



Biofuels from liquid phase pyrolysis oil: A two-step hydrodeoxygenation (HDO) process

Journal:	<i>Green Chemistry</i>
Manuscript ID:	GC-ART-09-2014-001741.R2
Article Type:	Paper
Date Submitted by the Author:	28-Oct-2014
Complete List of Authors:	<p>Pucher, Hannes; Technische Universität Graz, Institut für Chemische Verfahrenstechnik und Umwelttechnik Schwaiger, Nikolaus; Graz University of Technology, Institute of Chemical Engineering and Environmental Technology Feiner, Roland; Technische Universität Graz, Institut für Chemische Verfahrenstechnik und Umwelttechnik Ellmaier, Lisa; BDI-BioEnergy International AG, Pucher, Peter; BDI-BioEnergy International AG, Chernev, Boril; Austrian Centre of Electron Microscopy and Nanoanalysis, Siebenhofer, Matthäus; Graz University of Technology, Institute of Chemical Engineering and Environmental Technology</p>

Biofuel production from liquid phase pyrolysis oil:**A two-step HDO process****Biofuels from liquid phase pyrolysis oil:
A two-step hydrodeoxygenation (HDO) process**

Cite this: DOI: 10.1039/x0xx00000x

Hannes Pucher^a, Nikolaus Schwaiger^{a,b}, Roland Feiner^{a,b}, Lisa Ellmaier^b, Peter Pucher^b, Boril. S. Chernev^c, Matthäus. Siebenhofer^aReceived 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/^aInstitute of Chemical Engineering and Environmental Technology, NAWI Graz, Central Lab Biobased Products, Graz University of Technology, Inffeldgasse 25/C, 8010 Graz, Austria^bBDI-BioEnergy International AG, Parkring 18, 8074 Grambach/Graz, Austria^cAustrian Centre for Electron Microscopy and Nanoanalysis, Steyrergasse 17/III, 8010 Graz, Austria

New biomass utilization technologies and concepts are needed to suffice future increasing energy demand. This paper contributes to understanding of liquid phase pyrolysis (LPP) oil upgrading which significantly differs from fast pyrolysis (FP) oil upgrading processes. A two-step HDO process was established to convert the LPP oil into a biofuel with fuel-like properties. In the first HDO step (250°C, 85bar) the bulk of water and most of the highly oxygenated water soluble carbonaceous constituents were removed to lower hydrogen consumption in the second HDO step. In addition the highly reactive compounds were stabilized. In the second HDO step (400°C, 150/170bar) the product specification was improved. This paper shows the proof-of-principle of a two-step HDO process for converting LPP oil to a diesel-like biofuel.

Abbreviations

ATR-IR	Attenuated Total Reflection Fourier Transform Infrared Spectroscopy.
BCO	bioCRACK Oil
BtL	Biomass to Liquid
EY _{Phase}	Energy Yield
FP	Fast Pyrolysis
GC-MS	Gas Chromatography with Mass Spectrometry
GC-TCD	Gas Chromatography with Thermal Conductivity Detector
GPC	Gel Permeation Chromatography
H/C	Hydrogen to Carbon
HDO	Hydrodeoxygenation
H _{i,Phase}	Heating Value
LCV	Lower Calorific Value
LPP	Liquid Phase Pyrolysis
MY _{Phase}	Mass Yield
O/C	Oxygen to Carbon
VGO	Vacum Gas Oil
w	Weight Percent

Introduction

This process addresses producers of LPP oil to help increase efficiency of LPP oil upgrading technology. A two-step HDO process was established to convert LPP oil into a biofuel with fuel-like properties.

Expecting from renewable resources to close the rising gap in the world's future energy demand biomass is a high potential resource because it provides a nearly immeasurable quantity of renewable biologically fixed carbon (1.24×10^{12} tons)¹⁻³.

However there are still obstacles to overcome to make biomass to liquid (BtL)-processes economically and ecologically feasible. Standard refinery processes are currently not prepared for converting biomass to biofuels. The high transportation cost and low energy density of biomass demand cheap pretreatment to facilitate the conversion process. In this project LPP is used to convert the biomass to liquid intermediates.

Liquid Phase Pyrolysis (LPP)

The LPP process applied in this project converts any type of non-edible lignocellulosic biomass into bioCRACK oil (BCO), LPP oil, pyrolysis char and pyrolysis gas. Technology and process design of LPP and the upgrading of the pyrolysis char have been reported⁴⁻⁷. In 2012 a pilot scale LPP plant (bioCRACK plant) with a capacity of 100 kg of biomass per hour has started operation at OMV refinery in Vienna. This pilot plant uses VGO as liquid heat carrier. VGO has a high boiling range between 320°C and 580°C and an elemental

composition of 86wt.% Carbon 12wt.% Hydrogen. As shown in Figure 1, 20wt.% of the biogenous carbon of the biomass is transferred into LPP oil.

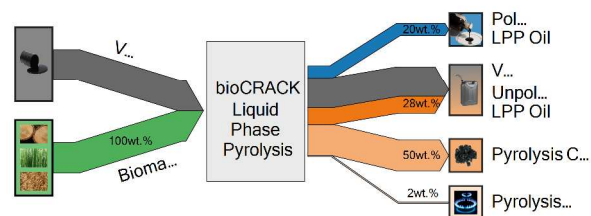


Figure 1: Biogenous carbon balance of LPP at T=350°C (mass balance inaccuracy 5%).

Due to the decomposition of holocellulose and lignin LPP oil is a mixture of different degradation products⁸. It contains a large amount of oxygenated constituents like low molecular weight acids, aldehydes and alcohols. It has a high water content and limited stability, especially during storage which is a major drawback. Therefore the improvement of product quality and stability of LPP oils are a highly desirable.

The produced BCO is a mixture of VGO and biogenous constituents (10wt.%). Table 1 shows selected properties of LPP oil, BCO and conventional diesel. BCO has almost fuel-like properties and can directly be refined in a conventional refinery.

Table 1: Comparison of LPP oil, BCO and conventional diesel.

	LPP oil	BCO	Diesel
Water Content (wt.%)	50	0.04	0.02
LCV (MJ/kg)	8.7	40.1	42.5
Density (kg/m ³)	1070	890	835
Viscosity (mPa s)	4	8	4
Biogenous carbon (wt.%)	100	10	<7
Elemental analysis on wet basis			
Carbon Content (wt.%)	25.6	83.6	85.9
Hydrogen Content (wt.%)	9.2	11.8	13.3
Oxygen Content (wt.%)	64.9	4.2	<1
Nitrogen Content (wt.%)	<1	<1	<1

Hydrodeoxygenation (HDO)

Hydrodeoxygenation (HDO) of FP oil has been reported⁹⁻¹³. Only little information is available regarding HDO of LPP oil¹⁴. LPP oils have (1) a higher water content (50wt.% to 30wt.%), (2) a lower carbon content (47.4wt.% to 51.1wt.%), (3) a higher oxygen content (44.1wt.% to 41.6wt.%), (4) a lower density (1070kg/m³ to 1200kg/m³) and (5) a lower load with inorganics and char⁴ than FP oils⁹.

During HDO different reactions occur in parallel¹². To achieve an insight into the HDO process and to determine the influence of the temperature and reaction time different studies were conducted. The results were published elsewhere¹⁴. Based on these results a two-step HDO process, see Figure 2, was established to convert LPP oil into a biofuel with fuel-like properties. Investigations focused on the mass/energy yield, the elemental composition, the density, the viscosity, the distillation characteristics and the biogenous carbon content.

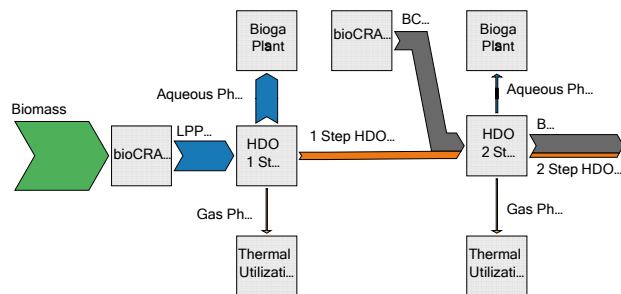


Figure 2: Scheme of the two-step HDO process.

Material and Methods

Materials

Raney Nickel as pre-activated catalyst (CAS: 7440-02-0, Merck 8208760250) consisting of 90% Ni and 10% Al weight on dry basis, obtained from Merck Millipore, was used for hydrodeoxygenation as Figure 3 shows.

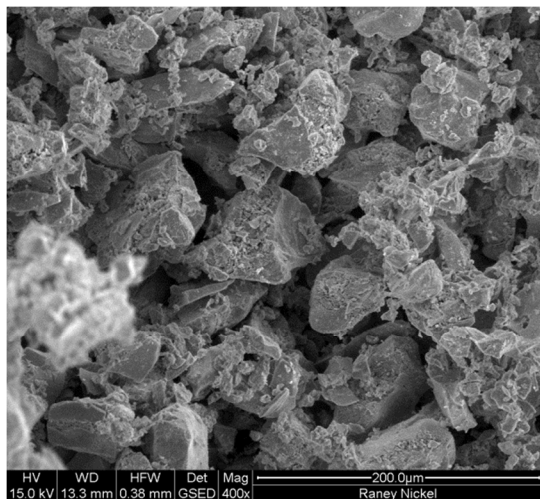


Figure 3: Raney Nickel as used for hydrodeoxygenation.

The LPP oil used for investigations was obtained from the pilot scale LPP plant (bioCRACK plant) at the OMV refinery in Vienna. It was produced from spruce wood pellets^{4,5}.

The LPP oil was analyzed and then stored in a refrigerator (6°C) to avoid aging. Selected properties of the LPP oil are shown in Table 1.

Experimental Set-Up and Procedure

LPP oil was hydrotreated in a 450ml batch reactor, type limbo, from Büchi Glas Uster AG. The reactor was equipped with a magnetically driven, gas-inducing, Rushton type impeller. The stirring speed was set to 500rpm during the experiment.

First HDO Step - Procedure

For each batch 100g of LPP oil and catalyst were fed to the reactor. The catalyst to oil ratio on wet basis was 0.05. The reactor was pressurized with 50bar of hydrogen at ambient temperature. Afterwards the reactor was heated with a heating rate of 10°C/min to the isothermal reaction temperature of 250°C. During the isothermal stage hydrogen was continuously metered at 85bar.

Second HDO Step - Procedure

For each batch 100g of a mixture of LPP oil, BCO and catalyst were fed to the reactor. Two different BCO to LPP oil ratios were conducted (2.5-4). The catalyst to feed ratio on wet basis was 0.10 in both experiments. The reactor was pressurized with 50 bar of hydrogen at ambient temperature. Afterwards the reactor was heated with a heating rate of 10°C/min to the isothermal reaction temperature of 400°C. During the isothermal stage hydrogen was continuously metered at 150/170bar.

Cooling Procedure

After the experiment was finished the reactor was rapidly cooled to ambient temperature. Then the reactor was depressurized and the gas composition was determined. The solid and liquid reaction products were recovered and separated in a separating funnel.

Apparatus and Methods

The gas composition was analyzed for CH₄, O₂, CO₂ and CO with a Mardur Photon II infrared gas analyzer.

The liquid products were characterized in CHN Mode with a Vario Macro CHNO-analyzer from Elementar Analysensysteme.

The water content of the liquid products was determined with a Gas Chromatograph with Thermal Conductivity Detector (GC-TCD) from Agilent Technologies and a HP-Innowax column.

The biogenous carbon content of the liquid samples was determined by Beta Analytic according to the standard EN 15440.

Distillation characteristics of BCO and 2nd step HDO oil were determined with a Gas Chromatograph-SimDist MXT 2887 with a 10m column from Restek and Agilent 7890A GC.

The IR-ATR spectra of the liquid products were recorded using a Tensor 37 spectrometer from Bruker. The samples were measured in attenuated total reflection (ATR) with a MIRacle® unit with diamond crystal. The spectra were accumulated with spectral resolution of 4cm⁻¹.

GC-MS analytics were performed by a GCMS-QP 2010 Plus from Shimadzu with a 60m DB-1701 column. Data comparison is performed in peak area units.

GPC of the liquid product was carried out with a Shimadzu RID-10A Refractive Index Detector and a Merck HITACHI L-6000A Pump. A SDV 5µm 8*50mm precolumn and two SDC 1000Å 5µm 8*300mm columns from PSS were used. GPC was calibrated against polystyrene of 163g/mol and 1890g/mol molar mass.

Results and Discussion

According to Figure 2 a two-step process was established to convert the LPP oil into biofuel with fuel-like properties.

In a first HDO step the LPP oil was stabilized at 250°C and 85bar hydrogen pressure. The bulk of water and highly oxygenated carbonaceous constituents were removed

In the second HDO step the 1st step HDO oil was mixed with the BCO from the bioCRACK plant and then treated at 400°C to improve the product specification. The 2nd step HDO oil has nearly similar properties to conventional diesel. The experimental matrix is illustrated in Table 2. Reaction time of preheating and isothermal operation is discussed separately.

The mass balance closure varied between 97% and 99%. The most likely reasons for inaccuracy were the complicated separations due to the high viscosity and stickiness of the 1st step HDO oil.

Table 2: Experimental matrix.

	Step	BCO/1 st step HDO oil Ratio	Catalyst amount [wt.%]	Temperatur [°C]	Pressure [bar]	Time [min]
HDO_1_4	1	-	5	250	85	240
HDO_2_4	2	4	10	400	170	120
HDO_1_2.5	1	-	5	250	85	120
HDO_2_2.5	2	2.5	10	400	150	120

Key Figures

For a better understanding different key figures were defined.

The mass yield MY_{Phase} , which is the fraction of product phase ($m_{Phase,dry}$) to the total of all product phases ($\sum m_{Phase,dry}$) on dry basis, is calculated according to Eq. 1.

In order to calculate the energy yield (EY_{Phase}) of a single phase, the lower calorific value ($H_{i,Phase}$) was calculated according to Eq. 2¹⁵. The energy yield of each phase (EY_{Phase}) is calculated by dividing the energy content of each phase ($m_{Phase} \cdot H_{i,Phase}$) through there sum (see Eq. 3).

$$MY_{Phase} = \frac{m_{Phase,dry}}{\sum m_{Phase,dry}} \quad \text{Eq. 1}$$

$$H_{i,Phase} = 34,0 \cdot w_C + 101,6 \cdot w_H + 6,3 \cdot w_N + 19,1 \cdot w_S - 9,8 \cdot w_O - 2,5 \cdot w_{H_2O} \quad \text{Eq. 2}$$

$$EY_{Phase} = \frac{m_{Phase} \cdot H_{i,Phase}}{\sum m_{Phase} \cdot H_{i,Phase}} \quad \text{Eq. 3}$$

First HDO Step

After the first HDO step formation of three product phases were observed, a clear slightly brown water phase which could be processed further in a biogas plant; a dark brown oil phase (1st step HDO oil) and a gas phase. It is important to mention that no solid phase was produced in the first HDO step. Densities and viscosities of the 1st step HDO oils were higher than the density and viscosity of the aqueous phase and the LPP oil (feed). The gas yield was between 1 and 2wt.%. The main gaseous components were unreacted hydrogen and carbon dioxide. Carbon dioxide was formed through the decarboxylation of organic acids, such as acetic and formic acid, common constituents in pyrolysis oils (8-10wt.%)¹⁶⁻¹⁸. This gas could be potentially recycled or burned directly to produce heat.

Second HDO Step

After the second HDO step also three product phases were found: an almost transparent aqueous phase which can be processed further in a biogas plant; a clear slightly brown oil phase (2nd step HDO oil) and a gas phase. It has to be mentioned that even at the high temperatures of the second

HDO step no solid phase was produced. This indicates that the constituents of the LPP oil were stabilized in the first HDO step. Dilution of 1st step HDO oil with BCO does retard polymerization at high temperatures. Densities and viscosities of the 2nd step HDO oils were lower than the density and viscosity of the LPP oil and the BCO (feed). The gas yield was between 5 and 10wt. %. The main gaseous components were unreacted hydrogen, carbon dioxide and methane. This gas can be recycled or incinerated.

Mass and Energy Yield

In Figure 4 the corresponding MY_{Phase} and EY_{Phase} of each experiment and phase are shown. The elemental composition of the 1st/2nd step HDO oil on dry basis can be found in Figure 5.

In the first HDO step (experiment HDO_1_4 and HDO_1_2.5) 19 and 22wt.% of the LPP oil was converted into an oil phase (1st step HDO oil), which accumulated 67 and 70% of the energy content of the feed. On dry basis the 1st step HDO oil contained 70wt.% carbon and 8.0 wt.% hydrogen. Compared to the LPP oil on dry basis the amount of oxygen, was reduced to 21 wt.%.

In the second HDO step (experiments HDO_2_4 and HDO_2_2) 87% of the feed (1st step HDO oil and BCO) was transferred into an oil phase (2nd step HDO oil). This phase contained 92 to 96% of the accumulated energy of the feed. The 2nd step HDO oils contained less oxygen and more hydrogen and carbon than BCO. It can be concluded that through second HDO step the elemental composition is improved despite the accumulation of the biogenous carbon content. 62 to 67% of the energy content in terms of LCV was collected in the 2nd step HDO oil.

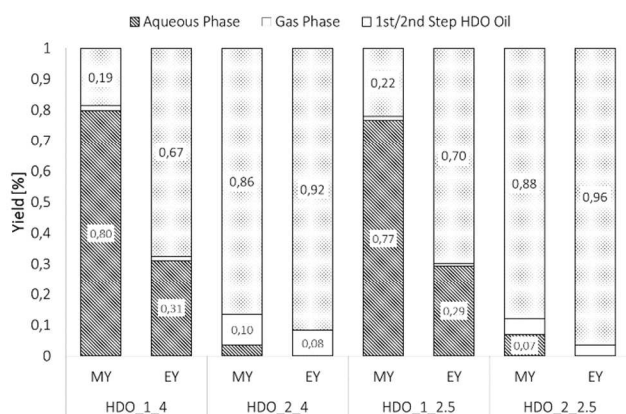


Figure 4: Mass (MY_{Phase}) and energy (EY_{Phase}) yield

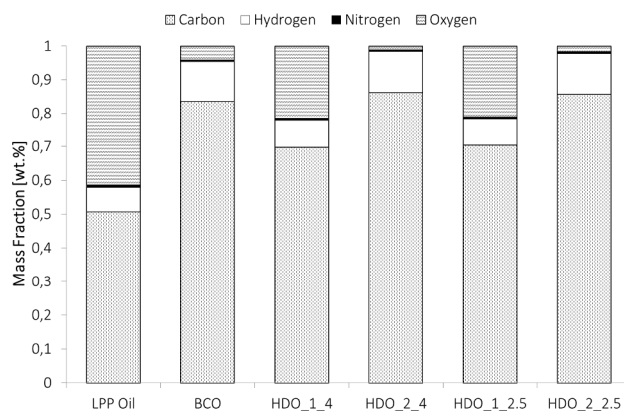


Figure 5: Elemental composition of the 1st/2nd step HDO oil on dry basis.

Van Krevelen Plot

To quantify the effect of HDO on the quality of LPP oil the molar ratios of oxygen to carbon (O/C) and hydrogen to carbon (H/C) are plotted in Van Krevelen Plot (see Figure 6) ¹⁹.

In order obtain a biofuel with fuel-like properties, the molar O/C ratio must be reduced and the molar H/C ratio must be increased. By decreasing the oxygen content the chemical stability, the lower heating value (LCV) and the energy density of the fuel can be improved.

In the first HDO step (experiments HDO_1_4 and HDO_1_2.5) the molar O/C ratio was reduced by 63% to 0.23 and 0.22. At the same time, the molar H/C ratio decreased significantly (HDO_1_4 by 16% to 1.43 and HDO_1_2.5 by 21% to 1.35). These results indicate that neither the reaction temperature (250°C) nor the reaction pressure (85bar) were sufficient to permit hydrogenation of LPP oil in the first HDO step.

The molar H/C ratio of 2nd step HDO oil was very similar to BCO. It was possible to reduce the molar O/C ratio of the 2nd step HDO oil by 75%.

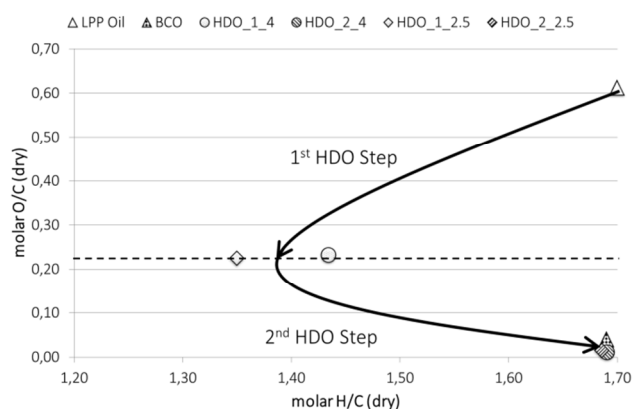


Figure 6: Van Krevelen Plot for the elemental composition of 1st step and 2nd step HDO oil on dry basis.

Density and Viscosity

Density and viscosity are key fuel properties. Especially in diesel engines, viscosity plays a crucial role during injection. It determines the size of the droplets and the quality of the atomization of the fuel. Too high viscous oils result in higher energy consumption with respect to the pump performance and the wear of injector equipment.

The reference values of the standard EN 590²⁰ diesel for density at 15°C (0.82 to 0.845 g/cm³) and for dynamic viscosity at 40°C (2.44 to 5.33 mPa s) are marked in Figure 7.

As shown, it is obvious that in the first HDO step the viscosity of the LPP oil was increased significantly. In HDO_1_4 the viscosity was increased by 1749% to 71.9 mPa s and in HDO_1_2.5 by 4079% to 162.6 mPa s. The density of the 1st step HDO oil however, was very similar to the LPP oil (HDO_1_4 1.07 kg/m³ and HDO_1_2.5 1.10 kg/m³).

In the first HDO step viscosity was increased enormously through water reduction of 80% and the low degree of hydrodeoxygenation. Density however, was not significantly altered by the first HDO step. In order to produce biofuels according to the specification of the standards the 1st step HDO oil had to be further processed.

As mentioned the 1st step HDO oil was processed together with BCO in the second HDO step. From Figure 7, it can be clearly seen that the 2nd step HDO oils had much improved regarding density and viscosity. Despite the increased biogenous carbon content, both specifications were lower than the specifications of BCO.

Compared to the 1st step HDO oil, the density was reduced in both experiments by 21%. The viscosity was decreased significantly by 96%.

It can be concluded that the two-step HDO process can convert LPP oil into 2nd step HDO oil with almost diesel-like density and viscosity. It was possible to improve the properties of the used BCO, despite the increase of the biogenous carbon content.

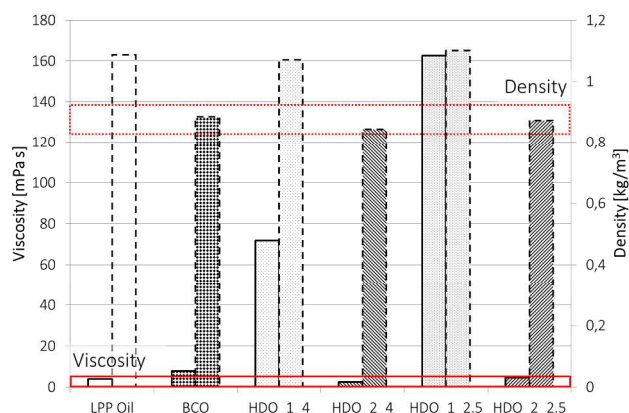


Figure 7: Density and viscosity of LPP oil, BCO and the 1st and 2nd step HDO oils.

GC-MS Analysis

Figure 8 shows the GC-MS chromatograms of LPP, HDO_1_2.5, and HDO_2_2.5. All 3 chromatograms show a gap at a retention time between 4.75 min and 6 min. This is the solvent gap, where the detector was switched off. It is hard to determine the chemical transformation of the liquids by the huge number of constituents which show up in GC-MS. Besides, GC-MS is limited by the boiling point of the compounds. GC-MS analysis seemingly suggests that only molecules with retention time below 35 min or a molecule size smaller than n-nonadecane are present in LPP oil or HDO liquids. To reveal the whole range of compounds GPC analysis was additionally performed. Figure 8 and Table 3 show the influence of the BCO carrier, which is providing fossil based long chain non branched alkanes into the fuel fraction.

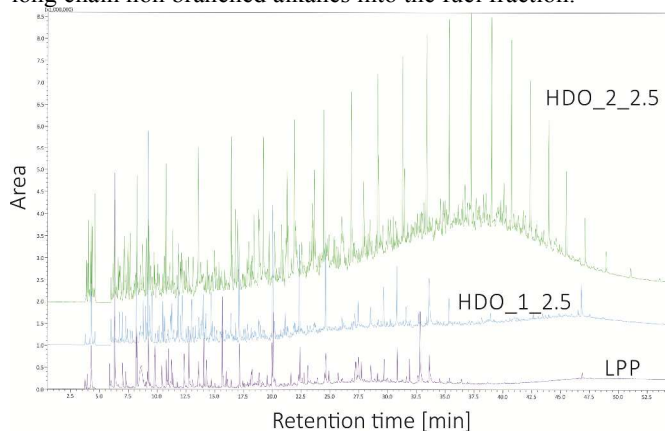


Figure 8: GC Chromatograms of LPP, HDO_1_2.5 and HDO_2_2.5

The effect of hydrodeoxygenation is well demonstrated by the vanishing highly oxygenated compounds as like levoglucosane (Retention time 32.8 min.) and 2-hydroxy-3-methyl-2-cyclopenten-1-one (Retention time 15.8 min.) during the first HDO step. 2-methylcyclopentanone which shows the highest peak in the HDO_1_2.5 chromatogram at 9.2 min is a major product of hydrodeoxygenation. This compound partly resists the second HDO step, so this is one of the sources of the

oxygen content of the final HDO fuel.

Table 3: Major constituents of LPP, HDO_1_2,5 and HDO_2_2,5

LPP	retention time	concentration
Compound Name	[min]	[area.%]
hydroxypropanone	6.3	15.3
levoglucosane	32.8	7.6
2-hydroxy-3-methyl-2-cyclopenten-1-one	15.7	7.4
2-methoxy-4-methylphenol	20.1	5.2
methoxyphenol	17.1	2.9

HDO_1_1,25

Compound Name	[min]	[area.%]
2-methylcyclopentanone	9.2	10.3
2-methoxy-4-methylphenol	20.0	8.3
2-methoxyphenol	17.1	6.1
2-methoxy-4-propylphenol	24.6	4.9
4-ethyl-2-methoxyphenol	22.3	4.7

HDO_2_1,25

Compound Name	[min]	[area.%]
heneicosane	37.2	2.3
nonadecane	33.4	2.2
eicosane	35.3	2.1
hexadecane	26.8	2.1
docosane	39.0	2.0

GPC Analysis

GPC analysis in Figure 9 shows the different molecule size ranges of LPP and the HDO products. Compared to FP oil LPP oil contains few compounds with an average molar mass of 2000g/mol.

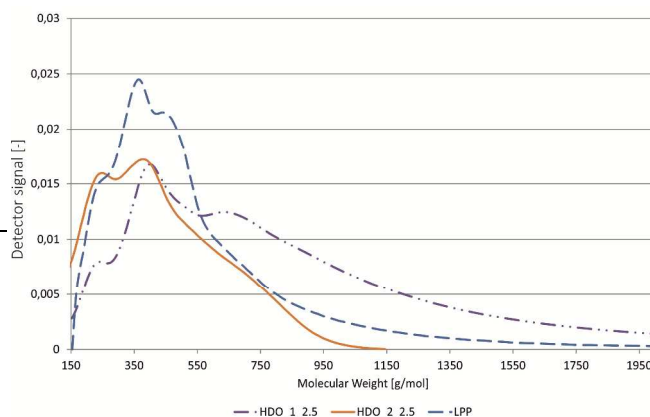


Figure 9: GPC Chromatograms of LPP, HDO_1_2,5 and HDO_2_2,5 (calibrated against polystyrene)

During the first HDO step, LPP oil is hydrophobized by loss of small highly oxygenated compounds and the water into the aqueous fraction, suggesting polymerization in the GPC. This effect is also the reason of viscosity density, as presented in Figure 7. Actually phase separation during the first HDO step by separating water from the nonaqueous phase increases the amount of polymers in the nonaqueous phase. Hydrogenation and cracking govern the second HDO step to produce final fuel, whereas the first step is mainly needed for deoxygenation and chemical dehydration.

Simulated Distillation

To quantify the volatility of BCO and 2nd step HDO oil simulated distillation experiments were performed. Figure 10 shows that the biogenous carbon content, obtained in the 2nd step HDO, does not have “negative” effect on the distillation characteristics.

Quality of the 2nd step HDO oils was closer to and partly above the reference curve of diesel fuel.

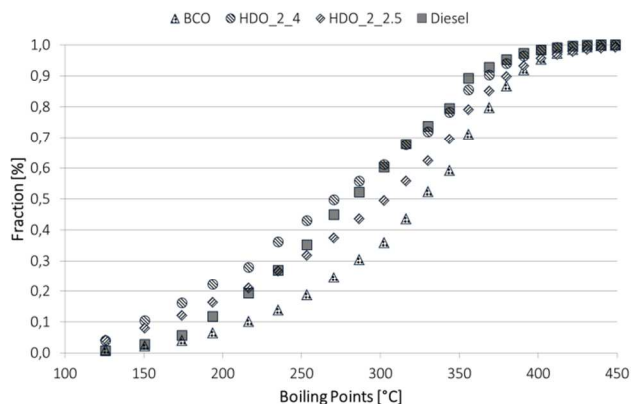


Figure 10: Distillation characteristics of BCO, Diesel and 2nd step HDO oils.

Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (ATR-IR)

As shown in Figure 11 the C-H peak at 3000cm⁻¹ is almost completely superimposed by the O-H peak at 3000 - 3500cm⁻¹. The C=O peak at about 1700cm⁻¹ represents the carbohydrate degradation products such as formaldehyde, hydroxy propanone, acetone, furancarboxaldehyde, in general substances with carbonyl groups. The stretching vibrations below 1000cm⁻¹ deplete, because only few hemiacetals and alcohols, as expected in carbohydrates, are present in the LPP oil.

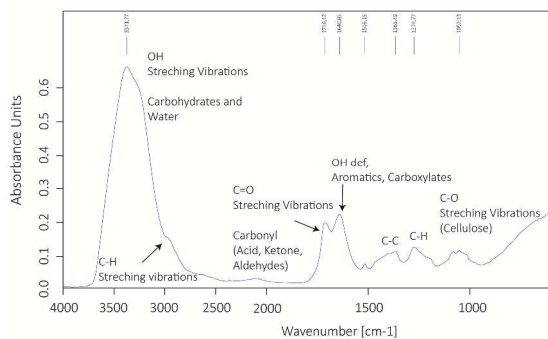


Figure 11 ATR-IR spectrum of LPP oil.

In Figure 12 to Figure 14 ATR-IR spectra of selected samples are shown. The interpretation of the different spectra is explained in Figure 11.

It is evident that in 1st step HDO oil (HDO_1_4) the water and oxygen content decreased and the fraction of aromatic carbon constituents increased.

1st step HDO (HDO_1_4) oil is converted into a biofuel through second step HDO. In 2nd step HDO oil (HDO_2_4 and HDO_2_2.5) CH absorption (3000cm⁻¹) and the characteristic absorption for aromatics (1500-1700cm⁻¹) is clearly confirmed through ATR-IR.

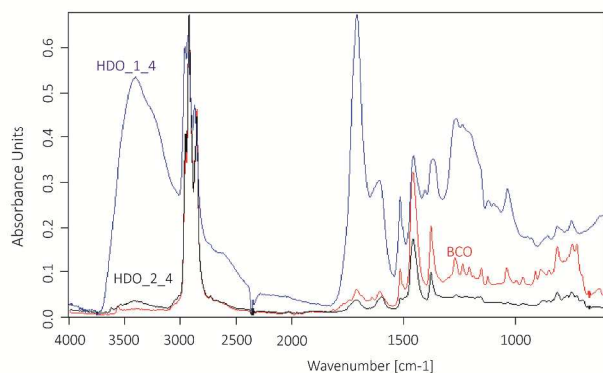


Figure 12: ATR-IR spectrum of BCO and 1st/2nd HDO oil.

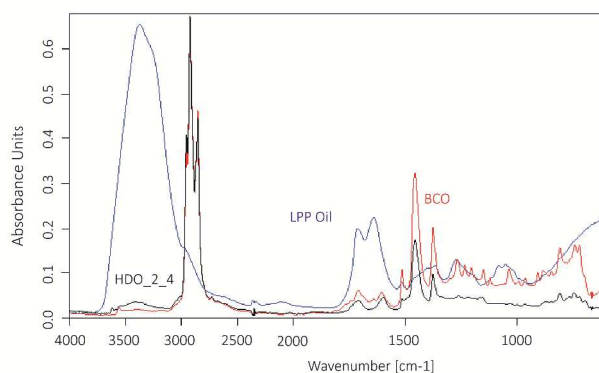


Figure 13: ATR-IR spectrum of BCO, LPP oil and 2nd step HDO oil.

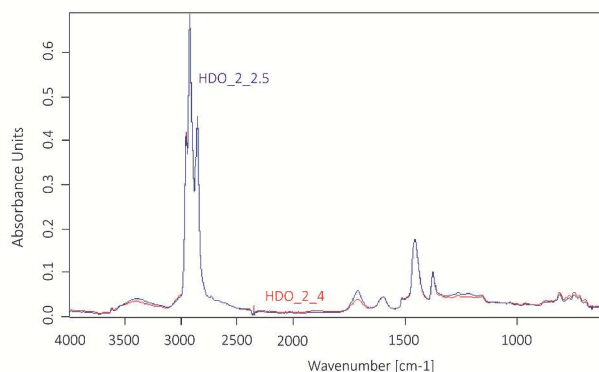


Figure 14: ATR-IR spectrum of 2nd step HDO oils.

Biogenous Carbon Content

In comparison to BCO the biogenous carbon content in the 2nd step HDO was increased as shown Table 4. These results show that with the two-step HDO process the LPP oil can be converted into a 2nd step HDO oil with diesel-like properties and high biogenous carbon content.

Table 4: Radiocarbon monitoring of 2nd step HDO oil and the BCO.

	Biogenous Carbon Content [wt.%]	Difference [%]
BCO	10	-
HDO_2_4	22.0	125
HDO_2_2.5	28.0	186

Balance of biogenous Carbon

In Figure 15 the balance of the biogenous carbon is shown for the two-step HDO process. It is apparent that 52wt.% of biogenous carbon of the LPP oil can be converted into biofuel with diesel fuel-like properties.

Most of the biogenous carbon was “lost” during the first HDO step in the aqueous phase since most of the unwanted highly oxygenated water soluble carbonaceous constituents like

hydroxypropanone, glycolaldehyde, acetic acid and formic acid were removed, to enable less hydrogen consumption in the second HDO step. As shown in Figure 15 these aqueous phases can be further processed in a biogas plant.

In the second HDO step 87% of the biogenous carbon (1st step HDO oil) from feed was be recovered. BCO was not converted into gaseous or aqueous products.

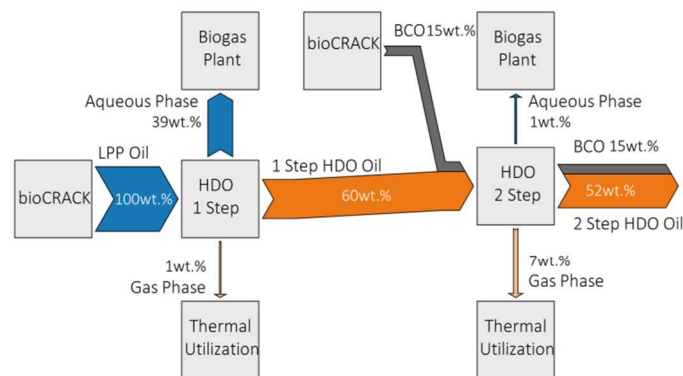


Figure 15: Balance of biogenous carbon of the two-step HDO process.

Conclusion

In this paper a two-step HDO process which is able to convert LPP oil in a biofuel with fuel-like properties is discussed. In Table 5 the key properties are summarized and compared.

It is apparent that:

- the water content was lowered by 99.6%
- the LCV was increased by 470% to 41.2MJ/kg
- the density and viscosity were lowered
- the carbon content of the product phase was increased by 330%
- the hydrogen content was increased by 30% and
- the oxygen content was lowered by 97%

The proof-of-principle of the two-step HDO process to convert LPP oil into a diesel-like biofuel was successfully investigated. The 2nd step HDO oil contained 52wt.% of biogenous carbon and 67% of the chemically fixed combustion energy .

Table 5: Comparison of LPP oil, 1st/2nd step HDO oil and conventional diesel.

	LPP oil	HDO _1_2.5	HDO _2_2.5	Diesel
Water Content (wt.%)	50	11	0.2	0.02
LCV (MJ/kg)	8.7	26.4	41.2	42.5
Density (kg/m ³)	1070	1100	870	835
Viscosity (mPa s)	4	163	4.5	4
Biogenous carbon (wt.%)	100	100	28	<7

Elemental analysis on wet basis

Carbon Content (wt.%)	25.6	62.5	85.5	85.9
Hydrogen Content (wt.%)	9.2	8.3	12.1	13.3
Oxygen Content (wt.%)	64.9	28.7	1.9	<1
Nitrogen Content (wt.%)	<1	<1	<1	<1

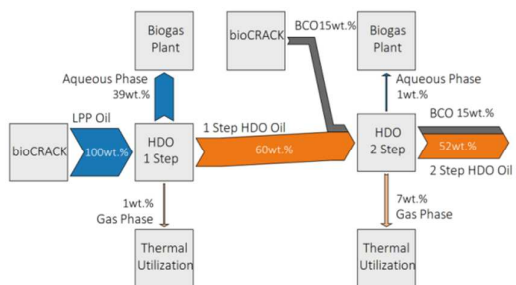
Acknowledgements

We thank A. Rollett, H. Kindermann, S. Krainer and A. Toth for assistance. This work was funded by the Austrian Research Promotion Agency (FFG) under the scope of A3 Plus Program.

References:

1. H. H. Nimz, U. Schmitt, E. Schwab, O. Wittmann, and F. Wolf, in *Ullmann's Encyclopedia of Industrial Chemistry 2000*, Wiley-VCH Verlag GmbH & Co. KGaA., 2000, pp. 454–503.
2. T. Bull, *Science (80-.)*, 1999, **285**, 1209.
3. T. Kaneko, F. Derbyshire, M. Eiichiro, D. Gray, and M. Tamura, in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, 2005, p. 37.
4. N. Schwaiger, R. Feiner, K. Zahel, A. Pieber, V. Witek, P. Pucher, E. Ahn, P. Wilhelm, B. Chernev, H. Schröttner, and M. Siebenhofer, *BioEnergy Res.*, 2011, **4**, 294–302.
5. N. Schwaiger, V. Witek, R. Feiner, H. Pucher, K. Zahel, A. Pieber, P. Pucher, E. Ahn, B. Chernev, H. Schroettner, P. Wilhelm, and M. Siebenhofer, *Bioresour. Technol.*, 2012, **124**, 90–4.
6. R. Feiner, N. Schwaiger, H. Pucher, L. Ellmaier, P. Pucher, and M. Siebenhofer, *RSC Adv.*, 2013, **3**, 17898–17903.
7. R. Feiner, N. Schwaiger, H. Pucher, L. Ellmaier, A. Reiter, M. Derntl, T. Glatz, P. Pucher, and M. Siebenhofer, *BioEnergy Res.*, in press, DOI:10.1007/s12155-014-9469-x.
8. F. M. Mercader, M. J. Groeneveld, S. R. A. Kersten, R. H. Venderbosch, and J. A. Hogendoorn, *Fuel*, 2010, **89**, 2829–2837.
9. J. Wildschut, F. H. Mahfud, R. H. Venderbosch, and H. J. Heeres, *Ind. Eng. Chem. Res.*, 2009, **48**, 10324–10334.
10. J. Wildschut, M. Iqbal, F. H. Mahfud, I. M. Cabrera, R. H. Venderbosch, and H. J. Heeres, *Energy Environ. Sci.*, 2010, **3**, 962–970.
11. F. de Miguel Mercader, M. J. Groeneveld, S. R. a. Kersten, C. Geantet, G. Toussaint, N. W. J. Way, C. J. Schaverien, and K. J. a. Hogendoorn, *Energy Environ. Sci.*, 2011, **4**, 985.
12. R. H. Venderbosch, a. R. Ardiyanti, J. Wildschut, a. Oasmaa, and H. J. Heeres, *J. Chem. Technol. Biotechnol.*, 2010, **85**, 674–686.
13. F. D. M. Mercader, *AIChE J.*, 2011, **57**, 3160–3170.
14. H. Pucher, N. Schwaiger, R. Feiner, P. Pucher, L. Ellmaier, and M. Siebenhofer, *Int. J. Energy Res.*, in press, DOI: 10.1002/er.3205.
15. *Dubbel: Taschenbuch für den Maschinenbau*, Springer Verlag, Berlin Heidelberg, 14th edn., 1981.
16. E. Laurent and B. Delmon, *J. Catal.*, 1994, **146**, 281–291.
17. Z. P. G. Masende, B. F. M. Kuster, K. J. Ptasinski, F. J. J. G. Janssen, J. H. Y. Katima, and J. C. Schouten, *Appl. Catal. B Environ.*, 2005, **56**, 189–199.
18. I. Kubičková, M. Snáre, K. Eränen, P. Mäki-Arvela, and M. Dmitry Yu., *Catal. Today*, 2005, **106**, 197–200.
19. D. W. Krevelen, *Fuel*, 1950, **29**, 269–284.
20. Austrian Standards Institute, *Kraftstoffe für Kraftfahrzeuge - Dieselmotoren - Anforderungen und Prüfverfahren*, 2010.

Table of contents entry:



A novel two step biomass liquefaction process for the production of a Diesel like fuel with 28% biogenous carbon content.