable jet fuels production are currently under approval. In Table 2 some requirements for JET A-1 are summarized.

Table 2: Some JET A-1 requirements according to DEFSTAN 91/91 [2]

Parameters	Limit
Flash point	> 38 °C

Crystallization (freeze) point	< - 47 °C
Viscosity at – 20 °C	< 8 mm <sup>2</sup> /s
Low calorific value	> 42.8 MJ/kg

The aviation fuel is monitored also in emissions limit (e.g. GHGs, NO<sub>x</sub>, SO<sub>x</sub>) and the chemical compatibility with materials and additives (included in ASTM D4054 approval process).

Critical issues in blending refer to hydrocarbon compounds, being aliphatic or aromatic: the conventional petroleum-derived fuels are composed of both types, while the renewable fuels are fully composed of paraffinic (i.e. aliphatic) hydrocarbons.

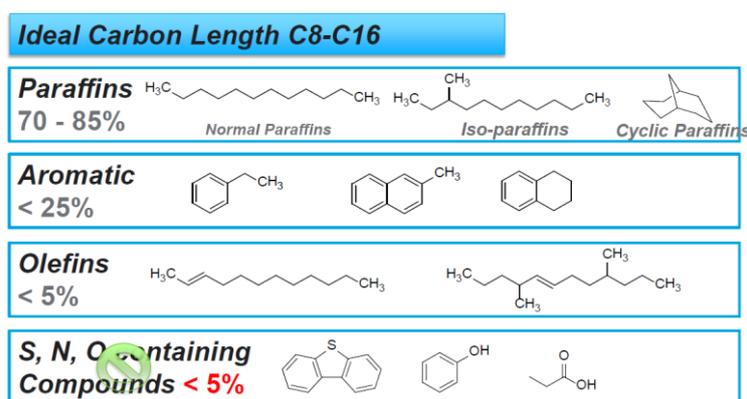


Figure 1: The desired compound classes in jet fuels [3].

The absence of aromatics content in the fuels provokes lower density value (below the minimum density requirement), and can be responsible of problems with seals (due to the property of some elastomers used in aviation to shrink), which may lead to fuel leaks [4]. An aromatic-free fuel leads also to a cleaner combustion reducing the soot emissions. Moreover, the renewable fuels are virtually free from sulfur- and nitrogen-compounds found in conventional jet fuel, thus the emissions are free from sulfur dioxide (SO<sub>2</sub>) or sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) aerosols [5]. ASTM D7566 allows the use of an approved alternative component in blend with conventional jet fuel.

## 2.3 Commercial pathways

Currently the commercial technologies for renewable jet fuel production are mainly based on either Fischer-Tropsch (FT) synthesis from coal, natural gas and possibly biomass, or hydrotreating of vegetable oil (hydrotreated renewable jet fuel, HRJ). Both routes implies significant constraints: in FT-synthesis the main bottleneck is capital cost, while in hydrotreating the main drawbacks are the cost of feedstock and the hydrogen demand of the process, which increases the operative costs.

Synthetic Fischer-Tropsch synthesis has been adopted in industrial processes for decades, based on synthesis gas produced from coal and natural gas. At least two separate consortiums (one composed by StoraEnso and Neste Oil, the other by UPM and Carbona) have been developing a BTL plant on the basis of biomass gasification and FT in Europe [6]. The fuel produced by means of FT technology from fossil sources (natural gas, coal) has been already tested in commercial airways, within the limits described in the previous paragraph.

The commercial technology of catalytic hydrotreating is based on the saturation of olefinic bonds of triglycerides-based material and the removal of heteroatoms (such as sulfur, nitrogen and oxygen), in order to obtain a green enriched fuel in paraffinic hydrocarbons. During the last years, several companies involved in petroleum refining started the production on renewable fuels adopting the hydroprocessing technology on lipid feedstock [7] [8] [9]. This treatment can be driven to the maximization of jet fuel by means of the separation of hydrocarbons jet classes to renewable diesel (i.e. the main product of the conventional process) [10].

An overview on the most significant tests on alternative fuels in aviation gas turbines has been carried out in the framework of this project [11].

## 2.4 Experimental pathways

One of the main issue in hydrotreating is the adoption of hydrogen in catalytic reactors working at severe thermodynamic conditions (around 350°C of temperature process up to 180 Bar of pressure). As said, the operative costs became relevant, thus the research on possible alternative routes was investigated. The scope of this WP focuses the study of UCO as possible feedstock for further non-commercial alternative thermochemical treatment to produce a bio-intermediate towards renewable jet fuel. A number of experimental pathways were tested and discussed in literature, adopting lipid-based materials as feedstock for thermochemical conversion [12]. RE-CORD investigated the catalytic conversion of UCO adapting its own pyrolysis pilot unit [13]. The UCO undergoes through a set of reactions to obtain an intermediate rich in hydrocarbons and still some oxygenated compounds derived from catalytic cracking of triglycerides. In particular, the process is conducted at atmospheric pressure with no hydrogen input, at 400 - 500 °C using low cost catalysts (compared to those used in hydrotreating). In order to reduce the global energy costs of hydrotreating, in particular the hydrogen demand, a possible route could be the integration of catalytic process before the first step of hydrodeoxygenation. This adds another step to the process but could reduce in part the global energy demand: the bio-liquid product could be either separated from oxygenated compounds and fractionated by hydrocarbon classes of interest (Figure 2), or processed in directly in hydrotreating. The hypothesis and pathways on these alternative routes will be investigated in the next

deliverable D2.8 “Development of UCO specification”, as well as the results of the next experimental catalytic conversion.

Other promising pathways as direct sugar fermentation to hydrocarbons, alcohol conversion to jet fuel and hydrotreated depolymerization of lignocellulosic material [14] will not be considered in this work.

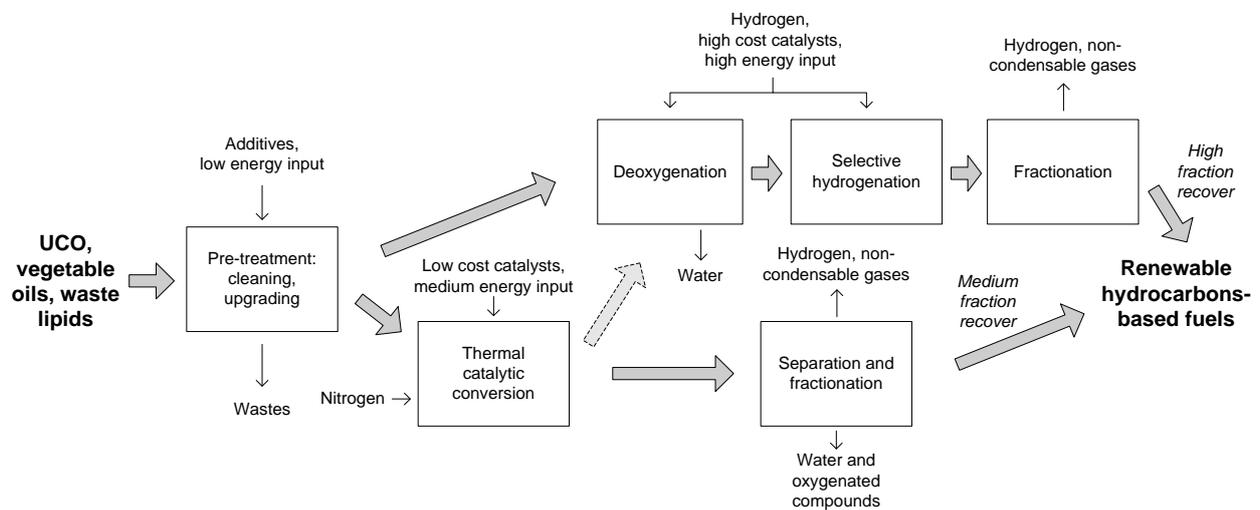


Figure 2: Possible routes for integrating the thermal catalytic conversion into hydrotreating [15].

### 3 Potential feedstock

The aviation sector has no real other alternative to biofuels for greening the sector, thus the role of used vegetable oil (UCO) as renewable feedstock for the development of drop-in renewable fuels could be significant. UCO collection follows a positive trend in terms of environmental issues and economic growing appeal, but today the largest amount is still used by the biodiesel industry [16], while the valorisation in aviation sector is very limited [1].

#### 3.1 The situation

Products derived from UCO as components of animal feed is forbidden in the EU due to risk of animal health hazards [17]. The disposal of large amounts of UCO is an environmental problem, thus is currently used in biodiesel industry, soap manufacture and oleo-chemical industries [18]. The discharge of UCO into drains or sewers leads to blockages, and if dumped in municipal solid waste landfills or into municipal sewage treatment plants, creating operation problems along with pollution of water and soil [19]. Seeking for the business opportunity behind this waste stream and thanks to EU UCO-biodiesel double counting, some companies are investing in the collection and treatment of used oils. After collection, the oil can be sold as biofuel or in the chemical industry.

The present work studied one private company currently operating in Italy, within the Florence urban area. This company is responsible for the collection and treatment of a large amount of vegetable oils for feed and/or biofuel industry. The strategies adopted for the oil sampling of ITAKA project and the treatments on UCO performed have been evaluated.

#### 3.2 Collection and recovery

The implementation of an industrial biorefinery for the Florence urban area is considered as an appropriate solution in terms of sustainability and environment. The first step to evaluate its feasibility is the creation of new technological pathways to promote a bioenergy source from a waste. From a technical point of view, a production chain for aviation biofuel could be considered. In this context, a local company SILO SpA [20] is working on exhausted cooking oil and fats from several years, collecting the feedstock by means of contracts with private companies of the Florence district .

UCO is considered as a non-hazardous waste to be destined to the recovery in accordance of art. 184 comma 2 from the Italian legislative decree 152/2006 (partially amended by Legislation Decree 205/2010 which implement the Directive 98/2008/EC). Therefore, UCO must be stored in appropriate containers until the authorized Companies (e.g. BACCIOTTI srl in the Florence area) collect the product. Vehicles discharge the UCO into a basement storage in SILO SpA, according to the current Italian regulation (provided with proper authorization n. 307, pursuant to art. 208 Legislative Decree no. 152/2006 and Decree n. 186 of 05/04/2006, from the Florence district).



Figure 3: UCO collection by means of special vehicles that discharge the feedstock into a basement storage.

### 3.3 Industrial treatments at Silo and sampling method

After collection UCO is filtered for subsequent treatments. Filtration and water removal are important initial cleaning steps. Filtration can remove solid impurities as well as water. The water content of UCO is greatly reduced by means of paper filters, a cost-effective solution with high removal efficiency. A part of the oil is treated in the esterification process, a method employed by SILO on UCO and PFAD (mainly to supply feedstock for biodiesel production). SILO esterification process works at about 220 - 230 °C, with the addition of glycerol (glycerine pure at 97 - 98%). This process restores the acidity of the UCO to values comparable with pure vegetable oil.

Critical issue at industrial scale is the sampling method for the liquid feedstock. Sedimentation due to the non-homogenous feedstock generally occurs. The Sonda Marsigliese [21] is adopted as sampling tool and simultaneously takes samples at different heights. This kind of probe is normally used by those who need to quickly check several loads (trucks) per day.



Figure 4: SILO Industrial filtration and the special probe (Sonda Marsigliese) for oil sampling.

### 3.4 Chemical characterization

An accurate analysis of the used cooking oil has been carried out in order to evaluate the feedstock characteristics. Currently there are no specifications on UCO as initial feedstock for biofuel production processes. Regarding the chemical analysis, typical parameters normally examined in vegetable oils have been investigated. A preliminary characterization of the used cooking oil properties was carried out according to DIN 51605 (i.e. the reference in specifications and test methods used for straight vegetable oil analysis). UCO has been collected from SILO every three months in order to analyse different batches, and the variability of parameters emerged. Seven batches were selected and characterized in table 3. Most of the values are comparable with the standard of raw vegetable oils. The total contamination is very high, as it could also be seen by visual observation (Figure 5). Water content is clearly high due to the cooking process, and its removal necessary. Also Phosphorous and Nitrogen content is generally above the limits.



Figure 5: Used cooking oil samples: pure and filtered at 0.7  $\mu\text{m}$  (according to UNI EN 12662).

Table 3: UCO analysis.

Parameter	Used Cooking Oil									
	Unit	Method	DIN 51605 limit	UCO 120126	UCO 130215 (1)	UCO 130215 (2)	UCO 130513	UCO 130528	UCO 130704	UCO 140417
Density	kg/m <sup>3</sup>	UNI EN ISO 3675	900 - 930	937	916	922	914	910	916	911
Kinematic Viscosity at 40 °C	mm <sup>2</sup> /s	UNI EN ISO 3104	max 36	n.a.	34.50	34.08	31.50	n.a.	35.64	29.51
Acid value	mg KOH/g	UNI EN 14104	max 2	5.52	2.40	3.30	2.60	20.07	1.88	3.21
Free Fatty Acid	%	ISO 660	-	2.76	1.20	1.65	1.30	10.03	0.94	1.60
Iodine Number	g Iodine/100g	UNI EN 14111	95 - 125	44	96	96	n.a.	n.a.	97	106
Iodine Value	g/100 g	ISO 3961	-	44	96	96	n.a.	n.a.	97	106
Water content	%	UNI EN ISO 8534	max 0.075	39.00	0.94	2.10	0.29	5.99	1.70	2.53
Ash	% (m/m)	UNI EN ISO 6245	max 0.01	0.60	0.03	0.04	0	0.01	0.03	0.01
Total contamination	mg/kg	UNI EN 12662	max 24	n.a.	628	1,895	n.a.	4,308	3,129	11,166
Insoluble impurities	%	UNI EN ISO 663	-	n.a.	n.a.	n.a.	n.a.	0.46	0.31	0.81
Sulphur	%	Internal method	max 0.001	0	0	0.01	0.02	0	0	0.01
Calcium	mg/kg	UNI EN 14538	max 20 (+Mg)	59.30	0	0.00	6.25	13.40	13.90	246.70
Magnesium	mg/kg	UNI EN 14538	max 20 (+Ca)	42.70	0	0	1.04	9.40	1.90	40.70
Phosphorus	mg/kg	UNI EN 15290	max 12	78.24	4.93	7.50	4.10	33.50	6.40	102
C	%	ASTM D5291	-	31.50	76.50	75.80	79.50	71.40	73.60	73.80
H	%	ASTM D5291	-	10.85	12.00	11.80	11.20	11.60	11.60	11.50
N	%	ASTM D5291	-	0	0.03	0.03	0.15	0.04	0.02	1.01
N	mg/kg	ASTM D4629	-	n.a.	n.a.	n.a.	106	428	227	1,002
O	%	calculated	-	57.59	11.44	12.32	9.13	16.95	14.75	13.67
Calorific value, higher	kJ/kg	DIN 51900-2	-	22,762	38,729.00	38,225	39,427	36,700	38,673	38,351
Calorific value, lower	kJ/kg	calculated	min 36,000	20,395	36,182.60	35,721.04	37,050.36	34,238.48	36,211.48	35,910.70

## 4 Materials and methods

### 4.1 Comparison of norms

Specific norms were selected for the comparison of UCO properties, different from those methods normally applied to measure similar parameters in other fields of bioenergy (e.g. DIN 51605 for straight vegetable oil in transports) as reported in Table 3. Thus, norms were compared and selected. Six parameters were selected for detailed investigation:

- Density
- Acid value and Free fatty acid
- Iodine Number and Iodine Value
- Total contamination and Insoluble impurities
- Phosphorus
- Water content and moisture & Volatile

#### 4.1.1 Density

Norm: Density UNI EN ISO 3675  
Density EN ISO 12185 (at 50°C)

Results can be directly compared only for samples analysed at the same temperature. However it is possible to calculate density for temperature different from 15°C by applying specific corrections.

	UNI EN ISO 3675	EN ISO 12185
<b>Main equipment</b>	Hydrometer.  Thermometer.  Optional constant-temperature bath.	Oscillating U-tube.  Circulating constant-temperature bath.
<b>Procedure</b>	Sample is transferred into a cylinder at the reference temperature (15°C), then an appropriate hydrometer is dunked in the liquid sample. Hydrometer is moved and rotated until floating is stabilized. Density is measured by reading a graduated scale.	Sample is introduced into a cell then instrument provides an electronic measurement of the frequency of oscillation, from which the density value is calculated.  The reference temperature for used cooking oil is 50°C.

#### 4.1.2 Acid value and free fatty acid

Norm: Acid value UNI EN 14104  
Free Fatty Acid ISO 660

	UNI EN 14104	ISO 660
<b>Sample treatment</b>	The sample is dissolved into a solvent mixture and titrated with a dilute solution of potassium hydroxide using phenolphthalein as indicator. Calculation for acid value only.	The sample is dissolved into a solvent mixture, the acids are titrated with a solution of ethanol or methanol with potassium hydroxide or sodium. Calculation of acid value and FFA.
<b>Reagents</b>	<ul style="list-style-type: none"> <li>Solvent mix: Diethyl ether and 95 % ethanol; ortoluene and 95 % (V/V) ethanol; or toluene and 99 % (V/V) 2-propanol.</li> <li>potassium hydroxide solution;</li> <li>phenolphthalein.</li> </ul>	<ul style="list-style-type: none"> <li>Solvent mix: ethanol 96% or 2-propanol; or diethyl ether or tert-butyl methyl ether, light petroleum, toluene;</li> <li>potassium or sodium hydroxide solution;</li> <li>phenolphthalein;</li> <li>thymolphthalein;</li> <li>alkali blue 6B.</li> </ul>
<b>Procedure</b>		3 different methods titration, depending on the expected magnitude of the acid value.
<b>Calculation</b>	<p>The acid value is reported as:</p> $(56.1 V c) / m$ <p>Where</p> <p>V is the volume, in milliliters, of standard volumetric potassium hydroxide solution used;</p> <p>c is the exact concentration, in moles per liter, of the standard volumetric potassium hydroxide solution used;</p> <p>m is the mass, in grams, of the test portion;</p> <p>56.1 is the molecular mass of potassium hydroxide. Results are expressed as mg KOH/g sample and shall be rounded to the second decimal digit.</p>	<p>The acid value, wAV, expressed as a mass fraction, is equal to:</p> $(56.1 V c) / m$ <p>where</p> <p>c is the exact concentration, in moles per liter, of the standard volumetric sodium or potassium hydroxide solution used;</p> <p>V is the volume, in milliliters, of standard volumetric sodium or potassium hydroxide solution used;</p> <p>m is the mass, in grams, of the test portion. The acidity or free fatty acid content, FFA, expressed as a percentage mass fraction, and according to fat type, is equal to:</p> $(V c M 100) / (1000 m)$ <p>where</p> <p>V is the volume, in milliliters, of the standard volumetric sodium or potassium hydroxide solution used;</p> <p>c is the concentration, in moles per liter, of the standard volumetric sodium or potassium hydroxide solution used;</p> <p>M is the molar mass, in grams per mole, of the acid chosen for expression of the result (see Table 2) according to the fat type;</p> <p>m is the mass, in grams, of the test portion.</p>

### 4.1.3 Iodine number and iodine value

Norm: Iodine value UNI EN 14111  
Iodine value UNI EN ISO 3961

The norms for Iodine value are essentially identical as regards reagents, procedures and calculations. Iodine value results obtained in accordance with UNI EN 14111 and UNI EN ISO 3961 are fully comparable.

#### 4.1.4 Total contamination and Insoluble impurities

Norm: Total contamination UNI EN 12662  
Insoluble impurities UNI EN ISO 663

	UNI EN 12662	UNI EN ISO 663
<b>Main equipment</b>	High retention glass-fiber filter of 0.7 µm mean pore size. Filter apparatus. Oven. Vacuum source.	Glass-fiber filter (as Whatman GF/D type, i.e. 2.7 µm mean pore size). Conical flask. Electric drying oven.
<b>Procedure</b>	For viscous samples (more than 5mm <sup>2</sup> /sec at 40°C): sample is diluted in a beaker with n-heptane then transferred into the filter apparatus. A low pressure is maintained by a vacuum source. Beaker and filter apparatus are washed and rinsed with heptane, then glass-fiber filter is dried in an oven at 110°C till constant weight.	200 ml of n-hexane are added to the flask containing the test portion. The flask is shaken, then left to stand at about 20 °C for about 30 min. Test portion is filtered through the filter in a suitable funnel using suction if necessary. Flask and filter apparatus are washed and rinsed with n-hexane, then glass-fiber filter is dried in an oven at 103°C till constant weight.
<b>Calculation</b>	$W = 1000 (m_2 - m_1) / m_E$ $m_2$ = mass of the filter with the residue in milligrams $m_1$ =mass of the filter, in milligrams $m_E$ =mass of the sample portion in grams Results are expressed in mg/kg.	$w = [(m_2 - m_1) / m_0] 100$ $m_2$ =mass of the vessel with its lid and filter paper containing the dry residue in grams $m_1$ =mass of the vessel with its lid and filter paper in grams $m_0$ =mass of the test portion in grams Results are expressed in percentage by mass.

Results obtained in accordance with UNI EN 12662 and UNI EN ISO 663 are not comparable because glass-fiber filters have different mean pore size. This parameter directly affects the amount of the residue collected.

#### 4.1.5 Phosphorus content

Norm : Phosphorus ASTM 5185  
Phosphorus UNI EN 15290

ASTM 5185 is applied for the analysis of wear metals, contaminants and additive elements in used lubrication oils. The concentration of metals and contaminants within a sample is then determined by direct analysis by ICP-OES (Thermo IRIS Intrepid II Inductively Coupled Plasma Optical Emission Spectrometry).

UNI EN 15290 is the norm applied for the determination of major elements – (Al, Ca, Fe, Mg, P, K, Si, Na and Ti) to solid biofuels, but it is also used in the case of liquid samples. ISO 10540-3, "Animal and vegetable

fats and oils - Determination of phosphorus content -Part 3: Method using inductively coupled plasma (ICP) optical emission spectroscopy", can also be used, but the sample has to be clear.

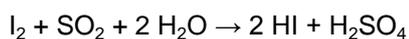
The sample is digested in a closed vessel by the help of reagents, temperature and pressure. The digestion is either carried out directly on the fuel. The detection of the elements may be done by ICP-OES, ICP-MS, FAAS or FES.

#### 4.1.6 Water content and Moisture & Volatile

The water content is measured by the two different method: Karl Fisher's titration, or through the heating of a test portion and then the determination of the loss in mass.

Norm:           Water content ISO 8534  
                  Moisture & Volatile ISO 662 (method B)

The water content is performed by the Karl Fisher's titration using 848 Titrino, Metrohm. The procedure is based on the oxidation of sulphur dioxide by iodine:



Among the advantages of this method compared to the measurement of water content by drying the sample in an oven there is the processing time - a few minutes versus a few hours - and the specificity - only the water reacts, not the other volatile compounds that may be present in the sample.

ISO 662 is based on the heating of a test portion at  $103 \text{ }^\circ\text{C} \pm 2 \text{ }^\circ\text{C}$  in oven until moisture and volatile substances are completely eliminated, and determination of the loss in mass. Several hours are required to achieve complete dehydration of water from the sample.

## 4.2 Other parameters

### 4.2.1 HHV and LHV

The higher heating value (HHV) was measured according to DIN 51900-2 by means of a Leco AC500 isoperibol calorimeter. A sample of about 1 g was weighed with a precision of 0.1 mg in a crucible, then the crucible and a nickel ignition wire were placed into the calorimeter. The equipment was closed and pressurized to 29 bar with high purity oxygen (99.999%), then settled into the bucket, which was previously filled with a fixed volume of distilled water. After a suitable period required to reach thermal equilibrium, the ignition was automatically started and temperature was measured by an electronic thermometer with an accuracy of 0.0001 °C. Certified calorific standard benzoic acid was used both for calibration and as a spike for samples. Analysis were carried out in triplicates.

### 4.2.2 Viscosity

Kinematic viscosity of UCO was measured according to UNI 3104 with a Lauda viscometer made by an Ubbelohde capillary tube controlled by iVisc software and a Proline PV 15 thermostatic bath filled with deionized water. Thermostatic bath allows to keep a constant temperature with a precision of 0.01 °C. Each

sample was introduced in the capillary tube and allowed to reach the selected temperature in the thermostatic bath before starting the analysis. After a suitable equilibrating time each measurement was carried out at the selected temperature for five times: two times in order to precondition the capillary tube, then the last three times for analyses: an interval of 90 seconds occurred between every measurement.

#### 4.2.3 Ash

Determination of the amount of ashes was performed in a Leco TGA 701 instrument. Samples were weighed, heated and incinerated in porcelain crucibles. A four step program was set to gradually heat samples under an air flow of 5 liters per minute from room temperature to 775 °C at oven heating rates of 10 °C/min, then samples were kept at 775 °C for 90 minutes for a complete incineration. Analysis were carried out in triplicates.

#### 4.2.4 CHNO

The CHNO content was determined by means of a Truespec CHN (LECO) following the method ASTM D5291. The sample weight range was 80 milligrams to 120 milligrams. The sample is dropped into a hot furnace (950 °C) and flushed with oxygen for very rapid and complete combustion. The product of combustion are passed through a secondary furnace (Afterburner, 850 °C) for further oxidation and particulate removal. The combustion gases are then collected in a collection vessel known as the ballast. The homogeneous combustion gases in the ballast are then purged through the CO<sub>2</sub> and H<sub>2</sub>O infrared detectors and the 3 cc aliquot loop. Once the gasses are equilibrated, carbon is measured as carbon dioxide by the CO<sub>2</sub> detector and the hydrogen is measured as water vapour in the H<sub>2</sub>O detector. The gases in the aliquot loop are transferred to the helium carrier flow, swept through hot copper to remove the oxygen and change NO<sub>x</sub> to N<sub>2</sub> and then flow through an absorber to remove carbon dioxide and water. A thermal conductivity cell is used to determine the nitrogen content.

#### 4.2.5 Sulphur

The Sulphur content was determined using a Truespec S (LECO) with an internal method. Analysis begins by weighing out a sample (range was 80 milligrams to 120 milligrams) into a combustion boat. The sample is placed in the combustion system, which is typically regulated at 1350 °C with pure oxygen environment. The combination of furnace temperature and analyse flow cause the sample to combust. All sample materials contained in the combustion boat go through an oxidative reduction process that causes Sulphur-bearing compound to break down and free Sulphur. The Sulphur then oxidizes to form SO<sub>2</sub>. From the combustion system, the gases flow through the Anhydron tube to remove moisture, through a flow controller and then through the infrared detection cell located in the instrument. The cell measures the concentration of Sulphur dioxide gas present.

#### 4.2.6 Mineralization with microwaves oven

The digestion or mineralization of a sample has been carried out following UNI EN 15290. Analysis begins by weighing out a sample (500 milligrams) into a PTFE container and treated with 8 ml of HNO<sub>3</sub> and 3 ml of

H<sub>2</sub>O<sub>2</sub>. A reaction time of minimum 5 min shall be kept before closing the vessel. The heating of the vessel was according the following heating programme for digestion:

Resistance heating:

- Step 1: Ramp to 220 °C over 1 h.
- Step 2: Hold for 1 h at 220 °C.

Microwave heating:

- Step 1: Ramp to 190 °C over 15 min.
- Step 2: Hold for 20 min at 190 °C.

Blanks determination were performed by using the same amounts of reagents but without sample. The solutions were finally analyzed by ICP.

#### 4.2.7 ICP

This method covers the analysis of major and minor elements in solution samples by ICP-OES (Thermo IRIS Intrepid II Inductively Coupled Plasma Optical Emission Spectrometry). An aqueous sample is converted to aerosols via a nebulizer. Aerosols are transported to the inductively coupled plasma which is a high temperature zone (8,000– 10,000°C). The analytes are heated (excited) to different (atomic and/or ionic) states and produce characteristic optical emissions (lights). These emissions are separated based on their respective wavelengths and their intensities are measured (spectrometry). The intensities are proportional to the concentrations of analytes in the aqueous sample. The quantification is an external multipoint linear standardization by comparing the emission intensity of an unknown sample with that of a standard sample. Multi-element calibration standard solutions are prepared from single- and multi-element primary standard solutions. Samples are measured with standardization blanks, other kinds of blanks, drift control samples, and quality control samples. The data are corrected in terms of standardization blanks, other relevant blanks, drift correction, and dilution factor application. The results are normalized to the internal reference standard if an internal reference standard is used.

#### 4.2.8 Determination of fatty acid composition with GC-FID

The composition of fatty acids in UCO samples was determined using a GC-FID apparatus according to UNI EN ISO 5508 norm, using the transesterification method according to UNI EN ISO 5509 norm. The glycerides contained in the sample are dissolved in hexane and converted to methyl esters by transesterification with a methanolic potassium hydroxide solution. After the reaction has finished, the potassium hydroxide is neutralized with sodium hydrogen sulfate to prevent saponification of the methyl esters. The sample is then analyzed in GC-FID to determine the fatty acid composition. In particular, the analysis was performed using a gas chromatograph GC 2010 Plus (Shimadzu) equipped with a flame ionization detector. The column used was a HP88 column (i.e. Agilent: length 60 m, diameter 0.250 mm, film 0.20 µm) and the analysis was performed with a column flow of 0.46 ml/min and an initial temperature of 120 °C increased to 230 °C, following three temperature steps. Helium was used as gas carrier.

The fatty acids were identified by comparing their retention times to known previously injected standards. Result were expressed as percentages assuming 100% was equal to total picks area.

### 4.3 Centrifugation

To evaluate the solid part contained into the cooking oil, some centrifugation test have been carried out. The RE-CORD laboratory is equipped with a small centrifuge (NF 400R) for this scope.

## 5 Experimental investigation and results

### 5.1 Literature review

The frying process causes various chemical decomposition reactions such as: hydrolysis, polymerization and oxidation [22]. Even the cyclization of the fatty acids can be expected [23]. As consequence, the physical and chemical properties of the oil can dramatically change during frying. Thus, the UCO is characterized by higher acid value, viscosity, water content and contamination respect to vegetable oils (as seen in Table 3). This increment is mainly due to the high temperatures (140 – 180 °C) of the frying process, and the interaction between oil and fried food. An increment of the level of saturation during frying has been already discussed, as well as the percentage of FFAs which tends to increase due to the decomposition of triglyceride molecules [24]. A method to restore the presence of FFAs could be the SILO esterification process (i.e. already discussed in paragraph 3.3), but this solution is mainly useful only in biodiesel production due to the maximum allowable level of 5% for direct alkali-catalyzed transesterification [25] as well as to allow the use of construction steel rather than expensive stainless steel tanks.

As the UCO can be a suitable feedstock for further upgrading processes, the presence of several elements, such as for instance the Nitrogen and the Phosphorous, has to be investigated. For example, if the UCO has to be used in combustion, Nitrogen should be limited to reduce the emission (i.e. *fuel NO<sub>x</sub>*). The presence of N and P can be a limiting factor even for the use of the UCO in several upgrading process.

Nitrogen is one of the most common element in the organic matter so it is naturally contained in different forms even in pure vegetable oil as well as in UCO. The amount of Nitrogen potentially contained in UCO can be higher respect to the original feedstock, as consequence of the “contamination” associated by the foods frying. In order to assess the effects of the frying process, a characterization of the Nitrogen content in commercial pure vegetable oil samples has been carried out.

### 5.2 Experimental investigation of commercial vegetable oil

In order to define figures to be used as reference for comparison with UCO, a commercial vegetable oil characterization (mainly sunflower oil) has been initially analysed. Results are presented in Tab. 4. In general, commercial vegetable oils are obtained by chemical extraction and refining, bleaching, winterization (de-wax), and deodorization before being used for edible purposes. The crude vegetable oils contains several impurities that must be reduced in order to make the oil commercially suitable for food application. There are two groups of impurities normally present in the crude sunflower oil:

- **macro impurities:** which can be measured as weight percentage;
- **micro impurities:** that are present in smaller amounts, generally at ppm or even ppb.

The presence or absence of some of the micro impurities can have significant effects on oil stability [26]. In order to assess the source of the Nitrogen in UCO, an experimental campaign has been carried out, analysing two batches of commercial sunflower oils.

Table 4: Commercial sunflower oil (CVO) analysis.

Parameter	Commercial Vegetable Oil (sunflower oil)					
	Unit	Method	DIN 51605 limit	CVO (1)	CVO (2)	FILTERED CVO (2)
Density	kg/m <sup>3</sup>	UNI EN ISO 3675	900-930	914	908	n.a.
Kinematic Viscosity at 40 °C	mm <sup>2</sup> /s	UNI EN ISO 3104	max 36	26.0	26.66	26.68
Acid value	mg KOH/g	UNI EN 14104	max 2	1.06	1.77	0.95
Free Fatty Acid	%	ISO 660	-	0.53	0.89	0.47
Water content	%	UNI EN ISO 8534	max 0.075	0.085	0.044	0.049
Ash	% (m/m)	UNI EN ISO 6245	max 0.01	0.007	0.005	0.005
Total contamination	mg/kg	UNI EN 12662	max 24	n.a.	209	0
Insoluble impurities	%	ISO 663	-	0.01	0.0045	0
Sulphur	ppm	Internal method	max 10	0	28	9
Calcium	mg/kg	UNI EN 14538	max 20 (+Mg)	n.a.	0.54	0
Magnesium	mg/kg	UNI EN 14538	max 20 (+Ca)	n.a.	0.1	0
Phosphorus	mg/kg	UNI EN 15290	max 12	0.110	0.29	0.13
C	%	ASTM D5291	-	77.8	81.7	80.8
H	%	ASTM D5291	-	11.9	11.2	11.2
N	%	ASTM D5291	-	0.01	0.026	0.008
N	mg/kg	ASTM D 4629	-	116	260	80
O	%	calculated	-	10.3	7.1	8.0
Calorific value, higher	kJ/kg	DIN 51900-2	-	39,482	39,530	n.a.
Calorific value, lower	kJ/kg	calculated	min 36,000	36,978	37,153	n.a.

The Nitrogen content for commercial sunflower oil reach high values (over 100 ppm); for this reason an up-grading by simple filtration has been implemented. All the other key values are lower than UCO, thus the real issue is where the Nitrogen is located.

As known, the most important oilseed crops as sunflower, soy and rapeseed are rich in proteins (i.e., a Nitrogen source). However, after oil extraction, the most of the proteins should remain in solid cakes, and the raw oil (after separation) should be composed of lipids. The source of the Nitrogen contained in the oil is so difficult to be identified: free fatty acids and triglycerides are Nitrogen free; only phospholipids can have a small percentage of N in the molecule (lower than 2% by weight).

Looking at phospholipids, the ones contained in sunflower seed oil are: phosphatidylcholine (PC), phosphatidylethanolamine (PE), phosphatidylinositol (PI) and phosphatidic acid (PA) [27]. PA is Nitrogen free

but PC, PE and PI contain both an atom of N per each atoms of P. Phosphorous content in sunflower oils is lower than 1 ppm (Tab. 4) so, considering the P amount as a marker for N, the Phosphorous from phospholipids source can contribute to the total N content for less than 1 ppm. So Nitrogen in the biofuel must be originated in compounds different than lipids.

Naturally sunflower seeds, during the oil extraction process, lose their protein fraction. However, a small amount of protein still remains in the vegetable oil. Nevertheless, even considering a conservative value around 20 ppm, the amount of Nitrogen due to this fraction (i.e. average 16% of N contained in the proteins [28]) is approximately 3.2 ppm (0.00032% of total lipids in the sunflower oil).

Another source of Nitrogen could be the vitamin B5-B6-B9. Pyridoxine (B6) is the highest vitamin contained in the sunflower oil (25 ppm, in a high-vitamin oil). This means a 2.5 ppm of Nitrogen contained in vitamin B6. Also vitamin B9 (folic acid) contains a big amount of Nitrogen, but its presence is usually really low. The total amount of Nitrogen contained in vitamins remains lower than 5 ppm. In the best case it has been identified approximately the 10% of the total Nitrogen contained in the sunflower oil. This means that probably the most important source of Nitrogen in commercial oils has to be find in the unsaponifiables or in the insoluble impurities which are not removed by standard refining treatments. Unsaponifiables are mainly composed by Nitrogen free steroids. The insoluble impurities are probably residues from oil-seeds squeezing. This hypothesis has been confirmed by the results obtained by filtering (pore size 0.7  $\mu\text{m}$ , according to UNI EN 12662) the sample nr.2 of commercial sunflower oil (i.e. last column in Tab. 4). After filtration the Nitrogen content has been limited, from 240 to 80 ppm. This promising results are the guidelines for the UCO characterization.

A CHNS analysis on sunflower meal pellets (test method, UNI 15104) has been carried out in order to identify the percentage of Nitrogen. The results show a value of 4.3%, probably from protein source. We can so conclude that high values of solid impurities may be the major Nitrogen source in commercial vegetable oils.

### 5.3 Experimental investigation on UCO

The UCO, previously characterized (Tab.3), has been centrifuged (described in 4.3) and filtered (according to UNI EN 12662) in order to assess the effect of the contamination on its composition. Two batches were examined, and three parameters considered:

- Nitrogen;
- Phosphorous;
- total contamination.

Table 5: UCO experimental filtration and centrifugation (first test).

Parameter	UCO 130528 sample							
	Unit	Norm	DIN 51605 limit	Pure UCO	Centrifuged UCO	Solid residual	Centr. and Filtered UCO	Solid residual
-	-	-	-	(initial feedstock)	-	(from centrifuge)	(> 0.7 micron)	(from filtration)
<b>N</b>	mg/kg	ASTM D 4629	-	428	278	-	249	-
<b>Phosphorus</b>	mg/kg	UNI EN 15290	max 12	33.5	2	208	2	-
<b>Total contamination</b>	mg/kg	UNI EN 12662	max 24	4308	177	-	-	-

First test (Tab. 5) shows a significant reduction in Nitrogen and Phosphorous content after centrifugation. This means that the presence of Nitrogen and Phosphorous were due to the solid particles. The content of the Nitrogen after a further filtration does not change. This leads to the consideration that other soluble compounds (formed during frying process) contribute to the N content in UCO. A large amount of Phosphorous is present on the solid residual, thus the value of the centrifuged and filtered UCO resulted very low: 2 ppm. Total contamination is widely reduced during centrifugation and it is almost below detection in filtered UCO (UNI EN 12662 normative equipment).

Table 6: UCO experimental filtration and centrifugation (second test).

Param.	UCO 130704 sample								
	Unit	Norm	DIN 51605 limit	Pure UCO	Centr. UCO	Solid residual	Centr. and Filtered UCO	Solid residual	Filtered UCO
-	-	-	-	(initial feedstock)	-	(from centrifuge)	(> 0.7 micron)	(from filtration)	Industrial filter (few micron)
<b>N</b>	mg/kg	ASTM D 4629	-	227	189	-	121	-	151
<b>P</b>	mg/kg	UNI EN 15290	max 12	6.4	3.1	-	1.7	-	3.7
<b>Total cont.</b>	mg/kg	UNI EN 12662	max 24	3129	252	-	-	-	-

The tests on the second batch of UCO confirmed the previous results. Here, the implementation of an industrial filter (in this case a paper filter from SILO, according to the UNI EN 12662) has been proposed as simple upgrading process on the raw UCO.

## 6 Conclusions

### 6.1 Barriers to innovation

Currently the commercial renewable jet fuel is produced either from hydrotreating of vegetable oils and other fats, or from microbiological synthesis. Aviation renewable fuel needs to meet specific requirements defined by ASTM D7566. Before a synthetic component can be considered for use in jet fuel, it has to be evaluated and approved according to the process defined in ASTM D4054.

This work investigated on used cooking oils as suitable feedstock for hydrotreating or alternative thermochemical treatments. UCO collection and recovery were investigated with the support of SILO SpA, an Italian company. Samples of UCO and commercial sunflower oil have been analysed. The critical parameters in the feedstock have been considered and monitored: Nitrogen, Phosphorous, total contamination, acidity and moisture content. The adoption of UCO as feedstock in hydrotreating is not possible without upgrading/cleaning pre-treatment. 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 an important reduction of Nitrogen and Phosphorous content with a high quality filtration. Despite the achieved improvements, the Nitrogen content of UCO still remains significant (80 ppm).

### 6.2 Recommendations for further research

Despite the experimental campaign on filtration and centrifugation, UCO remains a challenging feedstock for hydrotreating. The high Nitrogen content, even in filtered UCO, is maybe due to the Nitrogen oil soluble proteins, which are present in the used vegetable oil (maybe due to high protein content of the fried food). A more accurate characterization of the Nitrogen sources will be necessary in order to achieve the UCO specifications (i.e. next D2.8 "Development of UCO specification").

Even SILO's esterification process (described in paragraph 3.3) could be adopted as an upgrading route to restore the acidity of the UCO.

As real alternative to hydrotreating, RE-CORD investigated on catalytic conversion of lipid-based feedstock. In particular, RE-CORD adapted its pyrolysis pilot unit to process UCO in order to obtain a bio-intermediate towards further upgrading (e.g. hydrotreating). Next experimental campaign on thermochemical conversion is part of WP2 and will be completed by the end of the project.

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