BioSFerA
Biofuel for biotravels

H2020-LC-SC3-2018-2019-2020
EUROPEAN COMMISSION
European Climate, Infrastructure and Environment Executive Agency (CINEA)

Biofuels production from **S**yngas
Fermentation for **A**viation and maritime use

Grant Agreement No 884208

Deliverable D5.2

Selection of 2 catalyst and preliminary processing condition

Document Details

Due date	30/06/2023 (M39)
Actual delivery date	25/09/2023
Lead Contractor	CERTH
Version	Final
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Contents

1 Introduction

The current document is a short public version presenting the experimental study developed for the Task 5.2 entitled "Selection of 2 catalyst and preliminary processing conditions". The purpose of the study was to investigate the upgrading of Triglycerides that were produced in a previous WP 3 and 4. Biogenic residues and wastes were gasified and the syngas was fermented to produce bio-based triacylglycerides (TAGs). Thus, the aim of the current Task 5.2 is to deeply investigate the hydrotreatment process of TAGs targeting aviation and bunker fuels. To that aim three hydrotreatment catalytic systems suggested by KPRT and by CERTH were investigated at the TRL 3/4 plant of CERTH. For the catalytic system evaluation, various operating conditions were tested in order to investigate the optimum catalytic system based on product yields and quality targeting aviation and bunker fuels. The report was carried out by BioSFerA working group, led by CERTH.

2 Methodology

2.1 Feeds & catalysts

For the purpose of the current investigation a TAG feedstock was produced in WP 4 and 5. Biogenic residues and wastes were gasified and the syngas was fermented to produce bio-based triacylglycerides (TAGs). Bio-fuels were produced via TAG hydrotreatment. The overall process, combining thermochemical, biological and thermocatalytic parts is based on the gasification of biomass and other biogenic waste in a Dual Fluidized Bed gasifier and the 2-stage fermentation of the produced syngas. Through this process the syngas is converted to acetate (1st stage) and then the acetate is converted to TAGs (2nd stage). However, due to the limited availability of the TAGs, feed was simulated via a model compound. It is well known that vegetable oils also consist of TAGs with different chain lengths depending on the source of the oil. A wide range of vegetable oils was reviewed and in order to simulate the fatty acid composition of TAGs, four commercial vegetable oils were selected: Palm oil, Flaxseed oil, Olive oil and Pumpkin oil. These four oils were selected as they have the right chain length and are widely available on the Greek market where the research took place.

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In order to identify the best mix of the commercial oils that would simulate the composition of TAGs (based on the chain length) as close as posible, a mathematical solver was developed. Based on the mathematical model, the optimum blend that can simulate the TAGs fatty acid composition is 42.89 wt% Palm oil, 3.44 wt% flaxseed oil, 30.75 wt% Olive oil and 22.92 wt% Pumpkin seed oil.

Figure 1, presents the fatty acid composition of the TAGs and the model compound. It is observed that the blended feed match almost 80% the composition of the real TAGs, which can be characterized as a very good model compound for the purpose of the current investigation.

The mass recovery curve of the two feedstocks is presented in Figure 2, where it is observed that the two feedstocks consists of heavy molecules that need to be hydrocracked in order to produce jet and bunker diesel range hydrocarbons.

	Lauric acid	Myristic acid	Palmitic acid	Stearic acid	Oleic acid	Linoleic acid	Linolenic acid	Arachidic acid	Palmitolei c acid
TAG BioSFerA	0.00	0.00	24.00	14.00	48.00	9.00	2.00	0.00	3.00
Model compound	0.09	0.43	24.00	3.25	48.00	19.61	2.00	0.51	0.00

Figure 1 *Fatty acid composition of the TAGs and model compound feed*

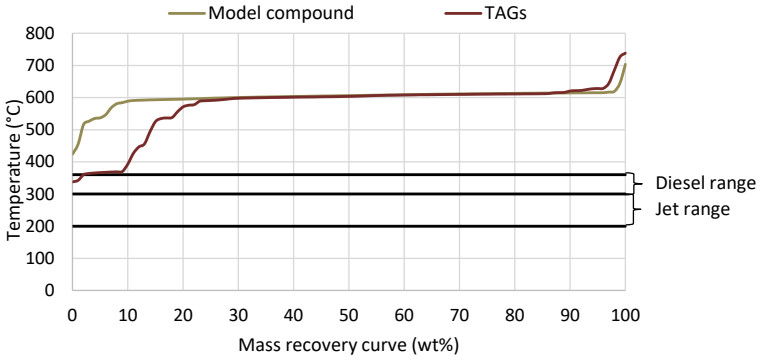

Figure 2 Mass recovery curve of model compound and TAGs

For the purpose of the current investigation three catalytic systems were explored. The two catalytic systems were suggested by KPRT as an effective hydrotreating catalytic systems for jet and bunker fuel production via TAGs while the third one was suggested by the HydPro team of CERTH. 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.

2.2 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 product flow was measured and analysed online via an on-line GC 7890 Agilent analyzer enabling accurate estimation of the H2 consumption during oils hydrotreatment.

2.3 Testing Infrastructure

For this study, all the experiments were carried out in a small-scale pilot hydroprocessing plant (TRL 3-4) 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 3**. 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.

Theunit consists of two reactors that can operate either in series or in parallel mode. For the goals of the current Project, the unit was operated in parallel mode. Each stainless-steel reactor operates in continuous flow and consists of six independent heating zones, sustaining the desired temperature profile within the reactor. The volume of each reactor is ~300 ml with an inlet diameter of 17.48 mm and a length of 1.289 m. The temperature of each catalyst bed is monitored and controlled via the six independent thermocouples placed inside a thermo-well. The hydrogen flow-rate is regulated by four mass flow controllers, two for each reactor, whereas the liquid feed system is regulated by three high-pressure liquid piston pumps, one for each reactor plus one spare. Furthermore, each reactor has each own feed tank with a capacity of 20 Litres. After the liquid feed is mixed with the high-pressure hydrogen at a regular T-joint, it enters the fixed-bed down-flow reactors, where the desired hydrotreating reactions take place. The product exits the reactors, condenses (at 35-40°C) and is finally flashed via low-pressure low-temperature separators, where the gas and liquid phase products separate. Each reactor has each own separator system when they operating in parallel mode. The gaseous products flow-rate is measured by a common wet-test meter and analyzed on-line via a common Agilent 7890 series gas chromatograph analyzer.

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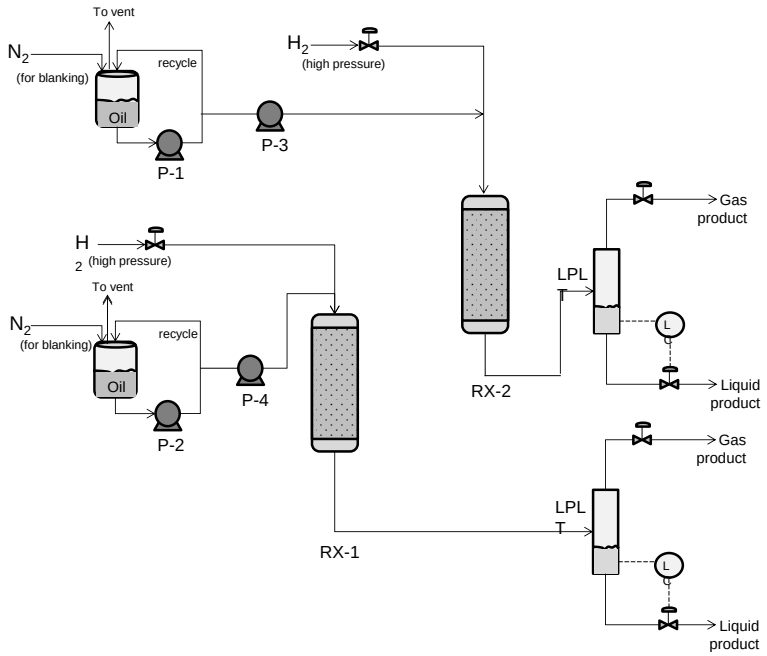

Figure 3 *Simplified diagram of the VB02 hydroprocessing pilot plant in parallel mode*

2.4 Experimental Procedure

The target of the current Task 5.2 is the investigation of three different catalytic systems that will end up to high quality bunker/marine diesel and jet fuels via hydrotreating of TAGs. Two catalytic systems were suggested by KPRT while the third one was suggested by the CERTH team. For each catalytic system various operating conditions were investigated in order to evaluate the efficiency of each catalytic system in terms of marine diesel

and jet fuel yields. The conditions used during the tests with the different systems are typical for the refinery operations of the selected catalysts.

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3 Results

3.1 Catalytic System A

The results from the 1st catalytic system will be presented below.

The mass recovery curves from the products of the three tested conditions and the model compound feed are presented in **Figure 4**. It is observed that the hydrotreating process was able to successfully break the heavy molecules of the initial feed to lighter hydrocarbons in the diesel and jet fuel range. Jet fuel range was defined from 200°C to 300°C while for marine diesel was defined from 300°C to 360°C. The jet and marine diesel yields are presented below:

- Condition 1: 32 wt% Jet yields and 68 wt% diesel yields
- Condition 2: 29 wt% jet yields and 71 wt% diesel yields
- Condition 3: 45 wt% jet yields and 53 wt% diesel yields

Based on the yields results, it is observed that the optimum condition is No. 3 as it can lead to the highest jet and marine diesel yields. Photos form the products of each condition are shown in **Picture 1**, where it is observed the similarity from the three liquid products.

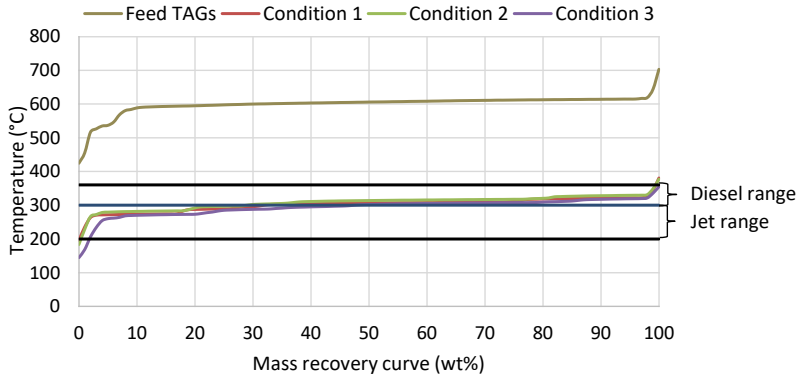
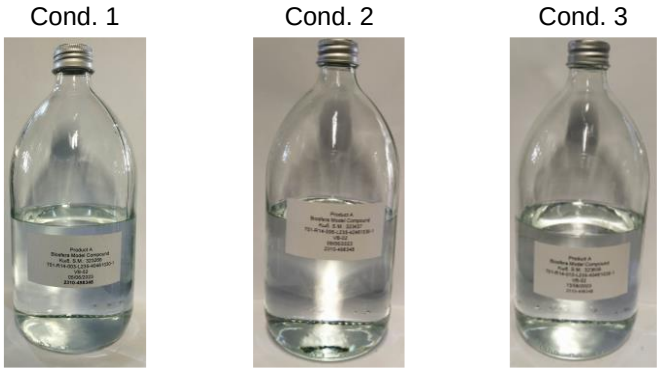


Figure 4 *Mass recovery curve from the model compound feed and the representative products from each condition*



Picture 1 *Products of the three conditions from the 1st catalytic system*

3.2 Catalytic System B

The results from the 2nd catalytic system will be presented below.

The mass recovery curves from the products of the three tested conditions and the model compound are presented in Figure 5. It is observed that the hydrotreating process was able to successfully break the heavy molecules of the initial feed to lighter hydrocarbons in the marine diesel and jet fuel range. Jet fuel range was defined from 200°C to 300°C while for diesel was defined from 300°C to 360°C.

The diesel and jet fuel yields are

- Condition 1: 41 wt% Jet yields and 56 wt% diesel yields
- Condition 2: 51 wt% jet yields and 44 wt% diesel yields
- Condition 3: 54 wt% jet yields and 39 wt% diesel yields

Based on the yields results it is observed that the optimum condition for high jet and marine diesel, is No. 1 as it can lead to the highest jet and marine diesel yields which is the main target of the current Project. Photos form the products of each condition are shown in Picture 2, where it is observed the similarity from the three liquid products.

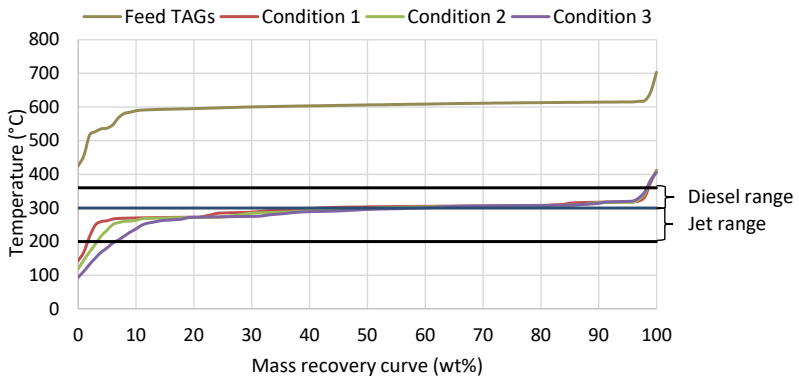
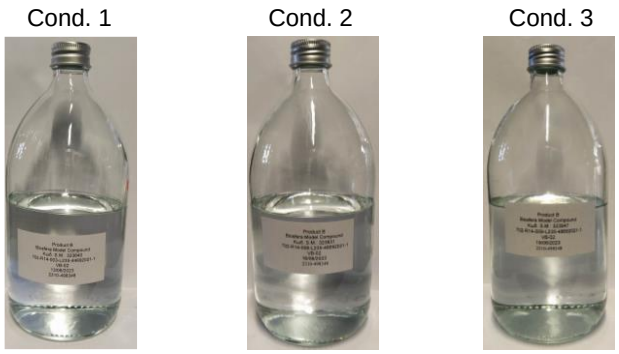


Figure 5 *Mass recovery curve from the model compound feed and the representative products from each condition*



Picture 2 *Products of the three conditions from the 2nd catalytic system*

3.3 Catalytic System C

The results from the 3rd catalytic system will be presented below.

The mass recovery curves from the products of the three tested conditions and the model compound (Feed TAGs) are presented in Figure 6. It is observed that the hydrotreating process was able to successfully brake the heavy molecules of the initial feed to lighter hydrocarbons in the gasoline, jet and diesel fuel range. Jet fuel range was defined from 0°- 200°C for gasoline, 200°-300°C for jet fuel and 300°-360°C for diesel/marine fuel.

The gasoline, jet and diesel fuel yields are

- Condition 1: 32 wt% gasoline yields, 47 wt% Jet yields and 21 wt% diesel yields
- Condition 2: 14 wt% gasoline yields, 52 wt% jet yields and 34 wt% diesel yields
- Condition 3: 24 wt% gasoline yields, 47 wt% jet yields and 29 wt% diesel yields

Based on the yields results it is observed that the optimum condition is No. 2 as it can lead to the highest jet and marine diesel yields. Photos form the products of each condition are shown in Picture 3, where it is observed the similarity from the three liquid products.

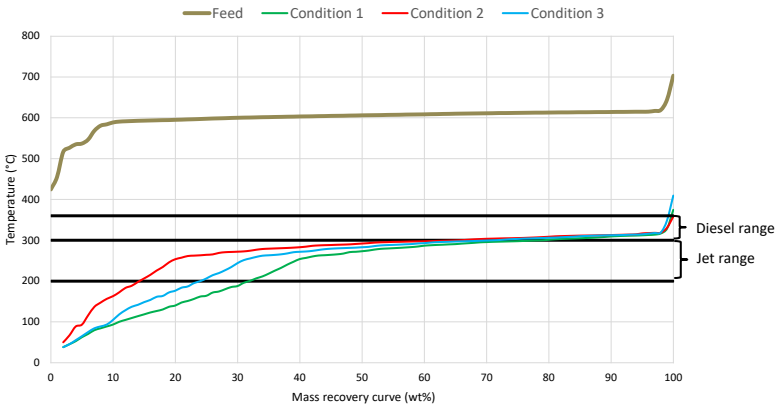
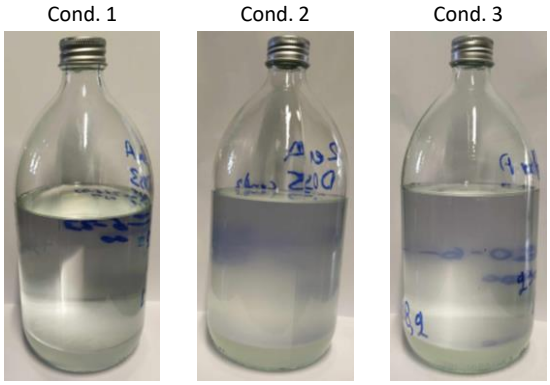


Figure 6 *Mass recovery curve from the model compound feed and the representative products from each condition*



Picture 3 *Products of the three conditions from the 3rd catalytic system*

4 Conclusions

All three catalytic systems have successfully converted the big/heavy molecules of the model compound feed to jet and marine diesel fuel range hydrocarbons and removed most of the non Hydrogen+Carbon atoms as intended. In case of Catalytic system, A, the optimum condition was found to be No.3, resulting in: 45 wt% jet fuel range HC and 53 wt% marine diesel fuel range HC. In case of Catalytic system, B, the optimum condition was found to be No. 2, resulting in: 51 wt% jet fuel range HC and 44 wt% marine diesel duel range HC. In case of Catalytic system, C, the optimum condition was found to be No. 2, resulting in: 14 wt% gasoline, 52 wt% jet and 34 wt% diesel range hydrocarbons.

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Crack molecules, remove hetero atoms and most desired product is Jet fuel range.

Comparing the three examined catalytic systems, system C has been chosen as it has the best potential for optimization testing (to maximize yield of Jet fuel) and input for economic modelling. To that aim, for the next phase, catalytic system C will be tested with both real TAGs and model compounds feed and an optimization of the operating window will be performed on deliverable 5.3.

With the current testing setup it is not possible to separate the Naphtha, Jet fuel and Diesel fuel range products as the amount of product is too low (due to the size of the pilot plant). Therefor it is not possible to check whether the products have the desired product specifications.

5 References

[1] J. HoraceK, D. Kubicka. Bio-oil hydrotreating over conventional CoMo & NiMo catalysts: the role of reaction conditions and additives, Fuel 198 (2017) 49-57 https://doi.org/10.1016/j.fuel.2016.10.003

[2] S.A. Channiwala, P.P. Parikh. A unified correlation for estimating HHV of solid, liquid and gaseous fuels. Fuel 81 (2002) 1051-1063. PII: S0016-2361(01)00131-4

[3] A. Dimitriadis, L. P. Chrysikou, A. I. Kokkalis, L. I. Doufas, S. Bezergianni. Animal fats valorization to green transportations fuels: From concept to industrially relevant scale validation. Journal of Waste Management. Waste Management 143 (2022) 242-252. https://doi.org/10.1016/j.wasman.2022.03.001

[4] S. Bezergianni, A. Dimitriadis, L. P. Chrysikou. Residual lipids incorporation in a petroleum refinery. Int. J. Global Warming, 13 (2017). https://doi.org/10.1504/IJGW.2017.087196

[5] S. Bezergianni, A. Dimitriadis, G. Meletidis. Effectiveness of CoMo and NiMo on Co-Hydroprocessing Heavy Atmospheric Gas Oil-Waste Cooking Oil Mixtures. Fuel 125 (2014) 129-136. https://doi.org/10.1016/j.fuel.2014.02.010

[6] S. Bezergianni, A. Dimitriadis. L. P. Chrysikou. Quality and sustainability comparison of one- vs. Two-step catalytic hydroprocessing of waste cooking oil. Fuel 118 (2013) 300-307. https://doi.org/10.1016/j.fuel.2013.10.078