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# **Deliverable D5.1** Pre-selection catalyst and set-up

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Prepared by	Xander de Jong (KPRT)
Input from	
Reviewed by	Leda Maragoudaki, Kostis Atsonios (CERTH)

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# Abbreviations

ATP	Adenosine triphosphate
GC	Gas Chromatography
GC-MS	Gas Chromatography–Mass Spectrometry
ICP	Inductively Coupled Plasma
LHSV	Liquid Hourly Space Velocity
SAF	Sustainable Aviation Fuel
TAG	Triacylglyceride
XRF	X-Ray Fluorescence



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# 1 Introduction

KPRT was initially the leader of Task 5.1&5.2, performing catalysts pre-screening experiments in their continuous pilot plant reactor placed. However, due to unforeseen difficulty of KPRT to undertake these activities due to unexpectedly lack of experienced catalyst testing staff, that impeded KPRT carrying out this task, all partners decided CERTH to undertake Task 5.2, ensuring the effective execution of the work plan. It was agreed that KPRT would prepare a literature study as input for the catalyst screening (WP 5.2) using extensive experience with refinery operations and Hydroprocessing of both conventional- and bio feedstock including Triacylglycerides and combining it with results from literature. Aim is to select catalyst systems and set operational conditions for the catalyst screening study.

The last step in the BioSFerA project will convert the Triacylglycerides (TAGs) into molecules that can be used in aviation fuel or in/as (marine) diesel. Triacylglycerides are a type of lipid (fat) molecules that are composed of three fatty acids esterified to a glycerol backbone. TAGs are the main storage form of lipids in living organisms and are commonly found in vegetable oils, animal fats, and human adipose tissue. TAGs are an important energy source for the body and can be broken down into fatty acids and glycerol to produce ATP (adenosine triphosphate), which is the energy currency of cells. TAGs are also used in various industrial applications, including the production of biodiesel and other biofuels. Up to date, there are many different thermochemical conversion technologies that are used for the production of alternative fuels from TAGs. Some of them are gasification, pyrolysis, hydrotreatment, hydrocracking etc. Hydrotreating is used in many processing steps in a refinery as it is a versatile process that uses hydrogen and a catalyst to process hydrocarbons in order to:

- Remove impurities such as Sulphur, Nitrogen and Oxygen
- Crack big molecules to smaller ones
- Hydrogenate unsaturated (reactive) bonds in hydrocarbons
- Isomerise or rearrange molecules to improve the specifications of the products (e.g. convert Normalparaffins to Iso-paraffins)

During the hydrotreatment the molecules are first deoxygenated and saturated to become normal paraffins, which can be (selectively) hydrocracked and isomerized yielding branched alkanes. The resulting organic product is a mixture of straight and branched hydrocarbons,  $C_xH_{2x+2}$ , that can be used as drop-in liquid fuel if it meets the requirements.



Figure 1 The Hydrotreatment process as the final step of the BioSFerA concept (Thermocatalytic part)

Triacylglycerides are characterised by a glycerol backbone connected by ester bonds (oxygen atoms) with three carbon chains that are usually straight chains (**normal paraffins**) with an even number of carbon atoms with some unsaturated (double) carbon bonds in the chain.

Fossil jet fuel is a middle distillate, or more specifically the jet fuel fraction of crude oil. It consists of molecules in the range of  $C_8$ - $C_{16}$ . The range is typically a normal distribution where the average  $C_{11}$  is the most present molecule.





In general jet fuel has to be stable so it should consist of non-reactive species with a mixture of different types of hydrocarbons (see Figure 2). The majority of the molecules are paraffinic with single carbon-carbon bonds with some having side-chains (**iso paraffins** or **normal paraffins**) or saturated cyclic (**cyclo paraffins**) and a small part of cyclic molecules with stable double carbon-carbon bonds (**aromatics**).

It is also critical to remove reactive species like olefins (chain with a double carbon-carbon bond) and it may be necessary to remove hetero atoms (like Sulphur, Nitrogen or Oxygen) by hydrotreatment to reduce corrosion and improve water draining of the jet fuel. Sometimes part of the molecules have to be converted to improve engine performance and/or meet the specification of the final product.



Figure 2 Type of molecules in Jet fuel with typical composition [2]

# 2 Thermocatalytic conversion (Hydroprocessing) in a refinery

Petroleum refineries already have a well-developed infrastructure to produce fuels and would not require additional capital-intensive investments to process alternative feedstocks. From this point of view, co-processing of biomassderived feedstocks with petroleum fractions is an attractive option. There is already a good amount of experience in hydrotreating Triacylglycerides to produce (green) fuels. Also, the hydroprocessing of crude based feedstock in refineries is a well-known process. At commercial level, the hydroprocessing of TAGs derived from fats and vegetable oils can be carried out using the same catalyst, reactor type and separation facilities that are used in the (vacuum) gasoil hydroprocessing or hydrocracking in the petroleum refineries. As the TAGs are very reactive compared to fossil fuel products, they can be converted to Jet Fuel or Diesel in existing units (both hydroprocessing and hydrocracking) with the existing catalysts but due to their nature they bring some challenges.

The operational challenges in the hydrotreating of Triacylglycerides are best overcome in a hydrocracker unit as the high content of oxygen and unsaturated bonds leads to a high hydrogen consumption which is orders of magnitude higher than used in hydrotreaters. Also, the associated heat release from the reactions is in the same order of magnitude as a hydrocracker which are specifically designed to handle this. Hydrocracking catalysts are also multifunctional and can be designed to change the length of the carbon chains of the end product. There are several literature articles describing co-processing tests with vegetable oils (also Triacylglycerides) in existing hydrocrackers with existing catalyst systems (e.g. see [3]). Another advantage of the hydrocracker is that in order to mitigate the effects of catalyst poisoning, hydrocracking units are designed with multiple catalyst beds, each of which is designed to remove different types of impurities to protect the (more sensitive) hydrocracking catalyst and maximize the conversion.



# 3 Hydroprocessing reactions with Triacylglycerides

Below is a short (incomplete) overview of the main reactions in hydroprocessing.

#### Catalytic hydroprocessing reactions and reaction pathways of Triacylglycerides

In Hydroprocessing of biobased feedstock, and specifically TAGs, to produce "Hydroprocessed Esters and Fatty Acids" (HEFA) the most dominant reactions are the following:



Figure 3 Hydroprocessing reactions for Triacylglycerides (TAGs)

The main reaction pathways are shown in the figure below. For a more complete overview see [1].





Figure 4 Hydrogenation & Deoxygenation pathways of Triacylglycerides [1]

It is crucial to test the behaviour of the TAG molecules in the first hydrotreatment step (removal of hetero atoms & saturation of the double bonds) as the reactivity & nature/composition of the feedstock depends strongly on the source. The second step is a well-known process. The product from step 1 only determines the chain length of the n-paraffins. Other properties are exactly the same for different sources (both fossil or bio based).

A complete overview of existing and potential strategies to control product selectivity for deoxygenation of fatty acids/esters to biofuels and fatty alcohols over heterogenous catalysts is given in [1]. It is also important to realize that not only the reaction (pathway) is important but also the resulting molecule. An example of this is that the position of a methyl group in an iso-paraffin will influence the freezing point of the product (e.g. 5-methyl-paraffins have lower freezing point than 2-methyl-paraffins). Also see [4].

# 4 Feedstock

In the BioSFerA project biomass is first converted to syngas (CO, CO<sub>2</sub> & H<sub>2</sub>). In the second step, the syngas is converted by fermentation to liquid products in the form of Triacylglycerides (TAGs). In the last step, the TAGs are hydrotreated to be converted into biofuels (Jet Fuel & Marine Diesel).

The produced TAGs (at small scale) for the pilot hydrotreatment testing were characterised, the product was screened on potential contaminants/poisons for hydroprocessing and a mild hydrotreatment test was performed. Based on these tests, decision is made on which purification steps will be used for the TAGs and whether it is possible to further upgrade them using hydroprocessing at lab scale at KPRT and CERTH. The mild hydrotreatment test was done to design the conditions for the pilot plant testing as molecule sizes of the product, reaction temperatures, saturation and (gaseous) by-products give important information for the reactions occurring during the hydroprocessing.



### 4.1 Fatty acids in TAGs

The carbon chain length of the fatty acids in the TAGs determine the main properties of the fuels that can be produced by hydroprocessing. The chain length and number of unsaturated bonds in the fatty acids of the Triacylglycerides was measured and shown in Table 1. Table 1 also contains the composition of 3 other vegetable TAGs for comparison.

Product	<b>C14:0</b> Myristic acid	<b>C16:0</b> Palmitic acid	<b>C16:1</b> Palmitoleic acid	<b>C18:0</b> Stearic acid	<b>C18:1</b> Oleic acid	<b>C18:2</b> Linoleic acid	<b>C18:3</b> Linolenic acid
TAGs produced	< 1%	20-30%	<5%	10-20%	45-55%	5-15%	<5%
Olive oil	<1%	10%	<1%	3%	78%	6%	<1%
Rapeseed oil	<1%	4%	<1%	2%	64%	19%	<1%
Cacao butter	-	25-34%	-	33-40%	26-35%	2-4%	-

Table 1 Experimental results from BioSFerA fermentation trials at BBEPP compared to other vegetable oils

Based on the composition in Table 1 and the reaction pathways, it is possible to estimate the Hydrogen consumption for saturation & deoxygenation reactions which is a critical parameter for the hydrotreatment process. When there is not sufficient hydrogen, the catalysts will start to convert the TAGs into coke. The coke will accumulate on the surface and deactivate the catalyst. Based on the structure and composition of the TAGs the following hydrogen consumption is needed for every TAG molecule for saturation & deoxygenation:

- Saturation, double bonds require 2.7 H<sub>2</sub> (average, calculated from Table 1): fatty acid contains an average of ~0.9 double bond, saturating a double bond consumes one H<sub>2</sub> molecule
- **Deoxygenation, ester bonds require 3 H**<sub>2</sub>: TAG contains 3 ester bonds, breaking an ester bond consumes one H<sub>2</sub> molecule (Propane + Fatty acid products).
- Deoxygenation, oxygen atoms require 0-12 H<sub>2</sub>: TAG molecule contains at least 6 oxygen atoms, removing 1 oxygen consumes hydrogen depending on severity, reaction products/pathway and varies between 0 H<sub>2</sub> (Glycerol + CO or CO<sub>2</sub> products) to 2 H<sub>2</sub> (Propane + CH<sub>4</sub> + H<sub>2</sub>O products) molecules per oxygen atom removed.

### 4.2 Non-Hydrocarbon composition of produced TAG

Especially the non-hydrogen and non-carbon atoms in TAGs can influence the reactions and lifetime of the catalyst as these atoms can deposit and plug the pores in the catalyst particles or block the active sites in the catalyst.

The TAGs are produced in a bioreactor via fermentation, so the product will contain other species, too. Prior to catalyst selection, TAGs are scanned to determine their composition. Several techniques were used to identify different species and gain insight into the different Triacylglycerides and carboxylic acids in the mixture.

Table 2 Compounds above	e the detection limit (Infrared a	and X-Ray Spectroscopy) in TAGs
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Compound		Concentration	Method <sup>1,2</sup>	Remark
Sulphur	S	22 [ppmwt]	ICP, ASTM D5185	
Phosphor	Р	6 [ppmwt]	ICP, ASTM D5185	
Silica	Si	14 [ppmwt]	ICP, ASTM D5185	
Boron	В	7 [ppmwt]	ICP, ASTM D5185	
Chloride	CI	Major	XRF, Q8 method	Qualitative measurement, ~10 %wt

1. ICP = Quantitative analysis with Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)

2. XRF= qualitative analysis with Wavelength Dispersion X-Ray Fluorescence Spectroscopy



In a hydroprocessing pilot plant test it is possible to handle these contaminants on a small-scale test or operation. However, for a commercial scale it is crucial to reduce Si in the product and keep also P, B preferably lower (< 5 ppm). These contaminants (if present in feed) have a significant impact on the catalyst lifetime as they can be absorbed on active sites or plug pores. The qualitative (XRF) analysis also detects a significant amount of chloride. This is also not desirable for commercial operation when present in higher amounts (>5 ppm) in the feed as it can damage the catalyst and equipment used due to the formation of hydrochloric acid (HCI) and ammonium chloride. In short, it is possible to perform hydroprocessing of this material, but, due to the presence of poisons, some catalyst deactivation will be seen in continuous lab-scale operation. Based on these measurements the purification of TAGs after the fermentation step was adjusted to minimise the amounts of the measured components.

### 4.3 Hydrocarbon Characterisation of produced TAGs

The hydrocarbons in the hydrotreatment feed sample should mainly contain Triacylglycerides and maybe some (short) carbon chain acids. Another important aspect is detecting which reactions will occur at different temperatures and estimating the amount of hydrogen needed for the hydrotreatment reactions. For more details on the different reactions and routes during the hydroprocessing of TAGs, see Section 3.

Therefore, the produced TAGs were hydrotreated at mild conditions with a noble catalyst (90 barg, 345 °C with 1% Pt on  $Al_2O_3$ ) in a batch reactor with heptane as solvent. The products in the gas phase and liquid phase give a good indication of the reactions. After hydroprocessing, the molecules are not reactive and can be characterised in more detail. The main components found with InfraRed combined with GC-MS in the liquid phase after the mild hydroprocessing are presented in Table 3.

Carbon #	Identified products	wt%	Remark
12	Dodecane	36.1 %	
	2-n-Heptylcyclopentanone	2.9 %	
	1,1-Bicyclohexyl-2-one	2.8 %	
15	Pentadecane	4.2 %	
16	Hexadecanoic acid	8.4 %	
17	Heptadecane	11.6 %	Main decarboxylation product
18	Dodecylbenzene	2.5 %	Some aromatisation and some deoxygenation
	Octadecane	1.4 %	
	Octadecanoic acid	18.5 %	
21	2,3-DiHydroxypropyl elaidate	0.4 %	Monoglyceride with C18 chain
27	Heptacosane	1.2 %	Paraffin from polymerisation

#### Table 3 Liquid composition from mild Hydrotreatment with 1% Pt catalyst on Al<sub>2</sub>O<sub>3</sub>

Below (Table 4) is the composition of the gas phase after the mild hydrotreatment reactions.

#### Table 4 Gas composition from mild Hydrotreatment with 1% Pt catalyst on AL<sub>2</sub>O<sub>3</sub>

Carbon #	Identified products	mol%	Remark
0	Hydrogen	94.6 %	
1	Methane	0.12 %	Products from Decarboxylation reaction
	CO	1.99 %	
	CO <sub>2</sub>	1.33 %	
2	Ethane/Ethene	0.14 %	Some ethene
3	Propane/Propene	0.14 %	~50% propene
4	Butane/Butene	0.02 %	
5	Pentane/Pentene	0.02 %	
>5	Carbon molecules	0.32 %	
-	Oxygen	0.29 %	



-	Nitrogen	1.03 %	

The composition of the gas phase in the batch reactor after hydroprocessing was analysed with GC. Nitrogen and oxygen are the only hetero atoms in the gas phase but others can/will be absorbed on the catalyst particles or in the liquid phase. It was not possible to prepare a mass balance for oxygen as there was only a very low concentration of water in the gas phase that could not be accurately measured. It was concluded that most of the water was in the liquid phase and absorbed on the catalyst particles.

# 5 Yields & product properties

Renewable fuel in the form of fatty acid methyl esters (produced from transesterification of Triacylglycerides with a selected alcohol) that are not hydrotreated have a higher oxygen content, lower stability and lower heating value than hydrotreated diesel & jet fuel. For marine diesel this is acceptable but it leads to lower performance in engines. For jet fuel it is not possible to meet the minimum specifications without hydrotreatment to remove oxygenates. The composition of the gas and liquid products will depend on the severity of hydrotreatment and the selected catalyst.

**Off-gas** composition is determined by both the composition of the TAGs and the reaction(s) being followed. In general, the gas phase contains propane (C<sub>3</sub>) from the Triacylglyceride backbone, water (H<sub>2</sub>O) from deoxygenation reactions and CO & CO<sub>2</sub> from the decarbonylation/decarboxylation reactions. In the presence of hydrogen, CO and CO<sub>2</sub> can be converted to methane (CH<sub>4</sub>) through the methanation reaction.

**Jet fuel** is the targeted product as it has the highest value but also the most strictly regulated specifications. The two most used jet fuels are, 'jet A' which is manufactured according to ASTM D 1655 in the US and 'jet A1' according to Def Stan 91-091 in Europe. The specifications are almost identical, with small differences in freezing point, acidity and conductivity.



Figure 5 Typical composition of Jet fuel [2]

The final product must meet all specifications according to ASTM D 1655. The most difficult ones to meet are shown in Table 5. **Figure 5Error! Reference source not found.** shows a typical composition meeting all Jet fuel specifications.

#### Table 5 Main specifications for Jet Fuel

Specification	Target
Density (15 °C)	775-840 [kg/m³]
Freezing point	< -47 [°C]
Flashpoint	>38 [°C]
Viscosity (-20 °C)	< 8 [mm²/s]
Heating value	> 42.8 [MJ/kg]
Aromatic content	8-25 [vol%]

**Marine diesel** contains molecules with higher boiling points that are too heavy for jet fuel. It consists of molecules in the range of  $C_{14}$ - $C_{29}$ . The range is typically a normal distribution with  $C_{17}$  being the most dominant molecule. From this distribution it is also clear that there is an overlap with jet fuel. As the TAGs predominantly contain carbon chains with  $C_{16}$ - $C_{18}$ , longer chains can only be formed by polymerisation (double bonds reacting) or bonds with oxygen (condensation). Specifications for marine diesel depend on the intended product being targeted. Typically, the severity and number of specs for marine diesel, as given in ISO 8217 Table 1, are much lower (easier to meet) than those for jet fuels. Additionally, marine diesel can meet these specifications with a broader range of composition compared to jet fuel.

The primary objective is to produce jet fuel, which is considered the most valuable product. Therefore, the focus is on generating molecules with the appropriate composition and carbon chain length. Longer carbon chains are typically directed towards the marine diesel product. To meet the general specifications, the composition of the different hydrocarbon species also has to be balanced (mild hydrotreatment will only yield normal-alkanes). During hydrotreatment it is difficult to produce aromatic compounds. However, as Sustainable Aviation Fuel (SAF) will be a drop-in fuel, the aromatics can also be sourced from other blend components to meet the requirements for jet fuel.

# 6 Hydroprocessing of produced TAGs

### 6.1 Types of metal catalysts

Main objective for the hydroprocessing in the BioSFerA project is to produce Jet Fuel & (Marine) Diesel. The most desirable is Jet Fuel, so for the produced TAGs this means:

- Saturation of hydrocarbons (Hydrogenation) and removal of heteroatoms like S, O and N to reduce corrosivity, reactivity and improve water draining/removal
- Optimization of molecule composition to meet the main specifications
  - Hydrocracking: right chain length & composition (viscosity, density & heating value)
  - Isomerization: convert n-paraffins to iso-paraffins (improve cold properties)

Several types of metal catalysts can catalyse these reactions.

**Transition metal sulphide** catalysts are widely used in petroleum refining for hydroprocessing to selectively remove heteroatoms in (fossil) fuels, saturate olefins and convert the molecules by cracking or reconfiguring (isomerisation & ring formation) the hydrocarbon chains. Therefore, the commercial sulphide catalysts (e.g. Ni, Mo and Co sulphides) are also a logical choice for the hydroprocessing of TAGs as they have a good balance between





cost, functionality and stability. Disadvantage of these catalysts is that the feedstock should contain some sulphides to prevent deactivation of the catalyst due to leaching of sulphur.

**Noble metal** catalysts (e.g. Pt, Pd and Ru) can also be used as they are very active, have a good catalytic stability and are also widely applied in (commercial) deoxygenation and cracking due to their high activity for H<sub>2</sub> dissociation to cleave C-O & C-C bonds. Main advantage is that due to their high activity they can work under mild conditions (low pressure & temperature). However, as these metals are rare, the cost of the catalysts is relatively high.

Recent studies [1], [4] contain a good summary of the different tests performed for hydrotreating natural oils with both transition metal sulphides and noble metal catalysts to produce biofuels. The main conclusion from these studies is that transition metal sulphide catalysts are a better option in hydroprocessing of both bio & fossil oils because they have a better balance between catalyst cost, availability and processing cost. Transition metal catalysts need a higher severity as they exhibit lower catalytic activity than noble metal catalysts. Only for the isomerisation of paraffins in the Naphtha range (C<sub>4</sub>-C<sub>10</sub>), Pt is used as the reactivity of these short paraffins is lower than for longer paraffins. In general, it is required that the catalysts have high metal dispersion, large pore sizes (or easy access to active sites) and sufficient acidity [4].

Hydro conversion of fossil feedstock typically requires higher reaction temperatures as bio-based feedstocks are more reactive. Therefore, the transition metal sulphide catalysts used in many existing hydroprocessing reactions for fossil fuels in a refinery will be able to convert bio-based lipids as well. Thus, it will also be possible to use **commercial catalysts** where the desired biofuels are produced using process conditions typically encountered in a refinery process. Furthermore, since TAGs are large molecules, diffusion of the products inside the catalyst particles/pores is important.

It is a known fact that the conditions for hydroprocessing of vegetable oil will vary depending on the specific oil being processed and the desired product characteristics, but some general conditions for Hydroprocessing of fossil fuels (sometimes including co-processing) in a refinery are:

- Temperature: Hydrotreatment (desulphurisation, denitrification, deoxygenation and saturation) is typically carried out at temperatures ranging from 150-350°C. Hydrocracking to reduce molecule size is performed at slightly higher temperatures (350-400 °C).
- 2. **Pressure**: The process is carried out at elevated pressures, between 40-200 barg, to ensure the availability of a sufficient amount of hydrogen during the hydrotreatment and hydrocracking process and depends on hydrogen consumption, selected catalyst and product specifications.

It is vital to choose the temperature, reaction time and pressure for the selected hydroprocessing catalyst but below are also other aspects influencing the hydrotreatment.

### 6.2 Catalyst poisoning

During hydrotreatment, catalyst poisons can accumulate on the surface of the catalyst and affect its activity, reducing its efficiency and effectiveness and, consequently, its lifetime. Catalyst poisons include:

- Sulphur is a common impurity in hydrocarbon feedstocks and can accumulate on the surface of noble catalysts, blocking active sites and reducing their effectiveness. Transition metal catalysts are used in sulphide form, so for these catalysts, some sulphur in the feed is needed to prevent leaching & deactivation of the active sites.
- **Nitrogen** is another impurity that can accumulate on the surface of the catalyst, reducing its activity. Especially acid activity for hydrocracking & isomerisation is impacted by the presence of (organic) nitrogen in the feedstock.



- **Metals such as Nickel, Vanadium and Iron** can also accumulate on the surface of the catalyst, interfering with its activity and reducing its effectiveness.
- **Chlorine/Chloride** will react with hydrogen to form hydrogen chloride, which can reduce catalyst activity, and corrode the catalyst and equipment.
- **Olefins** are very reactive and produce a lot of heat during hydrogenation which can lead to local hot spots and unwanted reactions (e.g. coking) resulting in blocking the catalyst pores.
- **Coke** is a carbonaceous material that can accumulate on the surface of the catalyst, reducing its activity over time.
- **CO/CO**<sub>2</sub> in the feed but also as reaction product can poison/reduce the activity of cobalt and noble metal catalysts if they are not protected.

### 6.3 Effect of reaction conditions

Hydrotreatment of bio-based lipids involves the removal of oxygen-containing compounds such as free fatty acids and other impurities to improve the quality of the oil. The process conditions for the hydrotreatment of bio-based lipids depend on the targeted reactions to meet the selected specifications and the selected catalyst. The effect of reaction conditions like temperature, pressure, residence time & ratio of hydrogen/oil on hydroprocessing of biobased lipids has been described in many studies [1], [4]. The main operating conditions for transition metal catalysts are described below.

The optimum **temperature** range for vegetable oils over Ni-based catalysts is reported to be between 250-400 °C. At the lower end of the temperature range, the goal is typically to remove heteroatoms and achieve saturation, while the higher end of the range is for the conversion of the hydrocarbon chains (isomerization and cracking). If the objective is to produce jet fuel, both isomerization and hydrocracking activities are needed.

In hydroprocessing, and especially for hydrocracking reactions, medium to high **pressure** is commonly employed. These reactions are promoted by hydrogen and also consume a significant amount of  $H_2$ . Therefore, it is preferred to operate at medium to high pressures, typically ranging from 80 to 200 barg. At these pressures, Ni is the optimal catalyst for hydroprocessing and also hydroconversion reactions in existing refinery processes. Increasing the pressure promotes the isomerization and hydrocracking reactions as the formation of hydrogen radicals on the catalyst surface is enhanced.

**Hydrogen to Oil ratio** is set to ensure that there is sufficient  $H_2$  for all the reactions. When hydrogen is not enough, the catalysts start to convert the TAGs into coke. Coke can accumulate on the surface and deactivate the catalyst. To prevent this, the composition of TAGs is measured to estimate the hydrogen consumption and ensure that the  $H_2$ /oil ratio is properly chosen. In Paragraph 4.1, the hydrogen consumption for saturation and deoxygenation is estimated based on the composition of TAGs and the reaction pathways.

In general, fatty acids have straight carbon chains (n-paraffins) that are too long for jet fuel, so they have to be cracked and converted to other hydrocarbons. Therefore, reaction conditions are selected for conversion (hydrocracking & isomerization) as well, so the H<sub>2</sub> consumption per TAG molecule will be high (see Section 4) but due to the pressure & temperature the Methanation reaction will not be complete. Thus, the main products will be CO/CO<sub>2</sub>, CH<sub>4</sub>, propane & water, and the hydrogen consumption will increase due to hydrocracking reactions. Therefore, the estimation for H<sub>2</sub> consumption is: 2.7+3+6=**11.7 mol H<sub>2</sub>/ per TAG molecule** for **saturation & deoxygenation**, while other conversion reactions will increase the hydrogen consumption (e.g. hydrocracking, isomerisation reactions and other impurities). During hydro conversion (hydrocracking & isomerisation) tests of waste cooking oil [5] [8], Jatropha oil [6] & palm oil [7], an optimum H<sub>2</sub>/feedstock molar ratio of 12.8 was found which is in line with the theoretical calculation. A general finding was that the conversion increases to a certain extent with increasing the H<sub>2</sub>/oil ratio. The optimal H<sub>2</sub>/oil ratio has to be determined by experimentation and should be above the calculated ratio as the project aims to convert the hydrocarbons that will need a higher severity.





**Space velocity** has a major effect on the conversion (hydrocracking & isomerisation), but a smaller effect on saturation and deoxygenation. Higher amounts of jet fuel components can be obtained with low space velocities that are typical for hydrocracking reactions (LHSV  $\sim$ 1-2 hr<sup>-1</sup>).

# 7 Conclusions

The processing of Triacylglycerides (TAGs) in existing refinery assets using available catalysts is a strategy that is already used by many refineries to reduce CO<sub>2</sub> emissions and/or to meet governmental mandates for renewable fuels in their products. (Co-)Processing of renewable feedstocks in hydrotreaters is widely used especially for diesel production to remove hetero atoms (e.g. oxygen and nitrogen) and saturate reactive double bonds. Thus, there is a huge amount of literature available for this topic. Nevertheless, in hydrotreaters the hydrocarbon chains do not change. Therefore, hydrocrackers are well-suited for the production of products within the BioSFerA concept as they are the most versatile units in a refinery and are able to overcome operational challenges related to hydrogen consumption, heat generation (exothermic reactions increase the temperature), contaminants and separation of renewable products in distinct streams (Jet Fuel and Marine Diesel).

The hydrocracker is particularly suitable for jet fuel production because, in addition to performing similar functions as hydrotreatment, it possesses the capability to modify the composition of hydrocarbon molecules. The TAGs contain predominantly  $C_{16}$ - $C_{18}$  side chains of normal paraffins, which require conversion (e.g., into iso-paraffins) and fragmentation into shorter carbon chains to optimize the product mixture and meet the specifications of the desired products (Jet fuel and Marine Diesel).

In order to minimise process modifications or investments in the existing hydrocracker units, it is also possible to co-process renewable feedstock, which is a strategy that helps mitigate the impact of known bottlenecks or limitations in the refinery. Adding a percentage of renewable fuels to the final products sold is also in line with government requirements. The activity requirements for catalysts involved in processing renewable fuels are lower compared to those for conventional fossil fuels, primarily due to the higher reactivity of renewable fuels. This co-processing can also serve as means to establish a baseline performance and effect on operation when introducing a certain amount of renewable feedstock into an existing hydrocracker.

Based on the composition of the TAGs, mild hydrotreatment tests in a batch reactor, actual experience from catalyst testing (see publications by CERTH [9]-[19]), refinery operations and information from literature, it was possible to select catalysts, estimate the process conditions and decide the parameters that are interesting to investigate during the pilot plant testing. It was agreed to perform the tests using real catalysts and process conditions employed in the existing (fossil) refineries. At later stages, it is also possible to conduct tests with biorefinery catalysts developed by different catalyst suppliers.



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## Annexes

### Results of TAG analysis

### Results from small-scale batch test (sample 2022-12906)

Fatty acid profile	C14:0 Myristic acid	C16:0 Palmitic acid	C16:1 Palmitoleic acid	C18:0 Stearic acid	C18:1 Oleic acid	C18:2 Linoleic acid	C18:3 Linolenic acid
Experimental results from BIOSFERA trials at BBEPP	< 1%	20%-30%	< 5%	10% - 20%	45% – 55%	5% – 15%	< 5%
Wild-type Y. <i>lipolytica</i> W29 on glucose (DOI: 10.3390/microorganisms8071054)	-	23%	6%	14%	39%	16%	1%
Y. <i>lipolytica</i> W29 on glycerol (DOI: 10.4141/CJAS2013-052)	-	6%	2%	1%	56%	27%	6%
Peanut oil (DOI: 10.15414/jmbfs.2014-15.4.3.231-237)	< 1%	9%	< 1%	4%	59%	20%	< 1%
Rice oil (DOI: 10.15414/jmbfs.2014-15.4.3.231-237)	< 1%	15%	4%	2%	45%	30%	< 1%
Olive oil (DOI: 10.15414/jmbfs.2014-15.4.3.231-237)	< 1%	10%	< 1%	3%	78%	6%	< 1%
Rapeseed oil (DOI: 10.15414/jmbfs.2014-15.4.3.231-237)	< 1%	4%	< 1%	2%	64%	19%	8%
Cacao butter (Naik and Kumar, 2014)	-	25% - 34%	-	33% - 40%	26% - 35%	2% - 4%	-

Test		Inspec	tion		Method	U	nit Result
401	Multielement Determination of Lubricating Oils and Base Oils by ICP ASTM D 5185						
		%-mass		mg/kg		mg/kg	
	Ba	<0.0005	Al	<1	V	<1	
	Ca	<0.0005	Cr	<1	Pb	<1	
	Mg	<0.0005	Cu	<1	В	7	
	Р	0.0006	Fe	<1	Mo	<1	
	Zn	<0.0005	Si	14	Sn	<1	
	S	0.0022	Na	<1	Ti	<1	
			Ni	<1			
1560 2905	Density at 15 ° Analysis of com	C aplex samples (Spectroscopy, IR)			ASTM D 4052 KPI 121	g/ml	0.9159
	Results						NO DATA
	Testtime					hour	1.5
	The infrared spectra in combination with GC-MS results indicate the presence of the following compounds:						
	<ol> <li>Triglyce</li> <li>Terephth</li> <li>1,2-Benz</li> <li>Oleic ac</li> <li>2-Decena</li> <li>n-Hexade</li> </ol>	ride (mainly glyceryl tri-ol alic acid, di(2-ethylhexyl) enedicarboxylic acid, diisoo id 1, (E)- canoic acid	eate) ester ctyl ester				
4652 4790	Water, ppm w l XRF qualitative	KF Proc. C (with KF-Oven red.interferer analysis	nce)		ASTM D 6304 KPI 178	mg/ł	g 325 NO DATA
	Major >10%: Minor 1-10% Trace <1% :	( P, S, Cl, Cs ) : Si, Cu 					

### Results from pilot plant tests (sample 2023-03828)

Similar as results above, with the difference that XRF results show no Chloride and Phosphorus appears to be a Minor instead of Major compound.

