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# Deliverable D5.4
## Validation of TAG upgrading technology in industrially-relevant scale

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**Document Details**

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# Contents

# 1 Introduction

The current deliverable is a continuation of deliverables 5.2 and 5.3 from WP5. In deliverable 5.2, three different catalytic systems were investigated for the hydroprocessing of TAGs. The results have shown that the optimum catalytic system was No. 3 because it has led to high jet and bunker diesel yields and presented the highest potential for optimization. However, during the pre-screening tests (Task 5.2), only three operating conditions were tested with the catalytic system No. 3. To that aim, on deliverable 5.3 the effect of different operating parameters with the optimal catalytic system No. 3, was explored to further optimize the TAGs hydroprocessing process. Based on the results of deliverables 5.2 and 5.3, the main task of deliverable 5.4 is the scaling-up of the process on a TRL5 hydrotreatment plant to produce 1-barrel bunker and 1-barrel jet fuel.

It should be mentioned here that, due to the limited TAGs feedstock, a Model Compound (MC or simulated feedstock) that was created via a blend of 4 commercial vegetable oils, was employed to simulate the TAGs as closely as possible. All the experiments in Task 5.4 were performed with the Model Compound feedstock.

# 2 Methodology

## 2.1 Experimental Scope and Procedure

The main objective of the current deliverable is the production of 1-barrel jet and 1-barrel bunker sustainable fuel via hydroprocessing of microbial oil. For the current scope a TRL5 hydrotreatment plant of CERTH was utilized. The optimal catalytic system obtained from Task 5.2 as well as the optimal operating window obtained from Task 5.3 were used. The produced total organic liquid product from TRL 5 hydrotreatment unit was further fractionated in a batch distillation unit of CERTH, aimed the separation of jet and diesel fuel fractions. The resulting renewable fuels were devaluated and their properties were compared with the specifications of Jet A1 (ASTM D1655), DMA marine diesel, EN 590 for road transport diesel and EN 15940 for paraffinic HVO fuels.

## 2.2 Feeds & catalysts

The main target of the current deliverable is to validate the TAGs upgrading technology on industrial relevant scale. To that aim a Model Compound feedstock that was prepared in Task 5.2 was utilized. The real TAGs as well as the Model Compound feedstock are presented in Picture 1. For the target of the current deliverable, approximately 300 litres of the Model Compound feedstock were prepared by blending for different commercial oils as described in detail on Task 5.2.

*Picture 1 Photos from the real TAGs on the left and from the Model Compound feedstock on the right*

The properties of both TAGs and Model Compound feedstock (MC) are presented in Table 1. It is observed that the Model Compound feedstock properties match with the properties of the real TAGs. More specifically, the density between the two feeds is very close, approximately ~0.91 g/ml. In addition, the elemental composition and the molecules (TAGs) in the products are the same in the Model Compound and the produced TAGs. The sulphur content of both feeds is below 100 wppm, more specifically for the TAGs the S content is 65.4 wppm and for the MC is 2.84 wppm. However, it should be noted here that the sulphur in the MC increased from 2.84 wppm to 784.5 wppm and for the TAGs increased from 65.4 to wppm to 863.3 wppm, during the experiments, with the addition of the DMDS, as the catalyst provider instructions mentioned that the S content of the feed should be higher than 700 wppm. DMDS is necessary to increase the sulphur content of the feed when Sulphided catalysts are used in the process. Furthermore, the Higher Heating Value (HHV) is close to 40 MJ/kg for both feedstocks. Finally, the mass recovery curve of the two feedstocks is presented in Figure 1, where it is observed that the two feedstocks consist of heavy molecules that need to be hydrocracked in order to lead to jet and bunker diesel range hydrocarbons.

*Table 1 TAGs and Model Compound properties*

| Properties | Units | TAGs | Model Compound |
|---|---|---|---|
| Density at 15°C | g/ml | 0.9159 | 0.9188 |
| Sulphur | wppm | 65.4 | 2.84 |
| Hydrogen | wt% | 11.75 | 11.86 |
| Carbon | wt% | 75.37 | 76.9 |
| Nitrogen | wppm | 87.6 | 9.3 |
| Oxygen | wt% | 12.86 | 10.54 |
| Water dissolved | wt% | 0.373 | 0.026 |
| TAN | mgKOH/g | 32.21 | 0.51 |
| Viscosity at 40°C | cSts | 46.24 | 35.46 |
| H/C ratio | - | 0.155 | 0.154 |
| O/C ratio | - | 0.170 | 0.137 |
| HHV* | MJ/kg | 40.01 | 40.88 |
| **Simulated Distl. Curve** | | | |
| Initial boiling point (IBO) | °C | 338 | 424 |
| 10 wt% | °C | 394 | 589 |
| 30 wt% | °C | 598 | 600 |
| 50 wt% | °C | 604 | 606 |
| 70 wt% | °C | 610 | 611 |

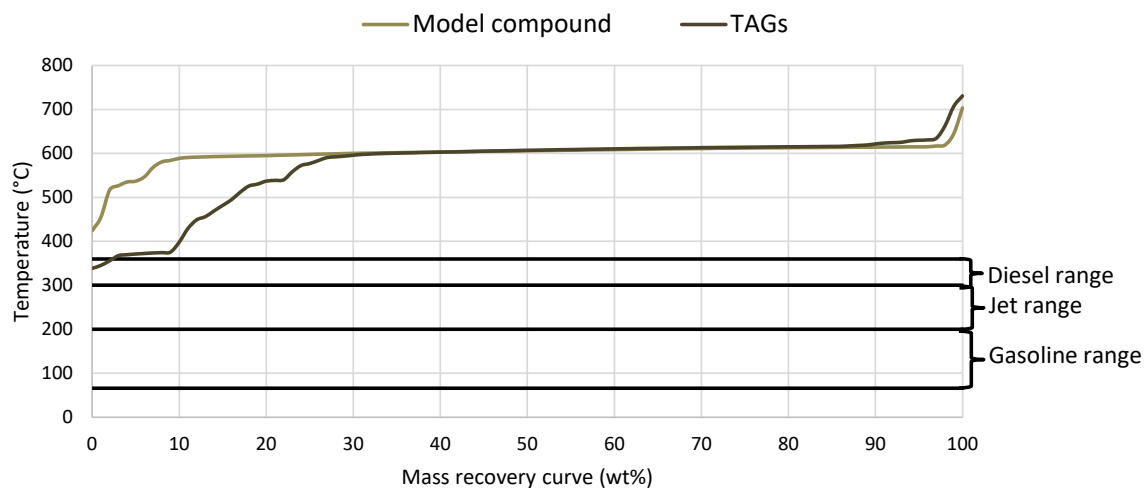| 90 wt% | °C | 621 | 614 |
|---|---|---|---|
| 95 wt% | °C | 628 | 615 |
| Final boiling point (FBP) | °C | 739 | 703 |
| *Heating value was calculated based on [2] | | | |



*Figure 1 Mass recovery curve of Model Compound and TAGs*

For the current investigation the optimum catalytic system from Task 5.2 and the optimal operating conditions from Task 5.3 were utilized. To maintain a desired Liquid Hourly Space Velocity (LHSV), the catalysts were diluted with glass beads for achieving good heat and mass transfer, while disabling feed channelling. Catalyst presulphiding was performed by a procedure defined by the catalyst manufacturer utilizing LAGO (Light Atmospheric Gas Oil) with DMDS. As the catalysts are commercial, no further details for the composition and structure of the catalysts could be provided. During the experiments, the Model Compound feed was mixed with a small quantity of DMDS (Dimethyl Disulphide) as it is necessary to maintain a certain sulphur level (up to 2 wt%) in the hydrotreating feedstock when a Sulphiding catalyst is employed. DMDS was selected as a hydrogen sulphide source, which can be in an industrial application partially replaced by $H_2S$ recovery from the off-gas from conventional hydrotreating processes [1] or the TAGs can be mixed with conventional (Fossil) fuels and co-processed in existing refinery systems.

## 2.3 Analysis

For the evaluation of the feed and liquid products, daily samples were collected and analysed in the CPERI/CERTH analytical laboratory. Several analyses were performed for products as well as for the corresponding feed samples. The liquid products were analysed off-line in the analytical laboratory of CERTH using existing analytical infrastructure. The gaseous products were analysed online via an on-line GC 7890 Agilent analyzer enabling accurate estimation of the $H_2$ consumption during oils hydrotreatment. In case of the liquid samples, the density was determined via ASTM D-4052, while the distillation curve was estimated via ASTM D-7169. Hydrogen and carbon content were determined using the LECO ASTM D-5291 method. The sulphur content was determined using a XRFS analyzer and ASTM D-8453 method. The oxygen concentration was indirectly calculated assuming a negligible concentration of all other elements in the measuring liquid sample. The water content was found via the ASTM D-1744 while the total acid number (TAN) was calculated via the ASTM D-664. Kinematic viscosity was determined via ISO 3104, cetane index on the products, via the ASTM D-976 and Pour point via ASTM D-97.

The HHV was estimated according to the following equation provided by Channiwalla et al. [2] given below:

HHV (MJ/Kg)=0.3491C+1.1783H-0.1034O-0.0151N+0.1005S-0.0211ash

Where, C, H, O, N, S, are the corresponding elemental composition on dry basis wt%. It was assumed that the ash content is zero in all samples.

For off-line characterisation of the products at Q8Research the mixed product from CERTH was first separated with certified equipment according to the ASTM 2892 (Standard Test Method for Distillation of Crude Petroleum (15-Theoretical Plate Column)). The fractions were Light Kero (BP 120-150 °C, included Naphtha and light end of Kero fraction), Kero (Medium BP 180-280 °C and Heavy 280-300 °C) and Diesel fractions. As the separation is done according to the ASTM standards, they have typical boiling point curves for refinery products. As the products are Parrafinic in nature, some key properties were selected to analyse the samples.

The density at Q8Research was measured using an ASTM D-4052 method a Simulated Distillation by GC according to EN-15199 method. For the light fraction the hydrocarbon composition was measured by GC using UOP-551 and inhouse databases. Electrical Conductivity was determined via ASTM D-2624, Flashpoint using ASTM D-93, Freezing point using ASTM D-5972 or Cloud point using ASTM D-5773 and Kinematic viscosity was determined via ISO 3104.

## 2.4 Testing Infrastructure

For this study, all the hydrotreatment experiments were carried out in a TPL5 hydrotreatment plant of the Chemical Process and Energy Resources Institute (CPERI) at the Centre for Research & Technology Hellas in Greece (CERTH), which is schematically depicted in Figure 2. This unit is a small industrial system which is operating to generate information about the behaviour of the system for use in design of larger facilities. Photo from the TRL5 hydrotreatment pilot plant of CERTH is depicted in Picture 2.

The current unit consists of two stainless steel continuous flow tubular reactors in line (with available volume of 555 cm$^3$ each, 28 mm inside diameter and 955 mm length). Each reactor contains five independent heating zones. The temperature of each catalyst bed is monitored and controlled via five independent thermocouples placed inside a thermo-well. The hydrogen flowrate is regulated by two mass flow controllers, whereas the liquid feed system is regulated by a high-pressure liquid piston pump. After the liquid feed is mixed with high pressure hydrogen at a regular T-joint, it enters the first fixed-bed reactor, where the desired hydrotreating reactions take place. The product exits the first reactor and enters the second downflow reactor. After the second reactor the product condenses and is finally flashed via a high-pressure low-temperature (36° - 60°C) separator, where the gas and liquid phase products separate. The gaseous product flowrate is measured by a wet-test meter and gas concentrations are analyzed off-line via a GC gas chromatograph. The gas flow rates and concentrations together enable mass balance and hydrogen balance calculations. The liquid feed flow capacity of the TRL 5 unit is from 250 ml/h to 600 ml/h depending on the catalyst volume and the desired LHSV.

For the current investigation the optimal catalytic system obtained from Task 5.2 was loaded on the reactor. The loading plan from both reactors is depicted in Figure 3. As far as the loading plan of reactor A is concerned, a catalyst specialized on HDO (hydrodeoxygenation), HDS (hydrodesulphurization) and HDN (hydrodenitrogenation) reactions was loaded at the top part. In the middle area of the reactor, a catalyst specialized on HDO and saturation reactions was loaded while at the bottom part the same catalyst with the top part was utilized as depicted in Figure 3. In case of reactor B, a catalyst specialized on isomerization and dewaxing reactions was loaded at the top and mid area of the reactor while at the bottom area a hydrocracking catalyst was selected. The operating conditions during the experiments were based according to the findings of Task 5.3. More specifically, the reactor pressure was set to 1500 psi, the temperature on both reactors was set at 330° and 350°C respectively, the H$_2$ to oil ratio was set to 5000 scfb and finally the liquid hourly space velocity was set to 1 hr$^{-1}$. To produce 300 litres of hydrotreated total organic liquid product two experiments were performed. The first experiment lasted 7 DOS (Days On Stream) leading to a production of 50 litres of organic liquid product and 4.3 litres of aqueous phase. The second

experiment lasted 33 DOS leading to a production of 265.5 litres of organic liquid product and 23.4 litres of aqueous phase. More details about the products of the two experiments will be presented on the following "Results" section below. It should be noted here, that 20 litres of hydrotreated organic liquid product was sent to KPRT laboratory for further fractionation and analysis.
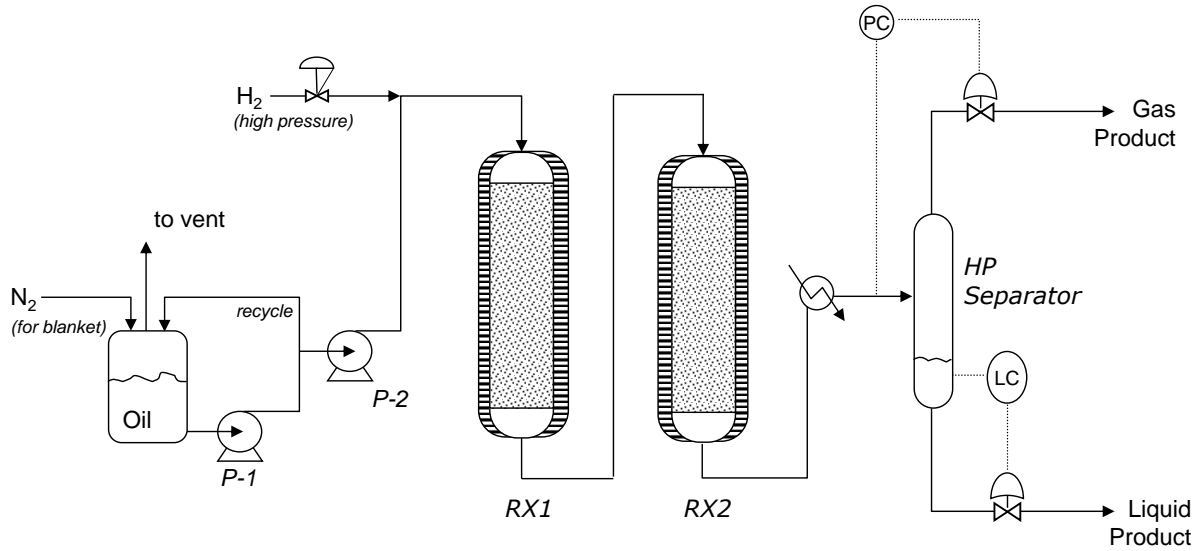


Figure 2 Simplified diagram of the VB02 hydroprocessing pilot plant at parallel mode
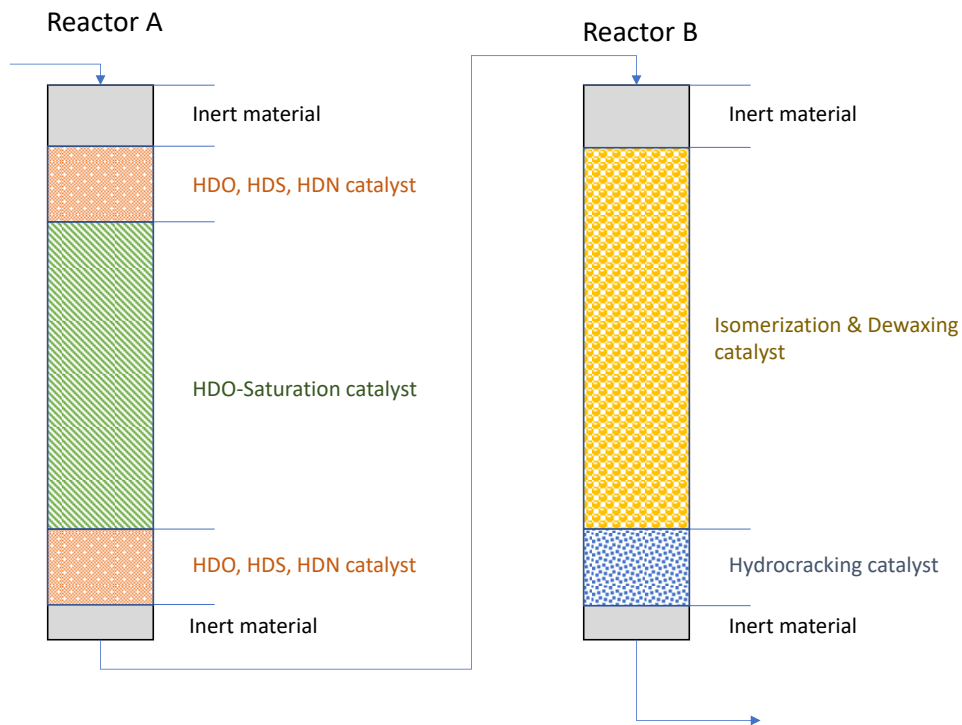


Picture 2 TRL 5 Hydrotreatment pilot plant at CERTH

*Figure 3 Catalysts loading plan*

For the fractionation of the total organic liquid product obtained from the TRL 5 hydrotreatment plant, a batch fractionation unit of CERTH was employed. The simplified plot from the batch fractionation unit is presented in Figure 4 while a photo from the unit is depicted in Picture 3. The current unit is a batch distillation unit with a minimum capacity of 10 litres and a maximum capacity of 20 litres per batch. The duration of one batch experiment is 8 hours of continuous operation. The operation is based under vacuum condition and can reach up to 365°C. The unit consists of the feed tank with a capacity of 30 litres, the fractionation column and the liquid product Flask with a capacity of 20 litres.
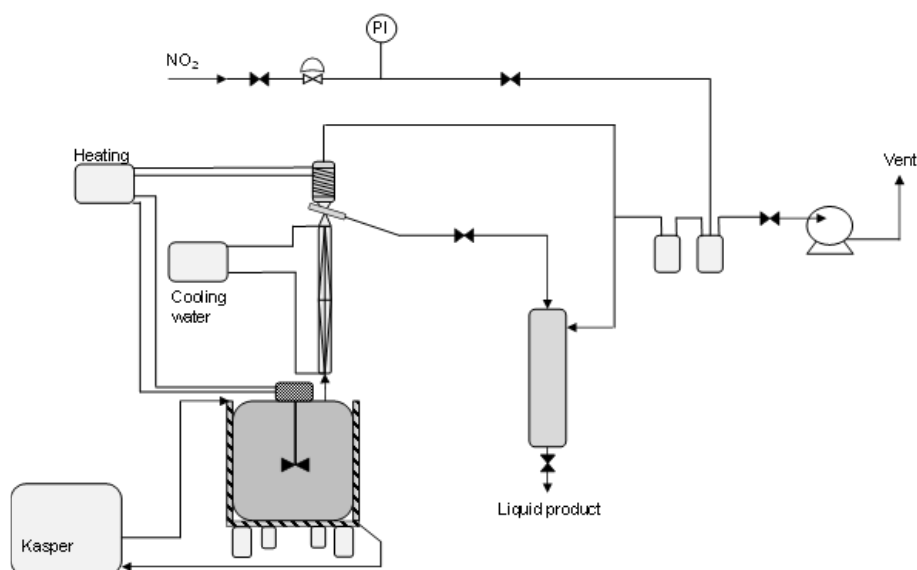


*Figure 4 Simplified diagram from the batch fractionation unit*

*Picture 3 Batch fractionation pilot plan at CERTH*

As already mentioned, 20 litres of the produced organic liquid product were sent to KPRT for product separation in order to compare the results from CERTH fractionation unit with the results from KPRT fractionation unit for better product evaluation, Photo from KPRT unit is presented in Picture 4.The unit is designed according to international standards (ASTM D-2892) that mimics a distillation column with reflux and 15 trays that mimics actual separation by distillation in a refinery. The system is fully automated and will slowly increase the temperature in the feed container. The vapors are sent into a distillation column with a set reflux so they are cooled back to a programmed temperature. The vapors from the top of the distillation column are cooled so they condensate and are send to a (selected) sample holder. As the temperature in the feed container and at the top of the distillation column slowly increases more heavy molecules will evaporate and condensate so at programed temperatures the sample holders are automatically switched to gather a heavier fraction. The liquid that remains after heating (residue) is the heaviest fraction (in this case Diesel).

*Picture 4 Fractionation unit of KPRT*

## 2.5 Storage stability study

Some of the hydrotreated product (organic liquid product) obtained from Task 5.3, with the TAGs, was stored for 6 months in an air tight metal container under a shed at ambient conditions to evaluate its stability over time. Storage containers are depicted in Picture 5. The weather conditions during storage were mild (average annual temperature ~19.4 °C, moisture content ~53,4 %wt). Samples were taken monthly and their stability was characterised by visual inspection, water content (WC), TAN, viscosity (measured at 40°C) and density (measured at 15°C). Before sampling the container was shaken to ensure homogeneity. The results from the storage stability study are presented on the results section below.



*Picture 5 Storage containers with upgraded TAGs*

# 3 Results

## 3.1 TRL5 Scale-up - production

The experiments performed on Task 5.3 on TRL3 unit have shown that the MC TAGs can simulate the TAGs with high accuracy leading to similar organic liquid products. To that aim, for the purpose of the current deliverable the Model Compound feedstock was utilized to produce the targeted fuels due to the limited availability of the real TAGs. As already discussed in the methodology section, two production runs (experiments) were performed on TRL 5 pilot plant. The first experiment had a duration of 7 DOS (Days On Stream) while the second experiment lasted 33 DOS. The resulting product from both experiments is a two-phase liquid product that consists of the organic and the aqueous phase. Water content analysis on the aqueous phase has shown that it consists of 99 wt% of water, thus no further analysis was performed on the aqueous phase. The two phases were separated via mechanical separation under gravity. The organic liquid product is the targeted upgraded TAGs product and is depicted in Picture 6. In total, 315.5 liters of organic liquid product were produced from both experiments. It should be noted here that 20 litres of the organic liquid product were sent to KPRT laboratory for fractionation in order to separate the fractions of gasoline, jet and diesel. This was agreed between CERTH and KPRT as the KPRT facilities are equipped with a high efficiency batch fractionation unit according to international standards (ASTM D2892 & D5236). The remaining 295.5 litres of the total organic liquid product were fractionated on the batch distillation unit at CERTH that was described in detail in the previous section 2.4 of this deliverable.



*Picture 6 Organic liquid product*

An average mass balance from the TRL 5 hydrotreatment unit operation is presenting in Table 5. It is easily observed that the mass closure is 97%, this is due to the measurement errors from the different analytical instruments that are used in order to calculate the mass flows between the products and the feed. However, for a TRL 5 pilot plant the 97% mass balance closure is very high. Furthermore, it is observed that from 1 g of feed, 0.87 g of organic product are produced as the aqueous phase is approximately 10 %v/v of the total liquid product. The organic phase of all days on stream was blended leading to a total organic liquid product of approximately 315.5 liters.

The operation of TRL 5 unit as well as the catalyst life was monitored via the sulphur and oxygen content in the daily products. Figure 5 presents the sulphur content from all products during the second run with a duration of 33 DOS, including also the max limits for EN590 specifications for road transport market diesel and the max limit for EN 15940 specifications of paraffinic fuels for comparison reasons. Oxygen content with days on stream is presented in Figure 6. According to the results of sulphur content, the catalyst life as well as the operation of the unit was constant during the 33 days of run. In general, the sulphur content in the products was very low and below

the max limits of EN 590 and EN 15940 specifications. Furthermore, according to Figure 6, the oxygen content remained very low and more specifically below 2.0 wt% confirming once again the catalyst activity. In addition, no DP was observed during the operation neither any coke formation on the catalyst. These results are very important as they can confirm that the described technology was easily scaled-up to TRL5 unit moving the technology one step closer to commercialization.

*Table 2 Average mass balance from TRL 5 hydrotreatment plant*

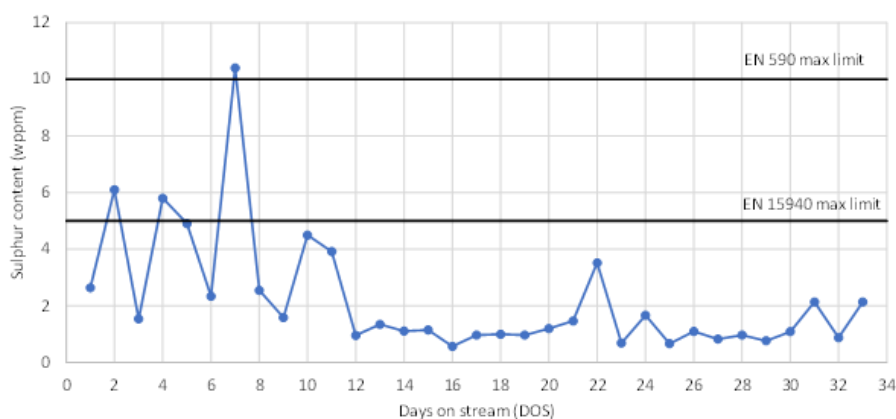|  | Units | Mass Flows |
|---|---|---|
| Liquid feed | g/h | 344.5 |
| Hydrogen feed | g/h | 30.7 |
| Liquid organic product | g/h | 299.8 |
| Aqueous liquid product | g/h | 33.3 |
| Gas product | g/h | 31.4 |
| Mass balance closure | % | 97.1 |



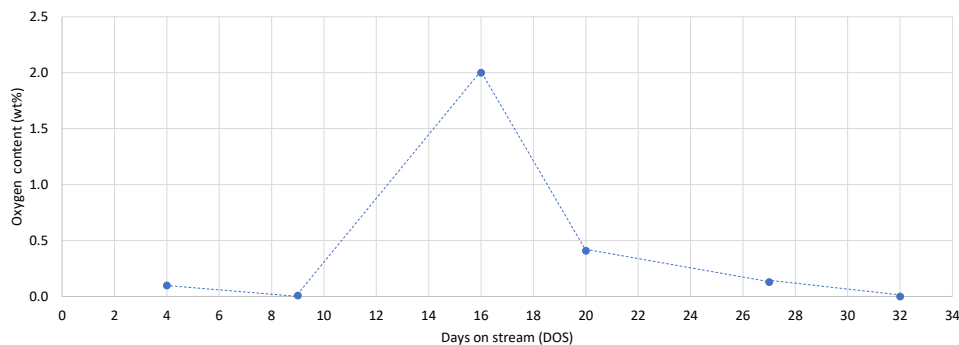*Figure 5 Sulphur content with DOS*



*Figure 6 Oxygen content with DOS*

The total liquid product from the TRL5 HDT plant (295.5 L) was fractionated in a batch fractionation unit as described in section 2.4. The target was to separate the jet from diesel fraction. The jet fraction range is from 200°C to 300°C and when the jet fraction is removed the diesel fraction range is from 300°C to 360°C. It should be noted here that the diesel range fraction can be also range from 200°C to 360°C including the jet fraction if the target is only the diesel fuel production. The fractionation of the 295.5 liters hydrotreated product was completed via 20 runs on the batch fractionation unit. The resulting diesel fraction of 165 litres, from the 20 fractionations was collected in one barrel which is depicted in Picture 7. The total jet fraction of 136 litres was collected in one barrel as depicted in Picture 7. However, due to its properties, the jet fraction was further separated in two different fractions the light jet and the heavy jet. The total light jet collected was 60 litres while the total heavy jet fraction collected was 76 litres. On the last phase of the study, one sample from each fraction analyzed and compared with the fuel specifications.



*Picture 7 Marine diesel and jet fuel products after fractionation*

In case of diesel fraction, the distillation curve is presented in Figure 7 from both KPRT and CERTH measurements. It is observed that the fractionation was successful for the diesel fraction. In case of the CERTH sample the diesel, fraction consists only of hydrocarbons with a boiling range in the diesel area. In case of KPRT sample the diesel, fraction consists of 95 wt% diesel range hydrocarbons and 5 wt% some heavier boiling range hydrocarbons. In both cases, the results are very good, the fractionation efficiency is above 95%. The two samples were also analyzed for several properties and compared with the DMA specifications for marine diesel, EN 590 specifications for the commercial road transport market diesel and with the EN 15940 specifications for HVO paraffinic fuels as presented in Table 3. The reason is that the diesel fraction presents some better properties compared to the fossil counterpart. More specifically, the produced diesel fraction has much higher calorific value (46.37 MJ/kg) compared to road transport diesel EN 590 (43.8 MJ/kg). Furthermore, the cetane index is very high (78.9) compared to DMA and EN 590 (>40) but also higher compared to the minimum limit of EN 15940 for paraffinic fuels (>70). The viscosity fulfills the requirements of all type of diesel fuels (EN 590, EN 15940 and DMA), in addition the flash point is really high 146° - 153°C while finally, the most important parameter, the sulphur content, is below 5 wppm fulfill even the strictest requirements of EN 15940 (<5 wppm). But especially the cold properties (e.g. cloud point) are not meeting the specifications of all Diesel type fuels due to the n-paraffinic nature of the molecules. Based on all the above results, it is easily observed that the diesel fraction can be used either as a road transport substitute or as a blending component improver for the fossil diesel fuel. But, can also be used as a high-quality bunker fuel or as an improver

additive for commercial marine diesel. For the purpose of the BioSFerA project, 165 litres of this marine diesel fraction was produced meeting the target production of 1 barrel. Photo from the diesel fraction is presented in Picture 8.
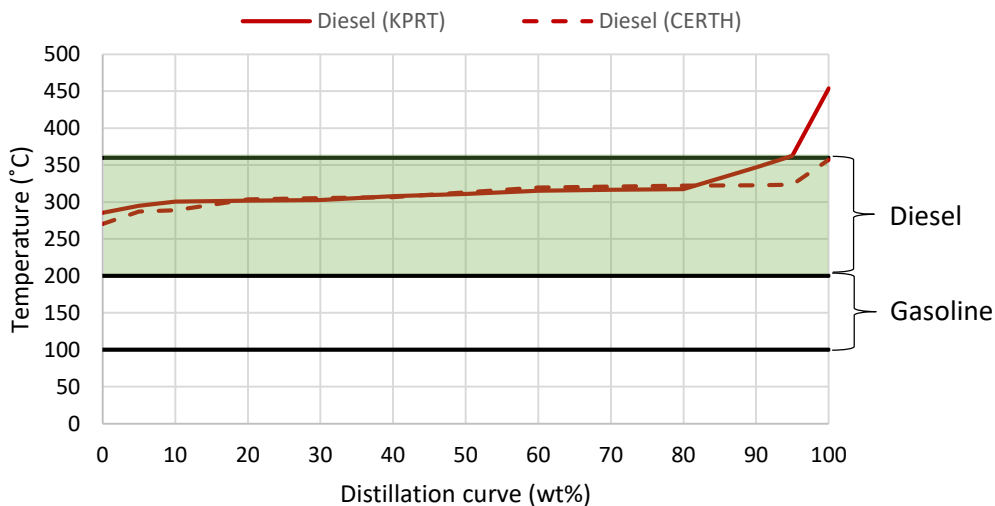


*Figure 7 Diesel fraction distillation curve*

*Table 3 Diesel fraction properties from CERTH and KPRT analysis and DMA, EN 590 and EN 15940 specifications*

| Properties | Units | DMA specs | EN 590 road transport diesel specs | EN 15940 paraffinic fuel specs | Bio-diesel fraction (CERTH results) | Bio-diesel fraction (KPRT results) |
|---|---|---|---|---|---|---|
| Density at 15°C | g/ml | <0.890 | 0.820-0.845 | 0.765-0.800 | 0.783 | 0.792 |
| Viscosity at 40°C | mm$^2$s$^{-1}$ | 2.00-6.00 | 1.9-4.1 | 2.0-6.0 | 2.826 | 3.925 |
| Cetane number | - | >40 | >40 | >40 | - | - |
| Cetane index | - | - | - | >70 | 78.9 | - |
| S content | wt% | <1.5 | <0.0005 | <5 | 0.0004 | - |
| Flash point | °C | >60 | >52 | >50 | 153 | 146.5 |
| Dissolved water | wt% | <0.30 | <0.05 | - | 0.0028 | - |
| Calorific value | MJ/kg | - | 43.8 | - | 46.37 | - |
| Cloud point | °C | - | | - | 22 | 21.8 |
| Total aromatics | v/v % | - | | <1.0 | - | 11 |
| 1-ring aromatics | v/v % | - | | - | - | 11 |

| 2-ring aromatics | v/v % | - | | - | - | <0.01 |
|---|---|---|---|---|---|---|
| 3-ring aromatics | v/v % | - | | - | - | <0.01 |
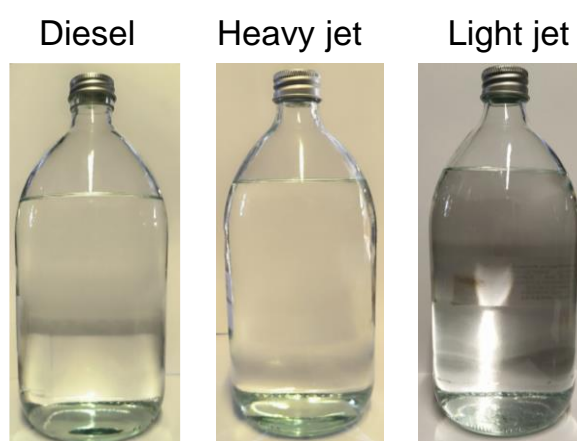


*Picture 8 Photos from the diesel, heavy jet and light jet fuels*

In case of jet fraction, it was separated on light and heavy jet fraction for better fuel fractionation. Photos from both heavy and light jet fuels are presented in Picture 8. The distillation curve from both light and heavy jet from both measurements (KPR and CERT) are presented in Figure 8. The light jet fraction obtained by KPRT fractionation consists of 10 wt% gasoline range hydrocarbons and 90 wt% jet range hydrocarbons. While the heavy jet fraction from KPRT fractionation consists of 90 wt% jet range hydrocarbons and 10 wt% diesel range hydrocarbons. The separation was more difficult than normal as the sample contains a lot of paraffinic molecules with exactly the same carbon chain length and thus boiling point, much more than a normal crude sample where the types of molecules and chain lengths are much more distributed. In case of CERTH fractionation, the light jet fraction consists of 5 wt% gasoline range hydrocarbons, 75 wt% jet range and 20 wt% diesel range hydrocarbons while the heavy jet fraction consists of 60 wt% jet range and 40 wt% diesel range hydrocarbons. It should be noted that the separation between the jet and diesel fraction was very difficult because a large fraction of the hydrocarbons has a boiling point very close to the separation limit between jet and diesel. As a result, some jet range hydrocarbons may pass to the diesel fraction or the opposite.

All measured properties by KPRT and CERTH for both light and heavy jet fractions are presented on Table 4. In general, the measurements from KPRT match with the measurements from CERTH in most of the properties. Both light and heavy jet fractions have low density that fulfill the specifications of jet A1. The sulphur content is also very low, below the limits of jet A1 specifications. In addition, the flash point is higher compared to the lower limit for jet A1 specifications. However, the freezing point is not met. Both light and heavy fractions have freezing point above 0°C while the higher limit for jet A1 specifications is minus -40°C. This is because the jet produced via the Project consists mainly of normal-paraffins (waxes), in order to overcome the drawback of high freezing point an extra isomerization step should be added in the process. Although, an isomerization-dewaxing catalyst was loaded on the second reactor, the products from the first reactor includes the organic liquid phase, the aqueous liquid phase as well as the gas products that contains various gasses including CO and $CO_2$. The aqueous phase, the CO and $CO_2$ poison the active sites of the isomerization-dewaxing catalyst on the second reactor reducing in that way its activity and for that reason the final organic liquid product consists mainly from normal-paraffins. From the experience gained during the BioSFerA project, to transform the normal-paraffins to iso-paraffins the isomerization-

dewaxing step should be performed as an extra step after removing the aqueous phase and the gas products from the feed of the second reactor. In that way the activity of the isomerization-dewaxing catalyst will be higher leading to iso-paraffins and thus to a jet fraction with very low freezing point. However, this step requires further investigation and optimization. The study of the extra isomerization-dewaxing step is very important for jet fraction to meet the jet A1 specifications and is a major subject for a future Project as a continuation of BioSFerA for further optimization of the technology. To summarize, a good quality jet fraction was produced during the current Task 5.4 that fulfill most of the jet A1 properties, but further optimization is need prior its commercialization.
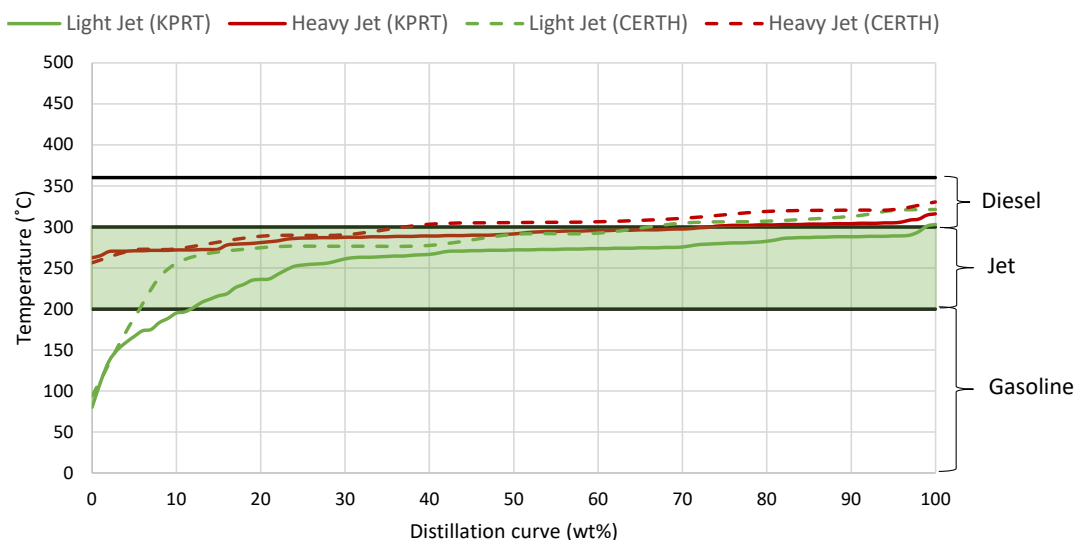


*Figure 8 Mass recovery curves for light and heavy jet fractions (CERTH and KPRT results)*

Table 4 Specifications for Jet-A1, EN 590 for market road diesel, EN 15940 for paraffinic HVO fuels, DMA for marine diesel and properties from the jet and diesel fraction of the study
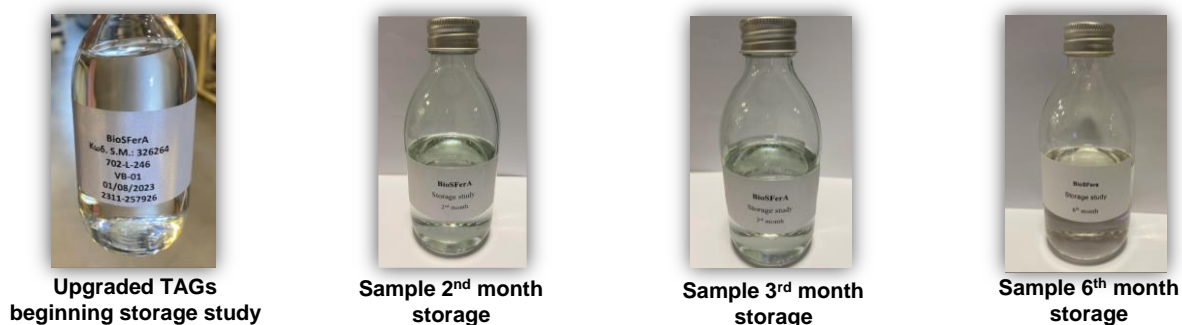
| Properties | Units | Jet A1 specs | Light Jet (KPRT) | Light jet (CERTH) | Heavy jet (KPRT) | Heavy jet (CERTH) |
|---|---|---|---|---|---|---|
| Density at 15°C | kg/m$^3$ | 775-840 | 770 | 777 | 778 | 783 |
| Viscosity at 40°C | mm$^2$s$^{-1}$ | - | - | 3.086 | - | - |
| Viscosity at 20°C | mm$^2$s$^{-1}$ | - | 4.772 | - | 3.245 | 4.076 |
| Viscosity at -20°C | mm$^2$s$^{-1}$ | <8 | - | - | - | - |
| Total Aromatics | wt% | <0.1 | - | - | - | 0.0 |
| Freeze point | °C | <-40 | 2.7 | - | - | - |
| S content | wt% | <0.3 | | - | - | 0.0004 |
| Flash point | °C | >38 | 62.5 | 59 | 136.5 | 140 |
| Calorific value | MJ/kg | >42.8 | | - | | 46.93 |
| Cloud point | °C | - | 2.6 | 8 | 11.7 | 17 |
| TAN | mg KOH/g | - | 0.08 | 0.0 | <0.03 | 0.75 |

| Smoke point | °C | - | >51 | - | >51 | >18 |
|---|---|---|---|---|---|---|

## 3.2 Storage stability study

As far as findings from the stability study is concerned, the product from the optimum condition 3 from Task 5.3 via hydrotreatment of the real TAGs feedstock, was selected for the current investigation. During storage, the product remained transparent, while solids were not formed. Photos from the product samples taken for the current investigation are presented in Picture 9. The results are presented in Figure 9 and Figure 10 showing the product stability over time, as TAN variation over time is negligible pointing limited oxidative variations. Moreover, the other monitored properties did not present a noticeable difference, further verifying the product's stability, while maintaining its quality. Therefore, it can probably be inferred that the MC TAGs hydrotreated products are stable and their storage is feasible for a maximum period of 6 months, whereas the regular monitoring of their quality characteristics is suggested.



**Upgraded TAGs beginning storage study**   **Sample 2ⁿᵈ month storage**   **Sample 3ʳᵈ month storage**   **Sample 6ᵗʰ month storage**

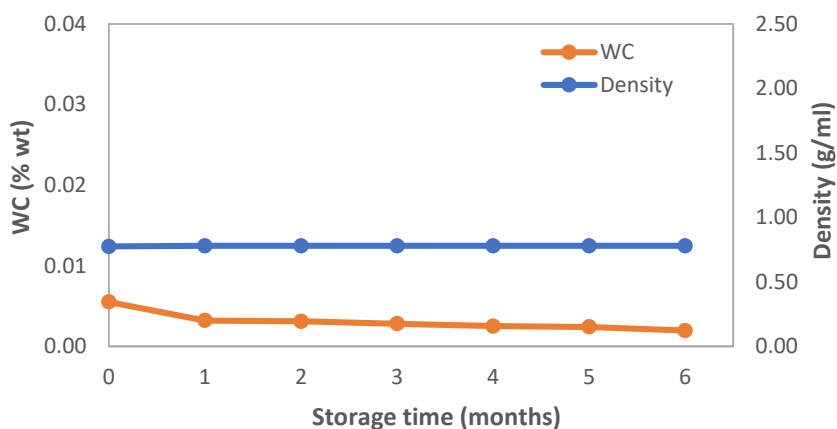*Picture 9 Photos from the samples taken for storage stability study*



*Figure 9 Water content (WC) and density of MC Tags hydrotreated products during storage*
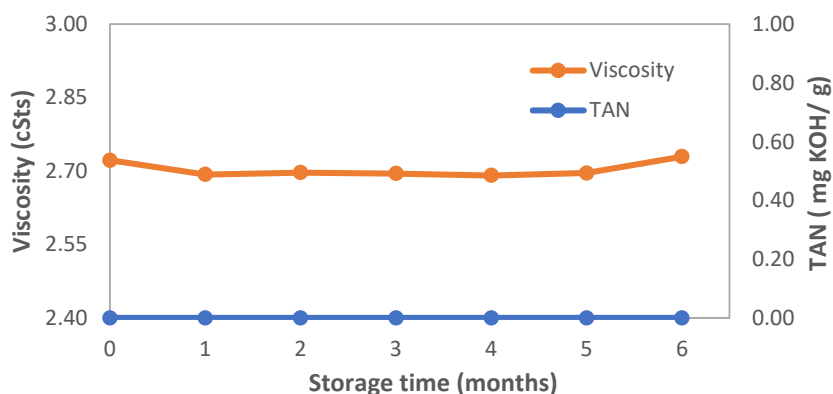
*Figure 10 Viscosity and TAN of MC Tags hydrotreated products during storage*

# 4  Conclusions

The main target of Task 5.4 was to use the data obtained from Task 5.2 and 5.3 to scale-up the process of microbial oil (TAGs) hydrotreatment, on a TRL5 pilot plant for the production of 1-barrel jet and 1-barrel bunker sustainable fuels. However, as the TAGs were limited, a Model Compound feedstock was employed to simulate the TAGs. The TAGs feedstock was simulated with a blend of 4 commercial vegetable oils (42.89 wt% Palm oil, 3.44 wt% flaxseed oil, 30.75 wt% Olive oil and 22.92 wt% Pumpkin seed oil). The analysis of the two feeds has shown that the blended feed match almost 80% the fatty acid composition of the real microbial oil TAGs. The prepared blended feed can simulate almost perfectly the two main acids of microbial oil TAGs, the Palmitic acid and the Oleic acid with an error of 0% and 0% respectively.

The results from Task 5.4 have shown that the process was successfully scaled-up on a TRL5 pilot plant utilizing 300 L from the model compound feed. The resulting total liquid product was a two-phase product consisting of the organic and the aqueous phase. The aqueous phase was separated via gravity while the organic phase was further processed in a batch fractionation unit to separate the jet and diesel fractions. A total of 20 litres of the organic phase was sent to KPRT for fractionation using equipment certified by international standards for crude fractionation, while the remaining 295 litres were fractionated in the batch distillation unit at CERTH. The produced diesel and jet fractions were analysed and compared with the Jet A1, DMA, EN 590 and EN 15940 specifications. The results have shown that the diesel fraction does not meet all specifications but in general is a high-quality diesel fuel that can be used as a high quality drop-in marine diesel fuel. The jet fraction was separated on a light jet and heavy jet. The results from the properties measurements have shown that both light and heavy jet fractions have very good properties fulfil most specifications of jet A1 apart from the freezing point which is high. The reason is that the jet fraction consists of normal-paraffins that have a high freezing point above 0°C. This means it cannot be used for blending compliant to ASTM D1655. In order to overcome this drawback an extra isomerization (dewaxing) step should be added in the process to transform the normal-paraffins to iso-paraffins that have appropriate cold flow properties (freezing point), however, the validation of this solution is requiring further experiments and optimization and it is suggested as a future work.

Finally, based on the storage stability study, the product from the hydrotreated of TAGs exhibited noticeable stability over the 6-month storage period at ambient conditions, as verified by the initial and final properties.

# 5 References

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