



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

Biofuels production from Syngas
 Fermentation for Aviation and maritime use
 Grant Agreement No 884208

Deliverable D5.3

Identification of optimal operating window for TAG upgrading

Document Details

Due date	30/09/2023 (M42)
Actual delivery date	25/09/2023
Lead Contractor	CERTH
Version	Final
Prepared by	Athanasios Dimitriadis, Stella Bezergianni, Vasilis Vasdekis
Input from	CERTH
Reviewed by	Maarten Van Haute, Xander de Jong

Document Details

<input checked="" type="checkbox"/>	PU - Public
<input type="checkbox"/>	PP - Restricted to other programme participants (including the EC)
<input type="checkbox"/>	RE - Restricted to a group specified by the consortium (including the EC)
<input type="checkbox"/>	CO - Confidential, only for members of the consortium (including the EC)



Disclaimer of warranties

This project has received funding from the European Union's Horizon 2020 research and innovation programme under Grant Agreement No 884208. This document reflects only the author's view and CINEA is not responsible for any use that may be made of the information it contains.

This document has been prepared by BioSFerA project partners as an account of work carried out within the framework of the EC-GA contract no 884208.

Neither Project Coordinator, nor any signatory party of BioSFerA Project Consortium Agreement, nor any person acting on behalf of any of them:

- a. makes any warranty or representation whatsoever, express or implied,
 - i. with respect to the use of any information, apparatus, method, process, or similar item disclosed in this document, including merchantability and fitness for a particular purpose, or
 - ii. that such use does not infringe on or interfere with privately owned rights, including any party's intellectual property, or
 - iii. that this document is suitable to any particular user's circumstance; or
- b. assumes responsibility for any damages or other liability whatsoever (including any consequential damages, even if Project Coordinator or any representative of a signatory party of the BioSFerA Project Consortium Agreement, has been advised of the possibility of such damages) resulting from your selection or use of this document or any information, apparatus, method, process, or similar item disclosed in this document.



Contents

1	Introduction	4
2	Methodology	4
2.1	Feeds & catalysts.....	4
2.2	Analysis.....	5
2.3	Testing Infrastructure	5
2.4	Experimental Procedure.....	6
3	Results.....	6
3.1	Model compound evaluation	6
3.2	Effect of operating parameter during hydrotreatment.....	7
3.3	Fuel Characterization	10
4	Conclusions	11
5	References	12



1 Introduction

The current deliverable is a continuation of deliverable 5.2 from WP5. In deliverable 5.2, three different catalytic systems were investigated for the hydroprocessing of TAGs using a model compound (blend of 4 vegetable oils). Based on the results, catalytic system C was selected because it has led to high jet and bunker diesel yields and presents the highest potential for optimization. However, during the pre-screening tests, only three operating conditions were tested with the catalytic system C and a model compound was used. This means that there is some room for improvements in terms of product yields if further optimization is performed. To that aim, in the current task 5.3 the aim is to explore the effect of different operating parameters with catalytic system C in order to further optimize the TAG hydroprocessing process.

In addition, as it was mentioned in Deliverable 5.2, due to the limited TAGs feedstock produced in the project, a model compound (blend of 4 commercial vegetable oils), was used to simulate the TAGs. All the experiments in Task 5.2 were performed with the model compound. To that aim, in order to evaluate the effectiveness of the model compound feed, in this deliverable the 20 litres TAGs were also tested on the first reactor parallel with the model compound feed on the 2nd reactor at the same operating conditions for comparison purposes to compare the behaviour of the catalyst system with the different feedstocks.

2 Methodology

2.1 Feeds & catalysts

The current deliverable has two targets, the first one is to evaluate the use of the model compound feedstock compared to the real TAGS and the second target is to explore various operating conditions in order to optimize the hydroprocessing of the model compound feed.

Thus, two feeds were explored, the first one is the real TAGs that were produced in a previous work package and the second one is the model compound feedstock that consists of selected vegetable oils based on the composition (chain length) of the acids in the TAGs as was presented in Deliverable 5.2

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 diesel range hydrocarbons.

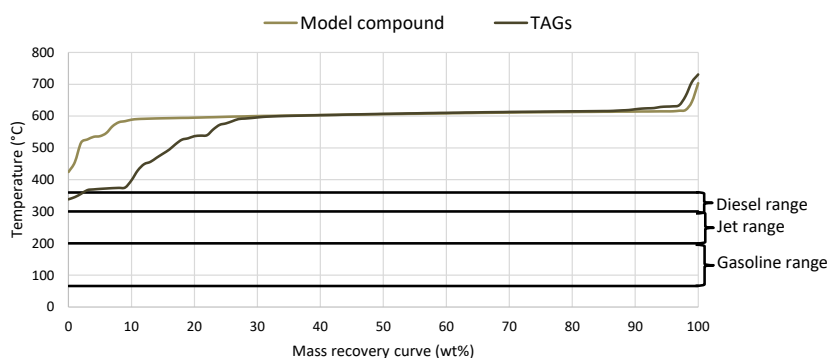


Figure 1 Mass recovery curve of model compound and TAGs



For the purpose of the current investigation the optimum catalytic system from Task 5.2 was utilized. In order 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.

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 products were analysed online via an on-line GC 7890 Agilent analyzer enabling accurate estimation of the H_2 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 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. The unit was deeply described on deliverable D5.2

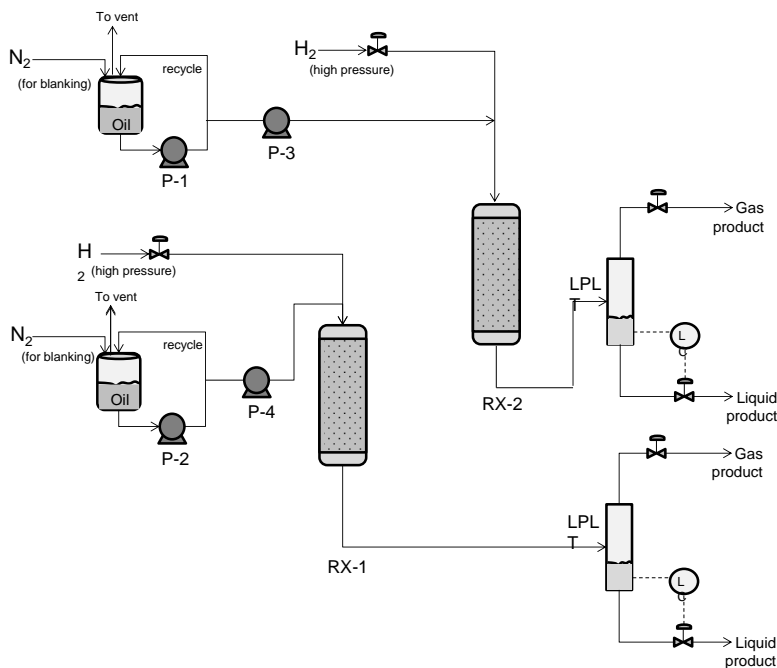


Figure 2 Simplified diagram of the VB02 hydroprocessing pilot plant in parallel mode



2.4 Experimental Procedure

The main targets of the current Task 5.3 is first to evaluate the behavior and products of the model compound feedstock compared to the real TAGs and secondly to investigate the effect of the process operating parameters on product quality. To that aim, the two reactors were operated in parallel mode. The same catalytic system was loaded in both reactors, however, in reactor A the feedstock was the real TAGs while the feedstock of reactor B was the model compound. Similar operating conditions were applied in both reactors. To that aim, the efficiency of the model compound to simulate the real TAGs was explored. In total, 5 conditions were investigated in order to optimize the technology for high jet and bunker fuel yields.

3 Results

3.1 Model compound evaluation

The first step of the current investigation is to evaluate the efficiency of the model compound (MC) blend to simulate the real TAGs. To that aim the two feedstocks were tested on the same 5 operating conditions. This section will present the results from both TAGs and model compound products after hydroprocessing. A very important analysis to evaluate the products after hydrotreating is the simulated distillation curve or the mass recovery curve of the products which is presented in Figure 3. The results show that the mass recovery curve of the TAGs product (lines) and MC products (dotted lines) are almost similar. This means that hydroprocessing of the model compound can lead to similar range hydrocarbons with the hydroprocessing of the real TAGs.

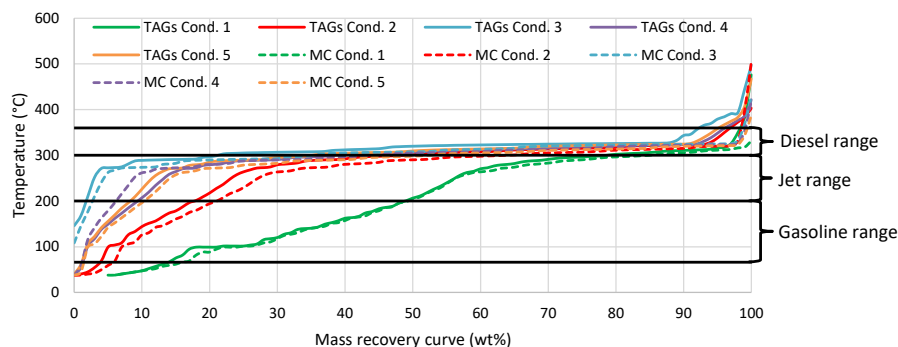


Figure 3 Mass recovery curve from products with real TAGs and Model Compound (MC)

The organic yields and aqueous phase from the products of both feeds are presented in Figure 4 and Figure 5 respectively. It is easily noticed that the hydroprocessing of both feeds can lead to similar organic yields confirming once again the ability of the model compound to simulate the real TAGs.

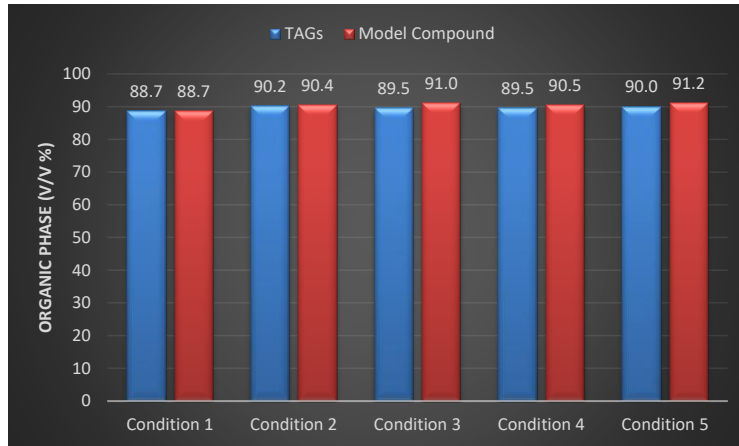


Figure 4 Organic yields results from the products of the TAGs and MC

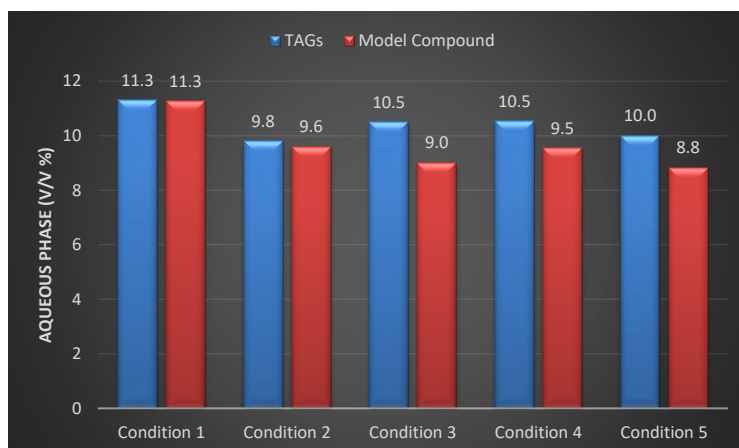


Figure 5 Aqueous phase yields results from the products of the TAGs and MC

From the above comparison, it was found that the properties of the products from the hydroprocessing of MC are very close to the properties of the products from the hydroprocessing of the real TAGs that were produced in the Project. Thus, the current results confirm the efficiency of the MC to simulate the TAGs during hydroprocessing. As a result, on the next section the effect of different operating parameters during hydroprocessing will be presented with the MC feed.

3.2 Effect of operating parameter during hydrotreatment

In order to optimize the process, the effect of the most important operating parameters was explored. The conditions used during the tests are typical for the refinery operations of the selected catalyst. The critical parameters during hydroprocessing is the reaction temperature, the LHSV and the reaction pressure. At first the effect of LHSV was

Commented [XdJ1]: Think you can even add the ranges of temperatures, pressures, LHSV and Hydrogen flow rates we used as you do not disclose the catalyst.



investigated with condition 1 and 2. The mass recovery curves of the products under conditions 1 and 2 is presented in Figure 6. It is observed that an increase of the LHSV leads to heavier hydrocarbons in the organic liquid products. In general, LHSV affects the reactor volume, higher LHSV required smaller reactors and thus lower investment cost. As a result, condition 2 is preferable compared to condition 1 as it can lead to higher jet and diesel yields and also half the catalyst and reactor size compared to condition 1. The yields in jet and diesel fuel at condition 1 are 36 and 15 wt.% respectively while at condition 2 are 43 and 35 wt.% respectively.

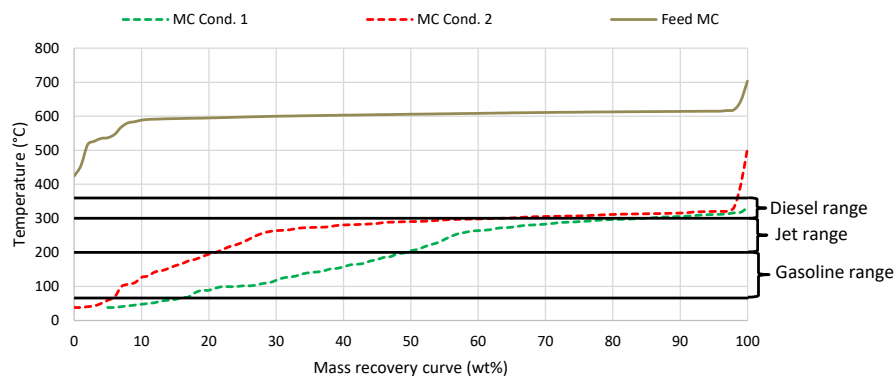


Figure 6 Mass recovery curve from the products of condition 1 and 2 with the MC (vary LHSV)

The effect of reaction temperature was investigated via condition 3. The mass recovery curve of condition 2 and 3 is presented in Figure 7. It is observed that reduction of operating temperature has led to less cracking reactions and thus heavier hydrocarbons in the products. The jet and diesel yield from condition 3 are 33 and 64 wt% respectively. In general, the higher the operation temperature the quicker the catalyst deactivation, in addition higher temperatures required high energy demands. From the above results, it is easily observed that condition 3 is preferable.

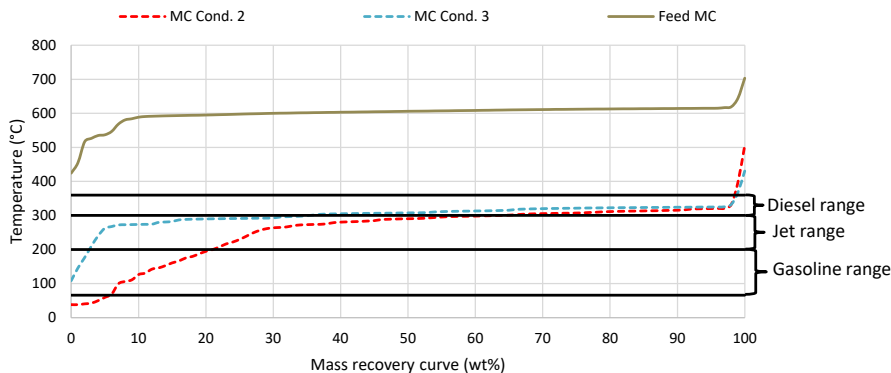


Figure 7 Mass recovery curve from the products of condition 2 and 3 with the MC (vary T)

In order to further improve the process, the LHSV was reduced in condition 4. Thus, the mass recovery curve of conditions 2, 3 and 4 is presented in Figure 8. It is observed that the reduction of LHSV leads to more hydrocracking



reactions as the retention time increased. However, lower LHSV demand bigger reactors and thus higher investment costs.

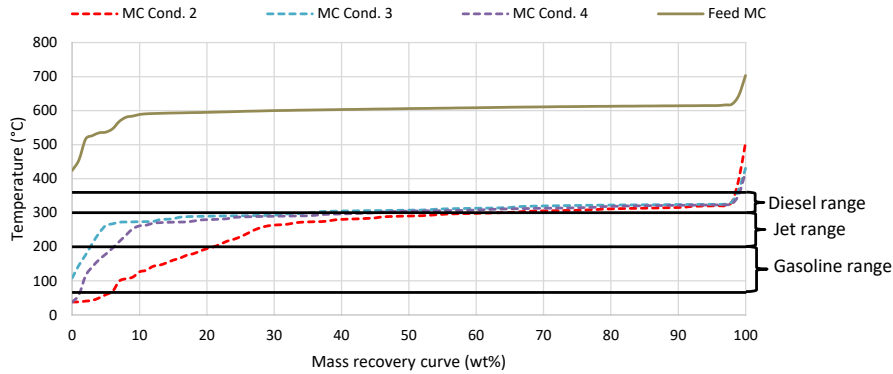


Figure 8 Mass recovery curve from the products of condition 2, 3 and 4 with the MC (vary LHSV & T)

Finally, in order to test the effect of reaction pressure, in condition No. 5. The mass recovery curve from conditions 2, 3, 4 and 5 is presented in Figure 9. It is observed that reduction of reaction pressure does not strongly influence the mass recovery curve of the products.

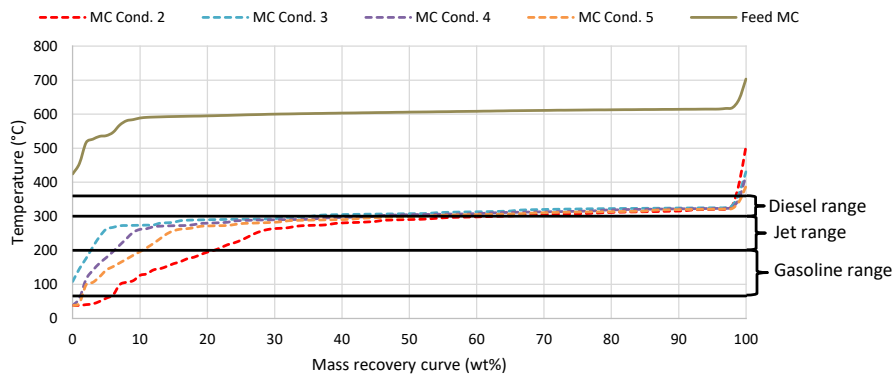


Figure 9 Mass recovery curve from the products of condition 2, 3, 4 and 5 with the MC (vary LHSV, T & P)

To summarize all the results, it was found that the optimum condition is No. 3 because it is characterized by high jet and diesel yields (43 and 35 wt% respectively), smaller catalyst volumes and average hydrogen consumption. The products from all conditions with Model Compound feed are presented in Figure 10 .

Commented [XdJ2]: In the conclusion below you select condition 2 as the optimum. Indeed I do agree that condition 3 is the optimum.



Cond. 1 Cond. 2 Cond. 3 Cond. 4 Cond. 5



Figure 10 Photos from the products of the Model Compound

Commented [XdJ3]: Why do you not add a photo of products from the actual TAGs?

3.3 Fuel Characterization

Based on the process optimization results, condition No.2 was selected as the optimum one. To that aim, the product from condition No.2 was fully analyzed and some of the properties are presented in Table 1 as a general reference. It should be noted here that all analysis were performed on the total liquid products and not on the jet and (marine) diesel range fractions, this means at this stage, it's not possible to assess fuels performance and analysis will be limited to a few environmental specs. On the next phase of the Project where the total liquid product will go under fractionation and the jet and marine diesel fractions will be separated, fuel performance analysis will be performed for jet and (marine) diesel fuel fractions in order to investigate if the targeted fractions fulfill the specifications for jet and marine diesel fuels.

Commented [XdJ4]: Condition 3 was selected not 2

Commented [MVH5]: which means we can limit conclusions to a few environmental specs, and not on fuel er

As noted before, the table shows a comparison between the total liquid product with selected JET-A and DMA specs. The total liquid product consists of both jet and diesel range hydrocarbons with a small percent of naphtha. On future Task 5.4, the process will be scaled-up in a TRL5 hydrotreatment plant where a quantity of approximately 400 liters of this total liquid product will be produced. The resulting total liquid product from TRL 5 unit will be fractionated in order to separate the fractions of jet and marine diesel. Thus, these fractions will be further evaluated and will be compared with JET-A and DMA specs. The only conclusion that can be drawn from table 1 is that both the TAN and Sulphur content of the product mixture are low compared to the specifications. Other properties can not be compared as a mixture behaves very different than separate fractions (specific blending rules apply).

Finally, during the current task 5.3 a quantity of 3 liters from this total liquid product utilizing the operating window of condition 2, was produced. The current quantity will be used for the storage stability study that will be completed on March of 2024. The total liquid product will be stored under control conditions and samples will be taken in during specific periods in order to evaluate its storage stability and oxidation. The results will be presented at the end of the study.

Commented [XdJ6]: Should be condition 3

Table 1 Properties from the products of MC from condition 3

Properties	Units	Cond. 2	JET-A	Marine Diesel DMA





Density at 15°C	g/ml	0.758	0.775-0.840	<0.89
Sulphur	wppm	11.6	3000	<15000
Hydrogen	wt%	15.1	-	-
Carbon	wt%	NA	-	-
Nitrogen	wppm	0.3	-	-
TAN	mgKOH/g	0.0	-	<25
Viscosity at 40°C	cSts	1.72	<8.0	2000-6000
Cetane index	-	91	-	>40

4 Conclusions

The main target of Task 5.3 was to optimize the hydroprocessing technology for TAG upgrading to jet and diesel range hydrocarbons. However, as the TAGs were limited, a model compound feedstock was employed in order to simulate the TAGs. Thus, the first target of Task 5.3 was to investigate the efficiency of the model compound feed to simulate the real TAGs feed during hydroprocessing. To that aim the two feedstocks were tested with the same catalytic system in 5 different operating conditions in order to evaluate if they can lead to similar quality products. The tests have shown that the fuels produced from the two feeds have very close results (conversion and Hydrogen consumption). This means that Model Compound feed can successfully simulate the real TAGs.

On the next phase, key operating parameters (the effect of LHSV, reaction temperature and pressure) was investigated in order to optimize the hydrotreating process and investigate the effect of the process parameters on product yields and quality. Thus, the MC was tested under 5 different operating windows. The results have shown that the optimum window is No. 3 because it was characterized by high jet and diesel yields with an average hydrogen consumption. Furthermore, the total liquid product from condition 3 was further analysed and compared with selected JET-A and Marine Diesel specifications. The only conclusion that can be drawn from the table 1 is that both the TAN and Sulphur content of the product mixture are low. Other properties can not be compared as a mixture behaves very different than separate fractions (specific blending rules apply).

The next step is to scale-up the process in a TRL5 hydrotreatment pilot plant in order to produce 1-barrel jet and 1-barrel marine diesel fuel based on the results of this test that will be separated and fractions will be analysed and compared with selected JET-A and Marine Diesel specs. It should be noted here that the TRL5 unit due to its size and capacity, has better performance compared to the TRL3 unit. Thus, it is expected that TRL5 will lead to higher quality liquid products compared to TRL3/4 unit from this deliverable. Further optimization of the process will also be performed on the next deliverable 5.4 utilizing the TRL5 unit.

Commented [XdJ7]: This should be condition 3 as mentioned.

Commented [MVH8]: not at all

Commented [XdJ9]: Jet fuel has many more specs than the one you show in the table. Only if all specifications are met it can be sold as Jet fuel.



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] Stella Bezergianni, Athanasios Dimitriadis. Comparison between different types of renewable diesel. Renewable and Sustainable Energy Reviews 21 (2013) 110–116. <http://dx.doi.org/10.1016/j.rser.2012.12.042>