www.BioBoost.eu

Biomass based energy intermediates boosting biofuel production

This project has received funding from the European Union's Seventh Programme for research, technological development and demonstration under grant agreement No 282873

Deliverable

Catalyst testing of catalytic pyrolysis oil with the selected route

Workpackage:	WP5
Deliverable N^{o}:	D5.9
Due date of deliverable:	30/09/14
Actual date of delivery:	06/03/15
Version:	Final / vers.1.0
Responsible:	NESTE
Authors:	Marina Lindblad, Steven Gust
Contact:	Marina.Lindblad@nesteoil.com
Dissemination level:	PU-Public / CO-Confidential

Publishable Summary

This report summarizes the experimental work conducted regarding the task to evaluate the applicability of catalytic pyrolysis (CP) oil as energy intermediate for biofuel production in oil refinery. The primary target for the upgrading process is to remove oxygen in order to improve the quality and stability of the bio-oil and to obtain appropriate chemical composition of the oil product. Due to the chemical nature of the CP oil hydrotreatment was considered the preferred upgrading route and the preliminary upgrading concept presented was based on this route.

The hydrotreatment procedure selected to be studied for the upgrading of CP oil to a hydrocarbon-like product was a two-stage process with an initial stabilization of the CP oil before the final oxygen removal by hydrodeoxygenation (HDO). The experimental study included screening tests for suitable hydrotreatment conditions and a comparison between two alternative hydrotreatment catalysts. This work was a co-operation between CERTH supplying CP oil samples, GRACE supplying two hydrotreatment catalysts with different composition and NESTE OIL preforming upgrading tests in batch and tubular reactors and analysing product properties.

Based on the experimental results of this study we found that:

1. the oil product yield was approximately 73 wt%
2. the hydrogen consumption (based on dry CP oil feed) was 6 wt%
3. the non-condensable gases (13 wt%) were primarily paraffinic hydrocarbons
4. the CP oil feed requires a stabilization but even then we found catalyst coking
5. under the operation conditions used, we were not able to remove all oxygen

Table of Content

Report

1 Introduction

The experimental study presented in this report is part of the task to evaluate the applicability of biomass derived energy carrier in oil refinery (WP 5 Task 5.3). The energy carrier selected to be upgraded by refinery processes was the catalytic pyrolysis oil (CP oil) due to its relatively low oxygen (15 - 20 wt-%) and water (<10 wt-%) contents. In the subtask 5.3.2 the experimental work was defined as reactor tests for hydrotreating or catalytic cracking of CP oil. The primary target for the upgrading process is to remove oxygen in order to improve the quality and stability of the bio-oil and to obtain appropriate chemical composition of the oil product.

The upgrading concept proposed for the CP oil in Deliverable 5.4 (Applicability of catalytic pyrolysis liquid for different upgrading methods including selection of the method) was based on a two-stage hydrotreatment process for oxygen removal. Hydrotreatment was the preferred route due to the highly aromatic nature of the CP oil. Aromatic compounds are known for their high tendency to form coke in catalytic cracking due to the lack of additional hydrogen present to compensate for the hydrogen consuming reactions taking place. The challenge with pyrolysis oil, in general, is the presence of highly active compounds prone to polymerize at elevated temperatures. In a two-stage hydrotreatment process excessive coke formation is prevented by an initial hydrogenation (stabilization) step at moderate temperature before the final oxygen removal (hydrodeoxygenation, HDO) step. The addition of hydrogen into the products formed will further improve their quality.

This study was a co-operation between CERTH supplying CP oil samples, GRACE supplying hydrotreatment catalysts and NESTE OIL preforming the upgrading tests and analysing product properties. The objective was to produce a hydrocarbon-like product with potential to be utilized as drop-in biofuel components in the gasoline and/or diesel pool.

2 Experimental

The experimental work carried out for the upgrading of catalytic pyrolysis oil comprised hydrotreatment reactions for the removal of oxygen from the bio-oil in order to produce a hydrocarbon-like product. This study included evaluation of reaction conditions for hydrotreatment of CP oils as well as a comparison between two different compositions of the hydrotreatment catalyst.

2.1 Feeds and catalysts

Catalytic pyrolysis oils used in upgrading test runs at Neste Oil were produced at the Biomass catalytic pyrolysis pilot plant of CERTH. The catalytic pyrolysis process produces a two phase product, an upper aqueous phase and a lower organic phase which are separated at the production plant. The bottom phase product was received by Neste Oil. The samples showed further phase separation upon standing. The upper highly acidic aqueous phase was removed before using the CP oil as feed. Analysis data for CP oil feeds refers to this organic bottom phase.

Samples were received in one litre glass bottles: in 2012 (one batch - 1 L), 2013 (one batch - 2 L) and 2014 (3 batches - 4 L), i.e. totally 7 litres for analysis and testing purposes.

Catalysts selected for upgrading of CP oils by oxygen removal were sulfided hydrotreatment catalysts supported on porous oxide materials. In test runs for pretreatment of CP oils and for screening of hydrotreatment reaction conditions a conventional refinery hydrotreatment catalyst was used. The catalyst comparison was carried out with two different catalysts supplied by GRACE, Catalyst A (CoMo-based) and Catalyst B (NiMo-based).

2.2 Test run equipments

Preliminary experiments were conducted in batch reactor (Figure 1) to study thermal pretreatments and evaluate suitable hydrotreatment reaction conditions for the CP oil. Screening of reaction conditions was continued in tubular reactor (Figure 2). The tubular reactor equipment was used for the catalyst comparison test runs.

For batch test runs a PARR stirred autoclave (90 ml) was used. In the experiments the reactor was filled with about 50 ml CP oil. Thermal treatments were carried out without catalyst in nitrogen flow. In catalytic reactions the hydrotreatment catalyst (3 gram) was placed in a wire mesh basket. These test runs were conducted either in closed system under hydrogen pressure (adding hydrogen while it is consumed) or in flowing hydrogen.

In thermal treatments the maximum temperature was between 95 - 280 ^{o}C and the reaction pressure from atmospheric pressure to 125 bar. In two-stage hydrotreatments the stabilization step was carried out at 240 - 260 ^{o}C (T1) and the oxygen removal at 310 - 320 ^{o}C (T2), both at a pressure of 50-150 bar.

All batch reactor test runs were conducted during a working day and the reaction time was 3-7 hours.

Figure 1. Batch equipment setup: PARR reactor with inlets (above) and catalyst basket after test run (below).

The continuous reactor test runs were carried out in tubular reactor equipment (called INTO). The reactor tube was loaded with a mixture of catalyst (24 gram) and inert SiC in 1:1 volume ratio. The test runs lasted between 96 and 120 hours.

The two-step hydrotreatment was conducted in the tubular reactor by applying a temperature gradient over the reactor tube. In the first test run reaction conditions (H_2 flow rate, liquid feed rate and reaction temperature) were screened. Problems with pressure control caused fluctuations in the pressure during the test run. This problem was resolved and a constant pressure of 150 bar was achieved in the subsequent tests. For the catalyst comparison the maximum temperature was set to 350 ^{o}C giving an average temperature of 300 ^{o}C.

Figure 2. INTO equipment setup: Continuous tubular reactor (feed container and reactor oven with heating elements).

2.3 Analyses

CP oil feed samples and their hydrotreated products were analyzed for physical properties and chemical composition. Physical properties such as density, viscosity and micro carbon residue (MCR) were frequently analyzed, while total acid number (TAN) and heats of combustion were analyzed for selected samples. Analysis of chemical composition for organic phases included at least the water content and elemental composition (C, H, N, S), but often also product identification by Gas Chromatography-Mass Spectrometry (GC-MS), molecular weight distribution by Gel Permeation Chromatography (GPC) and boiling point distribution by simulated GC-distillation (SimDist). The quantitative amounts of light acids present in the aqueous phases formed in hydrotreatments were analyzed by High-Performance Liquid Chromatography (HPLC). The chemical composition of the gas phase was determined by GC-MS.

Elemental concentrations (C, H, N, S) were measured for wet sample, but calculated relative to dry sample to enable comparison between samples with different water contents. The oxygen content was calculated by difference (O % = [100 - C - H - N] %). Atomic H/C and O/C ratios used in van Krevelen diagrams describe the degree of hydrogenation and oxygen removal during hydrotreatment.

3 Results and Discussion

3.1 CP oil properties and composition

Physical properties and elemental composition for CP oils are shown Table 1 (all properties analyzed are given in Appendix 1). The quality of the CP oils received varied to some extent and this will be taken into account when evaluating their performance in hydrotreatment.

Physical properties like density, viscosity, micro carbon residue (MCR) and total acid number (TAN) describe the quality of the CP oil for processing. Very high densities and viscosities give poor flow properties. MCR shows the tendency for the CP oils to degrade thermally and form coke. The MCR value is considered to be an indication for the processability of CP oils since coke deposition is one of the main reasons for HDO catalyst deactivation. The TAN value is a measure of the acidity of the oil indicating the potential for corrosion problems. The main acid component in the CP oil was acetic acid (~1.5 wt-%).

The CP oils received contained 16 - 22 wt-% oxygen per dry mass. At this level of polarity the CP oils were able to retain 5 - 7 wt-% water. Atomic H/C ratios close to one indicate that the CP oils are highly aromatic. The chemical composition is discussed in more detail in Chapter 3.4.

Table 1. Physical properties (per wet sample) and heteroatom contents (calculated per dry sample) for CP oil feeds.

Date on sample		15.11.2012	23.3.2013 Bottle 1	23.3.2013 Bottle 2	24.2.2014	29.8.2014	22.10.2014 Bottle1&2
Density	kg/m^3	-	-	-	-	1096 (20 °C)	1118 (15 °C)
Viscosity 20°C	mm^2/g	-	86	-	-	77	232
MCR	wt-%	20.4	15.1	15.3	-	14.5	16.8
TAN	mg KOH/g	40	41	-	-	-	-
Water	wt-%	7.4	7.0	4.9	6.5	5.0	5.0
O (dry)	wt-%	20.5	16.9	19.9	22.0	16.0	16.8
N (dry)	ppm	n.a.	960	1040	1390	860	650
S (dry)	ppm	-	150	-	-	130	65
Atomic H/C ratio		1.03	1.10	1.07	1.08	1.06	1.11

Other heteroatoms present in the CP oils were nitrogen (650 - 1400 ppm N) and sulfur (65 - 150 ppm S). Not only oxygen, but also other heteroatoms should be removed during hydrotreatment.

The CP oils - except the sample received in August 2014 - had a separate aqueous phase as an upper layer. This upper layer was removed before further processing and is omitted from feed analysis and mass balances.

Three of the aqueous top phases have also been analysed for acid content. The amount of some predetermined light acids was quantified by HPLC. The two most abundant acids were acetic acid (8 - 12 wt-%) and propionic acid (2 - 6 wt-%).

3.2 CP oil pretreatment

Pretreatments of CP oils were conducted to improve feed quality and stability before oxygen removal by hydrotreatment at elevated temperatures (>300 ^{o}C). Removal of water and acids present in CP oils improves the possibilities to use catalysts with low water tolerance and decreases the risk for corrosion problems. Partial hydrogenation of compounds highly reactive for polymerisation - such as olefins, aldehydes and ketones - suppresses catalyst deactivation and reduces the risk for reactor plugging. Analysis results for pretreatment experiments are shown in Appendix 2.

Heating under nitrogen

In these heating experiments, the goal was to drive off the water and acids using an inert gas such as nitrogen. Two tests were conducted where the CP oil sample was heated in the reactor at 95 and 135 ^{o}C, respectively, over a period of 4 hours. Compounds stripped off with the gas were collected in a cold trap. The trapped samples contained water and light acids, but also a complex mixture of other organic compounds from the CP oil. Partial water removal was achieved with 50 and 70 wt-%, respectively, of the amount originally present in the CP oil being stripped off. Heating under gas flow was not seen potential enough to be adopted as a pretreatment procedure for CP oils due to the incomplete water removal and, especially, the additional carbon loss by the removal of organic compounds other than acids into the cold trap.

Stabilization of CP oil

The blank test (without catalyst) and feed stabilisation tests were carried out in closed systems under H_2 pressure. In the blank test, where the temperature was raised to 280 ^{o}C causing an increase in pressure to 123 bar, no indication of hydrogen consumption was observed. The MCR value of the feed (20 wt-%) was not reduced in the blank test (23 wt-%) supporting the assumption that no improvement by hydrotreatment occurred.

The stabilization of CP oil was studied in two test runs at moderate hydrotreatment temperatures (240 and 280 ^{o}C) over a period of 6 hours. In the stabilisation tests the consumption of hydrogen in the catalytic reaction was compensated by adding more hydrogen into the reactor during the reaction and trying to keep the pressure constant at 75 bar. Improved stability of the CP oil was obtained according to the reduced amount of MCR (from 20 to 14-15 wt-%). The oil product was still highly polar as the water content was on the same level as for the initial CP oil.

3.3 CP oil hydrotreatment

Hydrogen consuming reactions in hydrotreatments include C=C double bond hydrogenation, C=O double bond reduction, oxygen removal by water formation in hydrodeoxygenation, hydrocracking and hydrogenolysis reactions. Part of the oxygen can also be removed by decarboxylation as CO_2 or decarbonylation as CO.

Screening of reaction conditions was conducted in order to find appropriate conditions for catalyst comparison tests. The target at this stage was to achieve high degree of oxygen removal, not an optimization of hydrogen consumption. The hydrogenation of aromatic rings will increase with the severity of the reaction conditions (until the reaction temperature reaches a point where dehydrogenation reactions prevail over hydrogenation).

The idea of a two-stage hydrotreatment was adopted from the work by Elliott[1] on hydrotreatment for fast pyrolysis oil.

Analysis results for oil products from batch and tubular reactor hydrotreatment test runs are collected in Appendix 2 and GPC chromatograms are shown Appendices 3-6.

3.3.1 Hydrotreatment condition screening

Screening of reaction conditions for the two-stage hydrotreatment of CP oils was started with small scale batch reactor experiments (Test 3-6), but continued in a flow reactor test run (INTO-1). In the continuous mode slow feed rates (WHSV = weight hourly space velocity) were studied since long residence times are known to be beneficial for oxygen removal.

In the batch reactor tests (Table 2) the hydrotreatment temperatures were held at 240 - 260 ^{o}C for a short period before raising temperatures to 310 - 320 ^{o}C. The first test run (Test 3) was carried out in closed system under H_2 pressure keeping the reaction pressure constant by compensating for the consumed hydrogen. The following tests were carried out under flowing H_2. The hydrogen pressure was increased from around 80 bar in Test 3 to 145 bar in Test 6.

Table 2. Properties for the CP oil used as feed and for oil products obtained in screening test runs in Parr reactor (T1 = stabilization temperature, T2 = oxygen removal temperature).

		Feed	Test 3	Test 4	Test 5	Test 6
Average T1	^{o}C		261	261	238	244
Average T2	^{o}C		310	309	318	321
Av. pressure at T2	bar		77	92	118	146
Oil sample, wet						
MCR	wt-%	15.1	13.0	6.2	5.3	6.0
Water	wt-%	7.0	6.3	5.1	4.3	3.4
Oil sample, dry						
H	wt-%	7.0	6.5	7.0	7.9	8.4
C	wt-%	76.0	76.2	76.5	79.8	81.3
N	wt-%	0.096	0.107	0.100	0.125	0.124
O, calculated	wt-%	16.9	17.2	16.4	12.2	10.2
H/C	mol/mol	1.10	1.02	1.09	1.17	1.23
O/C	mol/mol	0.17	0.17	0.16	0.11	0.09
Degree of HDO	%		6	18	42	46
Degree of HDN	%		-3	11	-5	-15

Negative values for the degree of nitrogen removal are unrealistic and probably to be due to inaccuracy in analysis of the amount of nitrogen. Anyhow, the degree of nitrogen removal is proposed to be low in these experiments.

[1] D.C. Elliott, "Historical developments in hydroprocessing bio-oils", Energy & Fuels 21 (2007) 1792 - 1815.

The trends in oxygen removal, hydrogenation, water content and micro carbon residue for the oil products, when going towards more severe hydrotreatment conditions, are depicted in Figure 3.

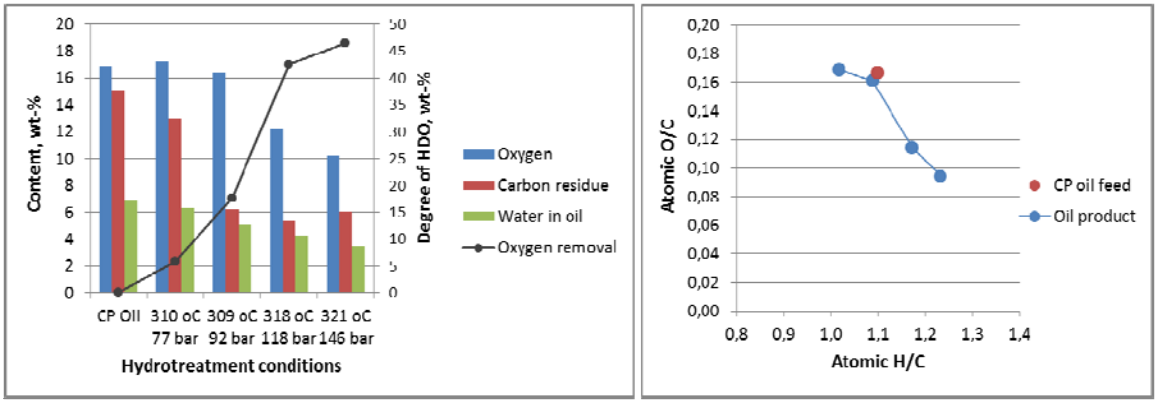


Figure 3. Oxygen removal (degree of HDO or atomic O/C), hydrogenation (atomic H/C), water content and micro carbon residue (MCR) for oil phase of hydrotreatment products.

With increasing efficiency for hydrotreatment a simultaneous decrease in oxygen content and increase in hydrogen content was observed. This change in composition decreased the polarity and increased the stability of the oil phase seen as decreased water content and micro carbon residues.

With a first stage prehydrogenation at about 240 °C and a second stage hydrotreatment at 320 °C and 150 bar in our batch reactor set-up (Test 6) the degree of oxygen removal achieved was only about 45 %. In addition, no nitrogen removal was observed. Screening of reaction conditions was decided to be continued in tubular reactor equipment (INTO).

In the first tubular reactor test run (INTO-1) the CP oil was dissolved and diluted with 15.7 wt-% tetrahydrofuran (THF, C_4H_8O) in order to ensure good flow properties of the feed. In the reaction THF was mainly converted to butane and removed in the gas phase, but some butane and THF was also detected in liquid phase. Results from this test run are shown in Table 3. The two stage hydrotreatment was carried out by applying a temperature gradient over the reactor tube. The reaction temperature is described by the average temperature over the whole catalyst bed and the maximum temperature within the bed. Due to difficulties in controlling the reaction pressure and hydrogen flow these are given as average values over the sampling time. At the end of the experiment (about 70 to 105 hours on stream) stable conditions were achieved.

In order to improve the degree of oxygen removal the feed rate was decreased (WHSV 0.39 → 0.16 h^{-1}), hydrogen flow rate increased (6 → 16 l/h) and the maximum reaction temperature slightly increased (340 → 350 °C). The main differences in reaction conditions compared to the batch reactor tests were higher maximum reaction temperatures, better contact between feed and catalyst as well as better hydrogen availability.

Table 3. Properties for the CP oil used as feed and for oil products obtained in screening test run (INTO-1) in tubular reactor.

		Feed	S5	S8	S10	S12	S13
Run time	h		23.2	47.2	71.1	98.7	122.1
Average T	°C		291	289	297	~298	~298
Maximum T	°C		342	340	349	352	352
Av. pressure	bar		153	152	154	148	144
WHSV	h^{-1}		0.39	0.31	0.21	0.19	0.16
Av. hydrogen	l/h		6	9	8	16	11
Oil sample, wet							
MCR	wt-%	-	0.7	1.8	-	0.3	-
Water	wt-%	6.3	1.4	1.0	1.0	0.4	0.2
Oil sample, dry							
H	wt-%	7.6	10.3	9.6	10.7	10.9	10.8
C	wt-%	71.4	81.4	78.1	78.2	82.4	82.6
N	wt-%	0.128	0.122	0.141	0.101	0.068	0.076
O, calculated	wt-%	20.9	8.2	12.2	11.0	6.6	6.6
H/C	mol/mol	1.26	1.51	1.46	1.63	1.58	1.56
O/C	mol/mol	0.22	0.08	0.12	0.11	0.06	0.06
Degree of HDO	%		71	58	60	82	87
Degree of HDN	%		30	20	41	70	76

Both the degree of oxygen and nitrogen removal was improved. With an average reaction temperature of 300 °C and a maximum temperature of 350 °C at 150 bar (Samples 12 and 13) the degree of oxygen removal was about 85 % and the degree of nitrogen removal about 75 %. In Figure 4 the deoxygenation and hydrogenation of the CP oil during hydrotreatment is depicted by the changes in atomic O/C and H/C ratios, respectively. The performances in tubular and batch reactor tests are compared. Due to the different ways to carry out the two-stage reaction in the tubular and batch reactor tests the comparison between reaction temperatures is not straightforward.

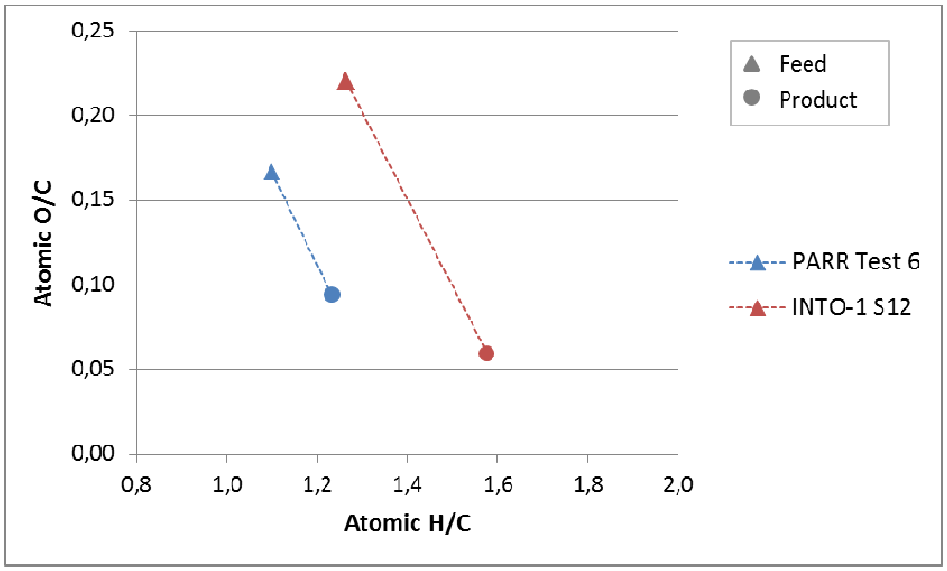


Figure 4. Van Krevelen diagram for tubular reactor (INTO-1 S12) and batch reactor (PARR Test 6) oil products obtained with a conventional refinery hydrotreatment catalyst.

The clearly improved performance for hydrotreatment in the tubular reactor set-up is proposed to be mainly due to the better feed-catalyst contact and hydrogen availability than a possible difference in reaction temperatures. The decision to favour the tubular reactor was further supported by the possibility to follow catalyst deactivation with time on stream. Since the use of THF as diluent complicated the evaluation of the results, the CP oil feed will be used without dilution in the catalyst comparison tests.

3.3.2 Hydrotreatment catalyst comparison

The performance of the two catalyst samples supplied by Grace was studied in tubular reactor test runs at reaction conditions found suitable for high oxygen removal based on previous screening test runs. The aim with these tests was, in addition, to achieve a reasonable mass balance and to get an estimate of the hydrogen consumption. The results for Catalyst A and Catalyst B are given in Table 4 and 5, respectively.

Table 4. Properties for the CP oil used as feed and for oil product samples obtained in tubular reactor test run (INTO-2) with Catalyst A.

		Feed	S2	S4	S6	S8
Run time	h		21.5	45.9	69.3	96.9
Average T	°C		299	299	299	299
Maximum T	°C		353	354	354	354
Pressure	bar		147	148	148	149
WHSV	h^{-1}		0.42	0.40	0.40	0.34
Hydrogen	l/h		13.7	13.7	13.7	13.7
Oil sample, wet						
MCR	wt-%	14.5	0.04	0.46	0.88	1.1
Density at 20 °C	kg/m^3		889	912	919	921
Viscosity at 20 °C	mm^2/s		2.2	3.1	3.5	3.6
Water	wt-%	5.0	0.1	0.5	0.5	0.4
Oil sample, dry						
H	wt-%	6.9	11.2	10.7	10.6	10.5
C	wt-%	77.1	87.0	86.6	85.3	86.0
N	wt-%	0.086	0.024	0.056	0.066	0.065
O, calculated	wt-%	16.0	1.8	2.6	4.0	3.4
H/C	mol/mol	1.06	1.53	1.47	1.48	1.45
O/C	mol/mol	0.16	0.02	0.02	0.04	0.03
Degree of HDO	%		92	87	80	82
Degree of HDN	%		81	50	40	37

The initial degrees of HDO and HDN were high with Catalyst A, but the results gave a clear indication of catalyst deactivation during the test run carried out at constant reaction conditions. The trend for weaker performance was seen in both physical properties and chemical composition of the oil product. The increasing amount of high molecular weight products observed by GPC (Appendix 5) supported this conclusion.

Table 5. Properties for the CP oil used as feed and for oil product samples obtained in tubular reactor test run (INTO-3) with Catalyst B.

		Feed	S2	S4	S6	S8
Run time	h		25.8	70.4	94.7	118.1
Average T	°C		298	298	299	299
Maximum T	°C		352	352	353	353
Pressure	bar		148	148	148	140
WHSV	h^{-1}		0.35	0.33	0.31	0.31
Hydrogen	l/h		12.4	13.7	13.7	13.7
Oil sample, wet						
MCR	wt-%	16.8	0.03	0.17	0.24	0.15
Density at 15 °C	kg/m^3		871	882	889	889
Viscosity at 20 °C	mm^2/s		2.4	2.6	2.9	2.7
Water	wt-%	5.0	0.01	0.02	0.043	0.085
Oil sample, dry						
H	wt-%	7.1	12.4	11.8	11.5	11.7
C	wt-%	76.1	86.2	85.1	85.4	86.7
N	wt-%	0.065	0.001	0.011	0.015	0.015
O, calculated	wt-%	16.8	1.4	3.1	3.0	1.5
H/C	mol/mol	1.11	1.71	1.65	1.60	1.61
O/C	mol/mol	0.17	0.01	0.03	0.03	0.01
Degree of HDO	%		94	85	86	93
Degree of HDN	%		99	90	86	86

The initial degrees of HDO and HDN with Catalysts B were higher compared to Catalyst A. Catalyst deactivation was also observed with Catalyst B, but to a lower extent based on changes in oil product properties. Still this test run was stopped due to reactor plugging at the upper part of the reactor tube. Problems with the pressure in the reactor started after 70 hours on stream and fluctuations in hydrogen flow at about 100 hours on stream. Catalyst A was on the other hand easily unloaded from the reactor and only minor clogging of the catalyst was observed at the inlet. The rate of deactivation for the catalysts is compared in Figure 5, where the rate is represented by the change in density with time-on-stream. Similar curves can be drawn for other properties as well.

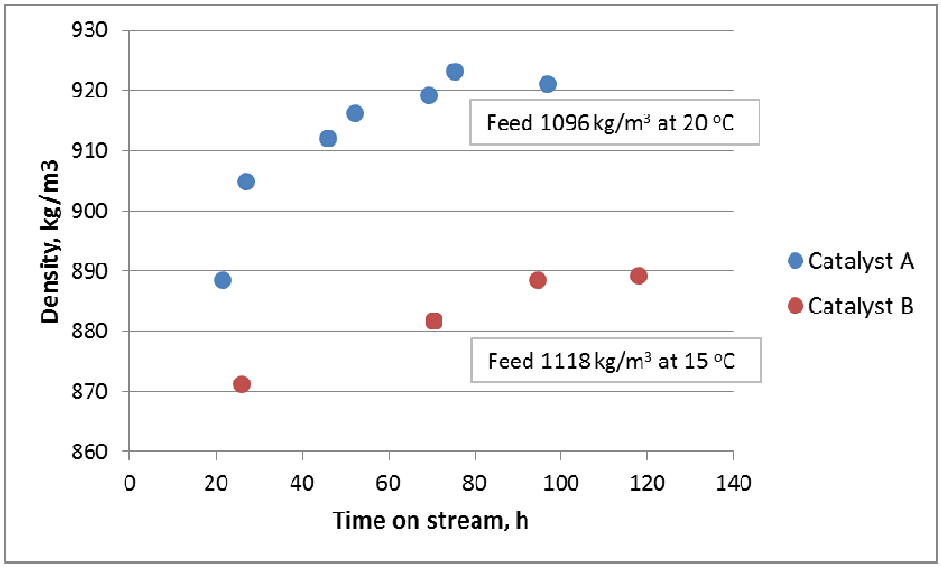


Figure 5. Density of oil products as a function of time on stream for Catalyst A (density at 20 °C) and Catalyst B (density at 15 °C).

The quality of the CP oils used as feed for Catalyst A and Catalyst B was similar, except for the higher viscosity of the feed for Catalysts B. The poorer flow properties might be one reason for the faster plugging of the reactor. It cannot be ruled out that the better quality of the oil products with Catalyst B is partly due to the clogging of the catalyst with high molecular weight products reducing their amount in the product.

Comparing the performance of Catalyst A and Catalyst B in HDO and HDN during about 95 hours on stream it was observed that

- similar average oxygen removal was achieved with Catalyst A (86 %) and Catalyst B (88 %)
- oxygen removal is restricted by the presence of phenolic compounds for both catalysts and, in average, about 2.5-3.0 wt-% oxygen remained in the products
- the quality of oil products produced with Catalyst B was slightly better compared to Catalyst A; especially the water content was reduced from an average amount of 0.4 to 0.02 wt-%
- significant difference was, however, observed in the HDN activity: the degree of nitrogen removal decreased from 81 to 37 % with Catalyst A, while it was at a much higher level with Catalyst B (decreasing from 99 to 87 %)

Figure 6 shows the van Krevelen diagram for Catalyst A and Catalyst B. The average atomic H/C ratio was 1.5 for Catalyst A compared to 1.7 for Catalyst B. The higher H/C ratio for Catalyst B indicated higher hydrogenation activity (see also Chapter 3.5).

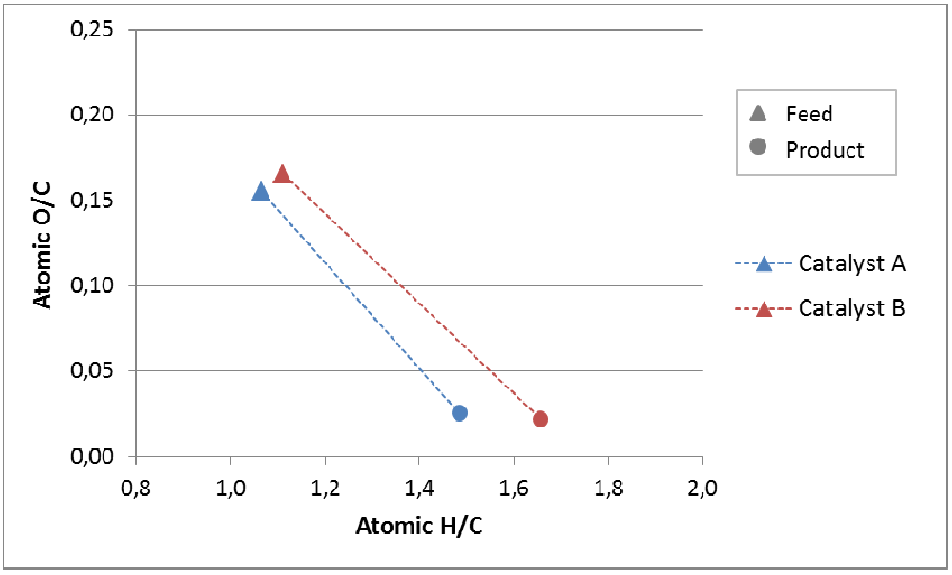


Figure 6. Van Krevelen diagram for tubular reactor (INTO-2 and INTO-3) oil products obtained with hydrotreatment Catalyst A and Catalyst B.

3.3.3 Nitrogen removal during hydrotreatment

All CP oil feeds contained some nitrogen. The degree of nitrogen removal taking place during hydrotreatments of CP oils is summarized in Figure 7.

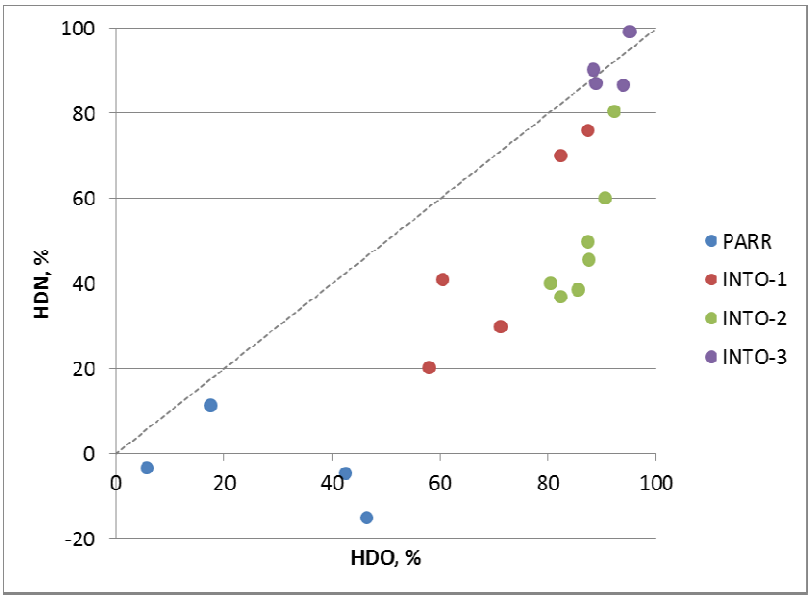


Figure 7. Nitrogen removal (HDN) as a function of oxygen removal (HDO) for oil products from batch (PARR Test 3-6) and tubular (all samples collected during INTO-1, INTO-2 and INTO-3) reactor test runs.

The degree of nitrogen removal seemed to follow the degree of oxygen removal, but stayed for most oil products at a lower level. The only exception was hydrotreatment with Catalyst B where a similar or even better HDN activity compared to HDO was achieved. The amount of nitrogen (hundreds of ppm N) remaining in the oil products is very high compared to nitrogen concentrations (<10 ppm) achieved in conventional

HDS/HDN of fossil fuel streams. A better knowledge of the type of nitrogen compounds present is needed to solve this problem.

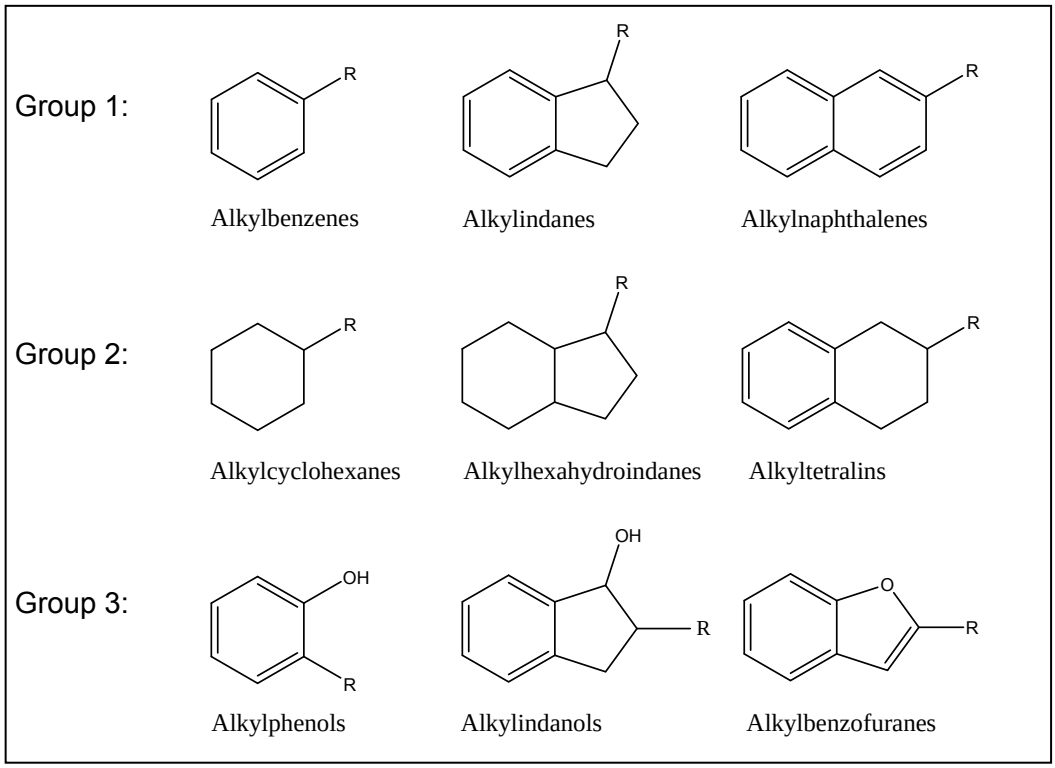
3.4 Hydrotreatment product composition

3.4.1 Liquid oil phase

Product compositions of oil phases were analysed by identifying compounds using GC-MS, estimating the molecular weight distribution by GPC and boiling point distribution by simulated GC-distillation (SimDist). The latter allows for simulated fractionations of the oil product into gasoline, diesel, bas oil and heavier components.

Compounds identified by GC-MS method were restricted to chain lengths C4-C13 and with maximum molecular mass around 180 amu for hydrocarbons and slightly higher (about 210 amu) for oxygen containing compounds. GPC and SimDist methods made it possible to clarify the presence of higher molecular weight compounds.

CP oils are complex mixtures of mainly aromatic hydrocarbons and aromatic oxygen containing compounds. These compounds can be grouped into alkylbenzenes, alkylindanes, alkylindenes, alkylnaphthalenes, alkylphenols, alkylbenzofuranes, alkylbenzenediols and methoxyphenol derivatives. Deoxygenation and hydrogenation reactions taking place during incomplete hydrotreatment are described in Appendix 7 for the oil product obtained in batch reactor Test 4 (degree of HDO 46 %). The main compounds present in the oil product at this stage belong to components present in Group 1 and 3 in Scheme 1. With increasing severity of hydrotreatment conditions Group 1 components are further hydrogenated to Group 2 components and deoxygenation of Group 3 compounds continues. The most difficult compounds to convert to hydrocarbons are the phenol based compounds.



Scheme 1. Groups of light compounds found in HDO products of CP oils.

In average about 2-3 wt-% oxygen was still present in oil products obtained with Catalyst A and Catalyst B during the most severe reaction conditions used in this study. The remaining oxygenates in the oil products for Catalyst A were identified by GC-MS to be phenol, C1-C14 alkylphenols, indanol and methyl-indanol.

The molecular weight distribution of oil products obtained in this study is shown in Figure 8.

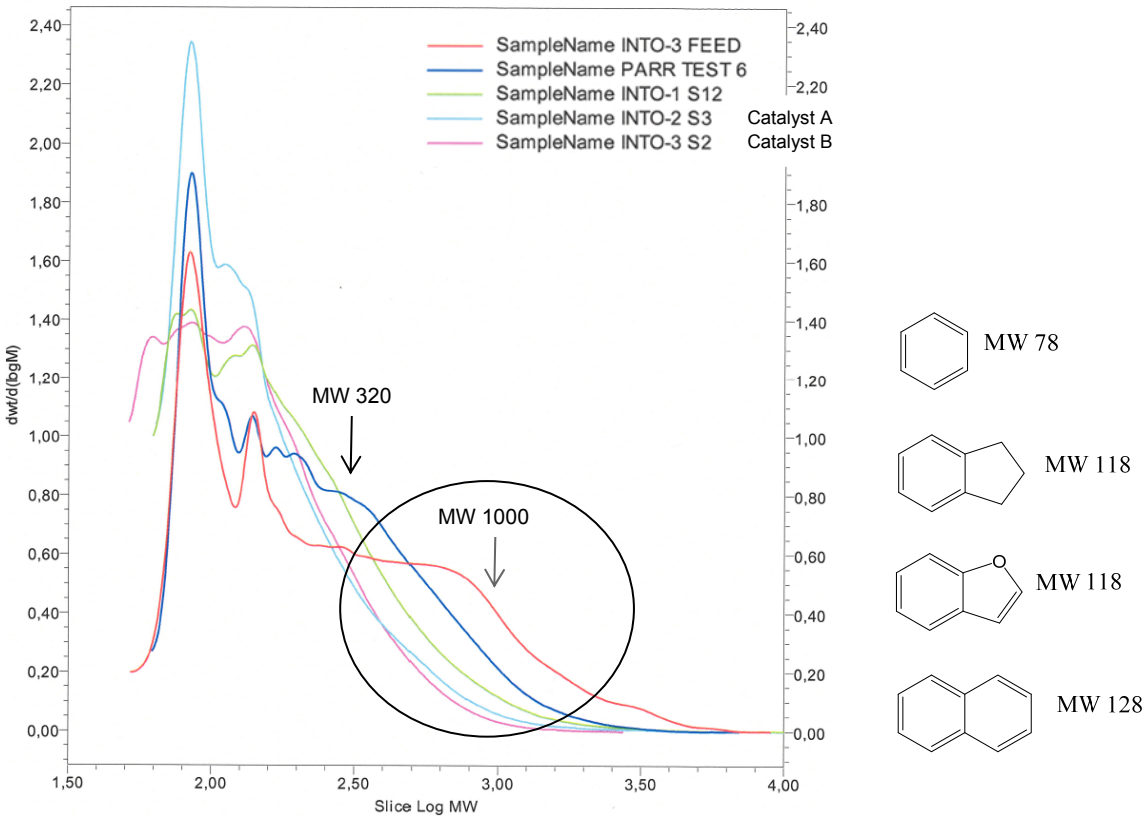
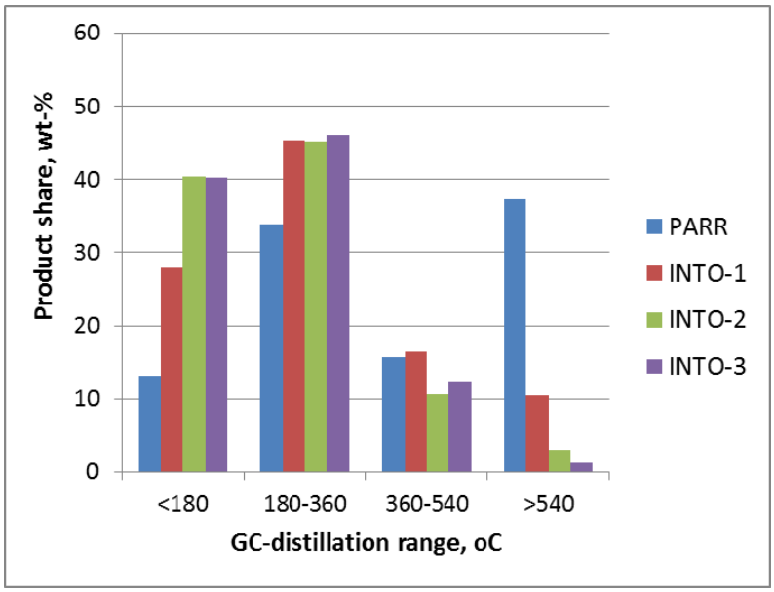


Figure 8. GPC chromatograms for oil products from a batch reactor test run (PARR Test 6) and tubular test runs (INTO-1, INTO-2, INTO-3) compared to a CP oil sample (represented by the feed used in INTO-3).

The molecular weight scale is based on oligomers of styrene. For oil products this is not an absolute scale but indicates only orders of magnitude. In all test runs the product distribution becomes narrower as the heaviest components are converted to lighter ones. This is proposed to mainly be due to oxygen removal by hydro-deoxygenation as well as side chain removal from aromatic rings by hydrogenolysis or hydrocracking. As expected, based on physical properties measured, the hydrotreat-ments carried out with Catalyst A and Catalyst B gives the narrowest distributions. The chromatograms also show that Catalyst B produced very light components not observed with Catalyst A.

Simulated GC-distillations of oil products support the GPC results by showing the formation of very high boiling components - all components were not even necessarily recovered in the GC-distillations with maximum temperature at 740 °C. The lower the degree of oxygen removal was, the higher the amount of unrecovered components. To have an estimate of the amount of various product fractions formed the GC-distillation results were roughly divided into gasoline (<180 °C), diesel (180-360 °C), base oil (360-540 °C) and heavier (>540 °C) components. The unrecovered amount, probably

consisting of heavy and highly polar compounds, was added to the bottom fraction (>540 °C). The simulated fractionations are shown in Figure 9.



Test run	Equipment	Catalyst	T, °C	p, bar	WHSV, h^{-1}	Time, h	Recovered, wt-%
PARR	batch	Conventional	320	146		7	82.5
INTO-1	tubular	Conventional	350 max	148	0,2	99	96.3
INTO-2	tubular	Catalyst A	350 max	148	0,4	97	99.3
INTO-3	tubular	Catalyst B	350 max	148	0,3	95	100

Figure 9. Product distributions for oil products estimated from simulated GC-distillations for batch and tubular reactor tests (bottom fraction = SimDist fraction >540 °C + unrecovered amount in SimDist).

The fractionation of the oil product for Catalyst A and Catalyst B was very similar: about 40 wt-% gasoline and 45 wt-% diesel components were formed. For Catalyst B full recovery of the oil products was obtained with distillation end points <600 °C.

3.4.2 Gas phase

The compositions of gas phase samples obtained in tubular reactor test runs are shown in Appendices 11-13.

The main components in gas phases obtained with Catalyst A and Catalyst B were hydrocarbons - their amount being ~93 wt-% when omitting the surplus of hydrogen coming through the reactor. In addition, some carbon dioxide (~6 wt-%) and carbon monoxide (~1 wt-%) were detected. The compounds were primarily saturated aliphatic C1-C7 molecules. The compositions with the ten most abundant molecules - representing about 80 wt-% of all hydrocarbons in gas phase - are shown in Table 6.

Table 6. Composition of gas phases obtained with Catalyst A (sample INTO-2 S6) and Catalyst B (sample INTO-3 S4). Samples shown were collected after 70 hours on stream.

		Catalyst A	Catalyst B
Composition			
Carbon dioxide	wt-%	6.5	6.0
Carbon monoxide	wt-%	0.9	0.8
Hydrocarbons	wt-%	92.6	93.2
Most abundant compounds			
Methane	wt-%	16.0	14.7
Ethane	wt-%	9.8	12.2
Propane	wt-%	11.8	11.4
n-Butane	wt-%	9.1	8.4
iso-Pentane	wt-%	2.1	2.0
n-Pentane	wt-%	2.9	4.4
Cyclopentane	wt-%	7.6	6.5
Methyl-cyclopentane	wt-%	5.4	4.5
Cyclohexane	wt-%	8.0	9.9
Methyl-cyclohexane	wt-%	4.9	7.3

The compositions and hydrocarbon distributions were surprisingly similar taken into account that the gas phases were obtained in hydrotreatment reactions with different batches of CP oil as feed and with catalysts of different composition.

3.4.3 Aqueous phase

Acids analysed from aqueous phase samples obtained in tubular reactor test runs are given in Appendices 8-10.

In hydrotreatment with Catalyst A and Catalyst B the oxygen removal was high enough to decrease the density of the oil products below that of water. After separation of the lower aqueous phase the amount was weighted and its acid composition was analysed by HPLC. Examples of acids identified and quantified are shown in Table 7.

Table 7. Amount of small acids in aqueous phase for Catalyst A (sample INTO-2 S8) and Catalyst B (sample INTO-3 S6). Samples shown were collected after 95 hours on stream.

		Catalyst A	Catalyst B
Formic acid	ppm	29	29
Acetic acid	ppm	160	110
Propionic acid	ppm	37	18
Butanoic acid	ppm	15	7
2-Methylpropanoic acid	ppm	6	2
Pentanoic acid	ppm	8	2
Methylbutanoic acid	ppm	10	2
Hexanoic acid	ppm	16	2
Butanedioic acid	ppm	<1	2
Propanedioic acid	ppm	<1	7
Hydroxybutanedioic acid	ppm	<1	2
Pentanedioic acid	ppm	<1	1

Samples taken at the same time-on-stream show a higher amount of acids with Catalyst A (281 ppm) compared to catalyst B (184 ppm). There are also some differences in the composition.

3.5 Hydrotreatment product yields and hydrogen consumption

The mass balances for the gas, oil and aqueous phases produced in hydrotreatments with Catalyst A and Catalyst B are depicted in Figure 10 as a function of time-on-stream. For comparison also the average yields for these samples were calculated (Table 8).

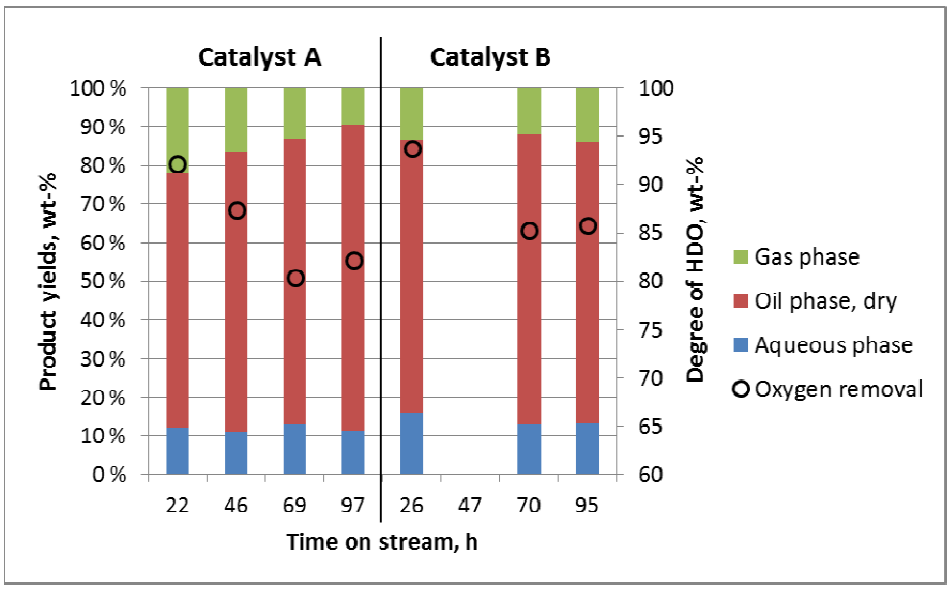


Figure 10. Mass balance for hydrotreatments: yields of gas, liquid oil and aqueous phases produced by Catalyst A and Catalyst B.

Table 8. Average product distributions for hydrotreatments with Catalyst A and B.

Average yields, wt-%	Catalyst A	Catalyst B
Gas phase	15	13
Oil phase, dry	73	73
Aqueous phase	12	14

No significant difference in product distribution between the two catalysts was observed. The oxygen mass balance and hydrogen consumption shown in Table 9 gives some more insight into the reactions taking place during hydrotreatment.

Oxygen can be removed as water in hydrodeoxygenation reactions or as CO_2 by decarboxylation (or CO by decarbonylation). The amount of oxygenates dissolved into the aqueous phase will also contribute to the removal of oxygen from the oil phase. The dissolved amount was calculated from the total oxygen removal by difference. No significant amount of oxygenates were observed in the gas phase.

Hydrogen is consumed in the formation of water, for the saturation of double bonds as well as in hydrogenolysis and hydrocracking. The latter is for example seen in the formation of highly saturated gaseous products. Since hydrogenation of C=C double bonds could not be separated from hydrogenolysis and hydrocracking reactions, they are all lumped together as "hydrogenation". From this follows that also the hydrogen consumed for saturation of aromatics is included in this lumped amount and cannot be reported separately. Only the hydrogen consumption for oxygen removal as water was calculated independently.

Table 9. Oxygen mass balance and H_2 consumption for Catalyst A and Catalyst B.

		Catalyst A	Catalyst B
Oxygen in feed	wt-%	16.0	16.8
Oxygen removed from feed	wt-%	13.7	14.7
Oxygen removal			
as H_2O	wt-%	82	97
as CO_2 + CO	wt-%	6	4
as oxygenates (by difference)	wt-%	12	-
H_2 consumed per CP oil, dry			
for H_2O formation	wt-%	1.4	1.7
for "hydrogenation"	wt-%	4.5	4.8
TOTAL consumption	wt-%	**5.9**	**6.5**
H_2 consumed per oil product, dry			
for H_2O formation	wt-%	1.8	2.2
for "hydrogenation"	wt-%	5.8	6.1
TOTAL consumption	wt-%	**7.6**	**8.3**

From Table 9 it is seen that oxygen is primarily removed as water. The low CO_2 formation indicates that acids are removed by hydrogenation and dissolution rather than by decarboxylation.

For both catalysts the hydrogen consumption for water formation is much lower compared to the consumption related to double bond hydrogenations, hydrogenolysis and hydrocracking.

A slightly higher degree of hydrodeoxygenation for Catalyst B is proposed by the higher oxygen removal and hydrogen consumption in water formation. The difference between the catalysts for the contribution from other hydrogen consuming reactions is minor. With the higher quality and higher H/C ratio for oil products obtained with Catalyst B a greater difference in the degree of hydrogenation would have been expected.

The total hydrogen consumption per dry CP oil was about 6 wt-% (with a difference of only 10 % between the catalysts).

4 Conclusions

The hydrotreatment procedure selected to be studied for upgrading of catalytic pyrolysis oil to a hydrocarbon-like product was a two-stage process with an initial stabilization of the CP oil before the final oxygen removal by hydrodeoxygenation (HDO). The study included screening tests for suitable hydrotreatment conditions and a comparison between two alternative hydrotreatment catalysts. Results presented in this report refer to the processing of the organic phase of the CP oils received.

Comments on processing:

- due to the polarity of the CP oil high **reaction pressure** (150 bar) was preferred for the hydrotreatment to ensure the availability of hydrogen in liquid phase; this is a higher pressure than those used in conventional HDS/HDN units in oil refineries (30 - 50 bar)
- complete oxygen removal was not possible mainly due to the presence of highly stable **phenol and alkylphenol compounds** (this type of compounds are known from literature to be highly resistant and may require HDO temperatures >350 ^{o}C); current traffic fuel specifications do not recognise phenolic compounds as components in the gasoline pool
- the **HDN activity** was generally lower than the HDO activity and very high amounts of nitrogen (hundreds of ppm) remained in the oil products; such high nitrogen contents could cause problems (e.g. catalysts deactivation) if further processing of the oil product is needed
- when aiming at high oxygen removal significant **saturation of aromatic compounds** occurred
- the **total hydrogen consumption** was about 6 wt-% H_2 per dry CP oil and about three times more hydrogen was used for hydrogenation compared to oxygen removal by water formation
- **carbon efficiency** was reduced by gas formation (hydrocarbons and carbon oxides) and dissolution of polar oxygenates into the aqueous phase

Comments on catalyst comparison and product properties:

- both catalysts showed deactivation during the test run
- similar total product compositions were obtained with Catalyst A and Catalyst B, consisting in average of 14 wt-% gas phase, 73 wt-% dry oil phase and 13 wt-% aqueous phase
- oxygen was mainly removed as water
- similar average oxygen removal was achieved with Catalyst A (86 %) and Catalyst B (88 %) and in average about 2.5-3.0 wt-% oxygen remained in the products
- oil products produced with Catalyst B showed better physical properties, lower water content and higher atomic H/C ratio all indicating a higher degree of hydrogenation, but this was not as clearly seen in the hydrogen consumption
- the higher degree of hydrogenation with Catalyst B (NiMo) compared to Catalyst A (CoMo) was to be expected due to the higher hydrogenation activity of nickel compared to cobalt
- the oil products were mainly within the gasoline (40 %) and diesel (45 %) range, but some higher molecular weight products were also formed

5 Appendices

1) Analysis results for catalytic pyrolysis oil samples received from CERTH
2) Analysis results for oil products (wet) from batch and tubular reactor test runs
3) GPC chromatograms for oil products from batch reactor test runs
4) GPC chromatograms for oil products from screening test runs in INTO-1
5) GPC chromatograms for oil products with Catalyst A in INTO-2 test run
6) GPC chromatograms for oil products with Catalyst B in INTO-3 test run
7) GC-MS results for oil products from batch reactor test run (Test 4)
8) Acids in aqueous phases from screening test runs in INTO-1 determined by HPLC
9) Acids in aqueous phases formed with Catalyst A in INTO-2 test run determined by HPLC
10) Acids in aqueous phases formed with Catalyst B in INTO-3 test run determined by HPLC
11) Composition of gas phases from screening test runs in INTO-1 by GC-MS
12) Composition of gas phases formed with Catalyst A in INTO-2 test run by GC-MS
13) Composition of gas phases formed with Catalyst B in INTO-3 test run by GC-MS

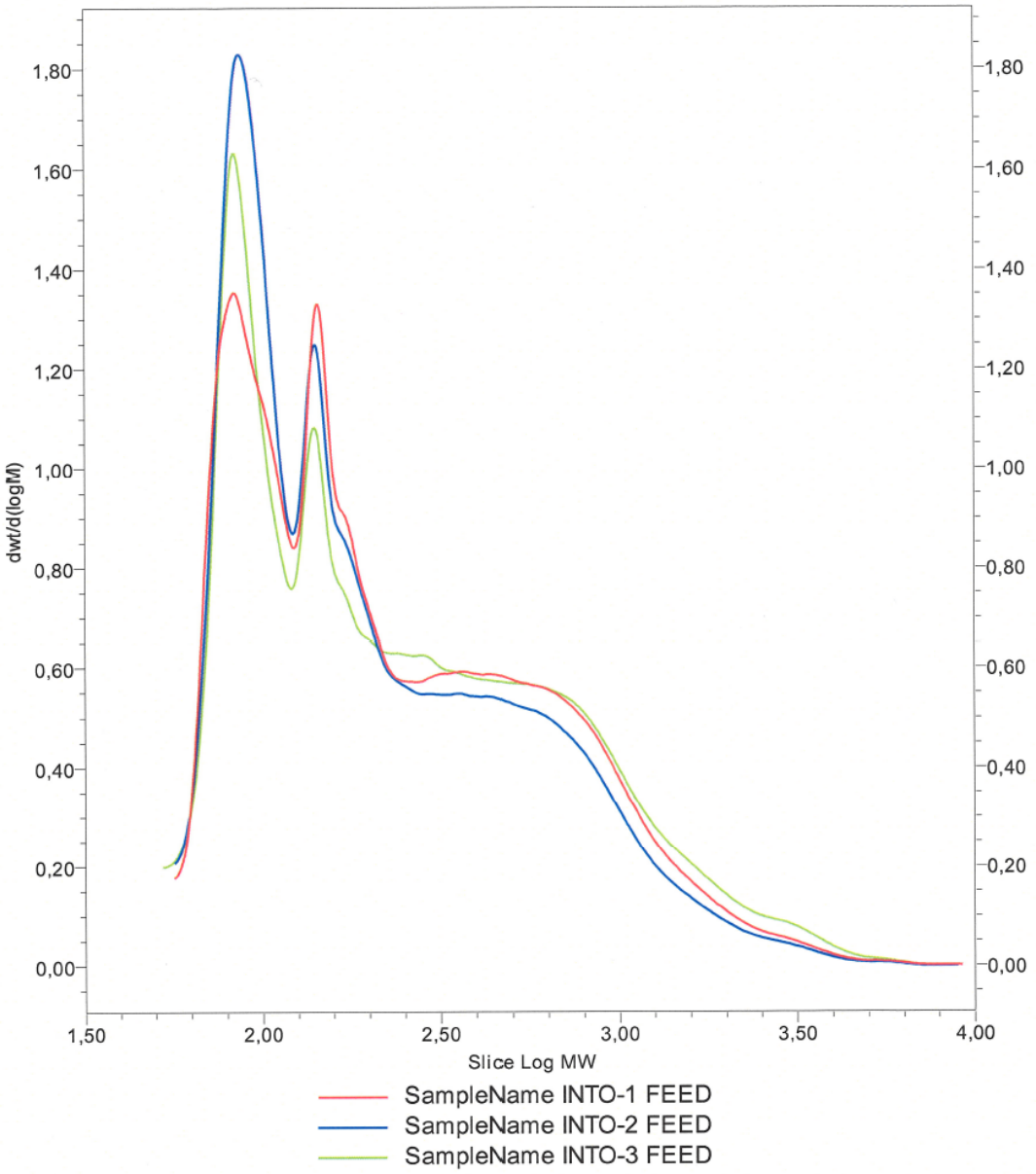
APPENDIX 1. Analysis results for catalytic pyrolysis oil samples received from CERTH

Table: Physical properties and elemental composition of **oil phase of CP oil samples**.

Date on bottle		**15.11.2012**	**23.3.2013 Bottle 1**	**23.3.2013 Bottle 2**	**24.2.2014 (*)**	**29.8.2014**	**20.10.2014 Bottle1&2**
Net heat of combustion	MJ/kg	27.9	-	-	-	-	-
Heat of comb. calorimetric	MJ/kg	29.3	-	-	-	-	-
Flash point	^{o}C	28.0	-	-	-	-	-
Density	kg/m^3	-	-	-	1098 (15 ^{o}C)	1096 (20 ^{o}C)	1118 (15 ^{o}C)
Viscosity (20 ^{o}C)	mm^2/g	-	85.7	-	-	76.9	232
MCR	wt-%	20.4	15.1	15.3	-	14.5	16.8
Ash, 775 ^{o}C	wt-%	<0.001	-	-	-	-	-
Unsoluble matters of fats	wt-%	0.03	-	-	-	-	-
TAN, mg KOH/g		40	41	-	-	-	-
Water	wt-%	7.4	7.0	4.9	6.5	5.0	5.0
C (wet)	wt-%	67.8	70.7	69.8	66.7	73.2	72.3
H (wet)	wt-%	6.7	7.3	6.8	6.8	7.1	7.3
N (wet)	mg/kg	<0.2 wt-%	890	990	1300	820	620
S (wet)	mg/kg	-	139		145	120	62
GPC		yes	yes	-	-	yes	yes
GC-MS			yes	-	-	yes	yes
FTIR		yes	yes	-	-	yes	yes
SimDist <750 ^{o}C		-	-	yes	yes	yes	yes

(*) this CP oil was diluted with 15.7 % THF before being used as feed in INTO-1 test run

The molecular weight distributions of CP oils delivered for the continuous reactor test runs (INTO-1, INTO-2 and INTO-3) are shown in following GPC chromatograms:



GPC Results

	Label	SampleName	Mn	Mw	MP	Polydispersity
1	03394661	INTO-1 FEED	163	391	82	2,4
2	03459203	INTO-2 FEED	152	349	86	2,3
3	03530050	INTO-3 FEED	165	433	83	2,6

Report Method: BIOBOOST_MWD_MULTI

30.12.2014

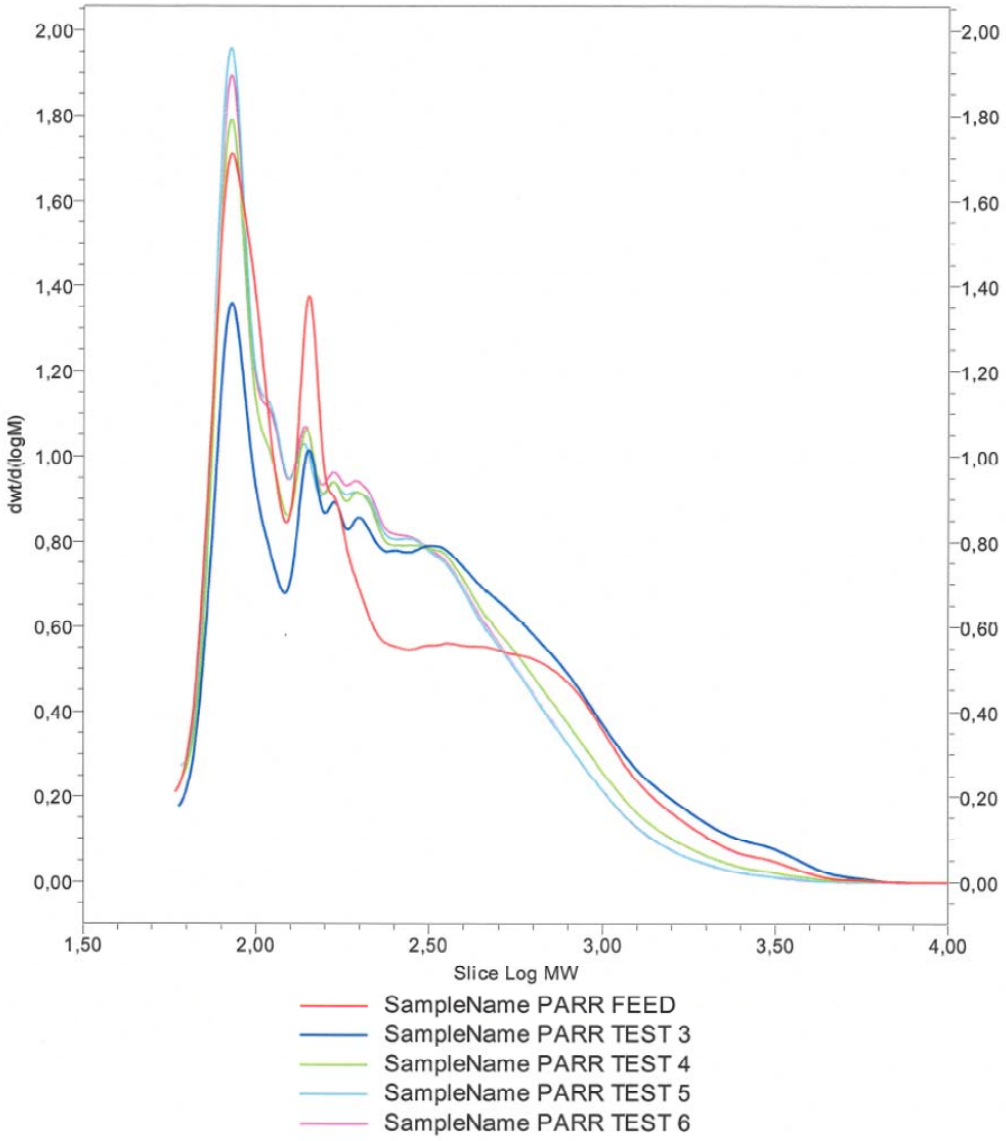
Project Name: LIGNIINI

APPENDIX 2. Analysis results for oil products (wet) from batch and tubular reactor test runs.

Sample	H	C	N	S	H_2O	MCR	Density 15 °C	Visco-city 20°C	Heat of comb.
	wt-%	wt-%	wt-%	ppm	wt-%	wt-%	kg/m^3	mm^2/s	MJ/kg[2]
PARR (Pretreatment and Screening of reaction conditions)									
Test 0.2	6.9	70.8	0.094	-	4.3	20.5	-	-	-
Test 0.3	7.1	73.0	0.110	-	-	23.2	-	-	-
Test 1	7.6	71.9	0.096	-	7.3	14.8	-	-	-
Test 2	7.8	73.5	0.110	-	8.0	14.4	-	-	-
Test 3	6.8	71.4	0.100	-	6.3	13.0	-	-	-
Test 4	7.2	72.6	0.095	-	5.1	6.2	-	-	-
Test 5	8.0	76.4	0.120	-	4.3	5.3	-	-	-
Test 6	8.5	78.5	0.120	-	3.4	6.0	-	-	-
Test 7	6.9	73.8	-	-	-	-	-	-	-
Test 8	8.6	72.3	0.093	-	11.0	4.9	-	-	-
INTO-1 (Screening of reaction conditions)									
Sample 5	10.3	80.3	0.120	-	1.4	0.68	907.3	4.2	36.9/39.1
Sample 8	9.6	77.3	0.140	-	1.0	1.80	945.7	8.1	38.0/40.1
Sample 10	10.7	77.4	0.100	-	1.0	-	908.5	-	-
Sample 12	10.9	82.1	0.068	-	0.40	0.27	903.7	4.9	41.1/43.4
Sample 13	10.8	82.4	0.076	-	0.20	-	910.3	-	-
INTO-2 (Catalyst comparison, Catalyst A)									
Sample 2	11.2	86.9	0.024	31	0.10	0.04	888.5[3]	2.2	41.2/43.5
Sample 3	10.9	86.6	0.045	25	0.50	-	904.8[3]	-	-
Sample 4	10.7	86.2	0.056	-	0.50	0.46	912.0[3]	3.1	40.1/42.4
Sample 5	10.3	86.4	0.062	-	0.70	-	916.2[3]	-	-
Sample 6	10.6	84.9	0.066	36	0.50	0.88	919.1[3]	3.5	39.9/42.0
Sample 7	10.5	85.9	0.068	-	0.60	-	923.2[3]	-	-
Sample 8	10.5	85.7	0.065	29	0.40	1.1	921.1[3]	3.6	-
INTO-3 (Catalyst comparison, Catalyst B)									
Sample 2	12.4	86.2	0.001	21	0.0095	0.03	871.3	2.4	-
Sample 4	11.8	85.1	0.011	10	0.02	0.17	881.7	2.6	-
Sample 6	11.5	85.4	0.015	9	0.043	0.24	888.5	2.9	-
Sample 8	11.7	86.7	0.015	21	0.085	0.15	889.1	2.7	-

[2] Net heat of combustion / Heat of combustion calorimetric (ASTMD240)
[3] Density determined at 20 °C

APPENDIX 3. GPC chromatograms for oil products from batch reactor test runs.



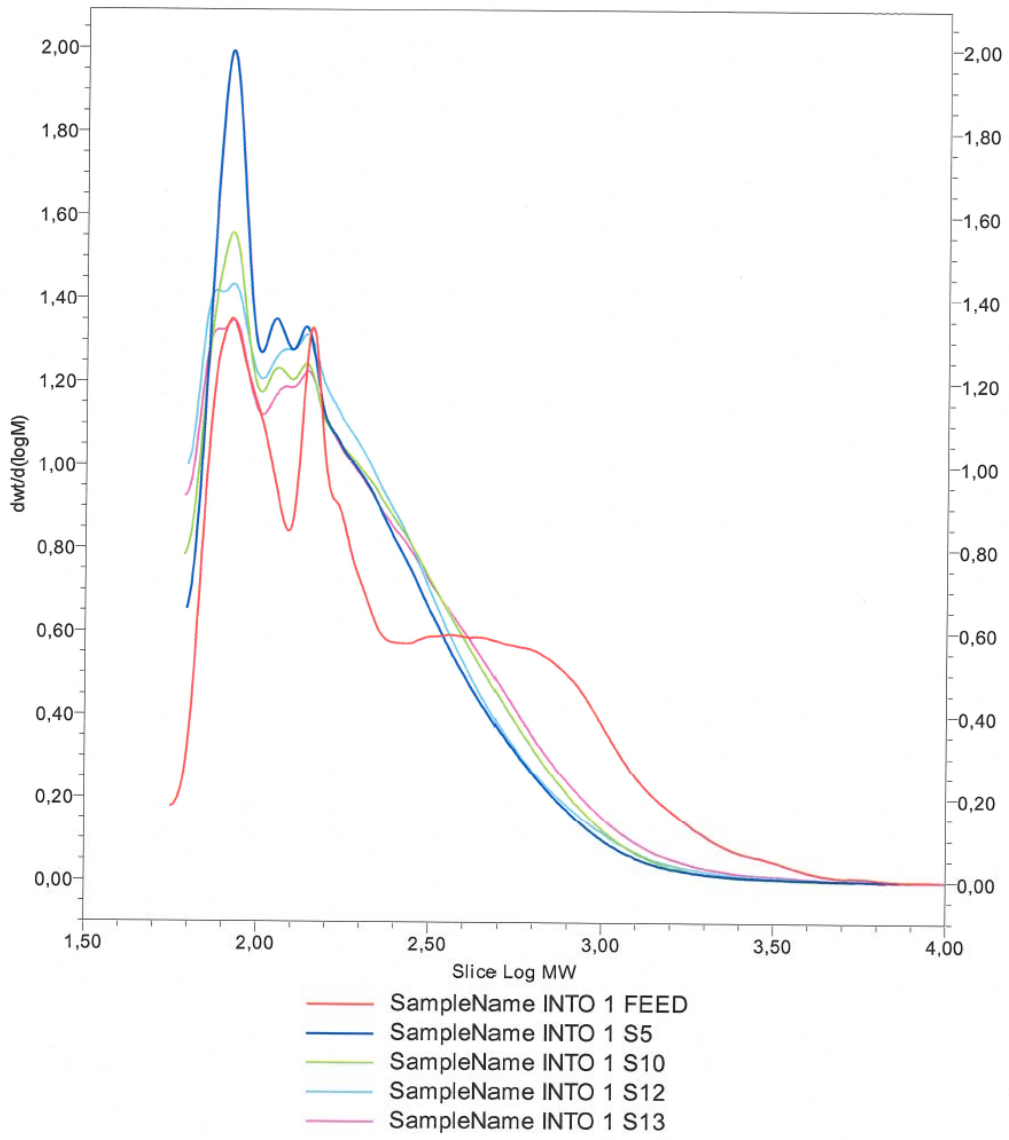
GPC Results

	Label	SampleName	Mn	Mw	MP	Polydispersity
1	03193058	PARR FEED	159	375	84	2,4
2	03189711	PARR TEST 3	186	442	85	2,4
3	03181123	PARR TEST 4	162	326	84	2,0
4	03229973	PARR TEST 5	155	293	84	1,9
5	03257203	PARR TEST 6	156	293	84	1,9

Report Method: BIOBOOST_MWD_MULTI 19.1.2015

Project Name: LIGNIINI

APPENDIX 4. GPC chromatograms for oil products from screening test runs in INTO-1.



GPC Results

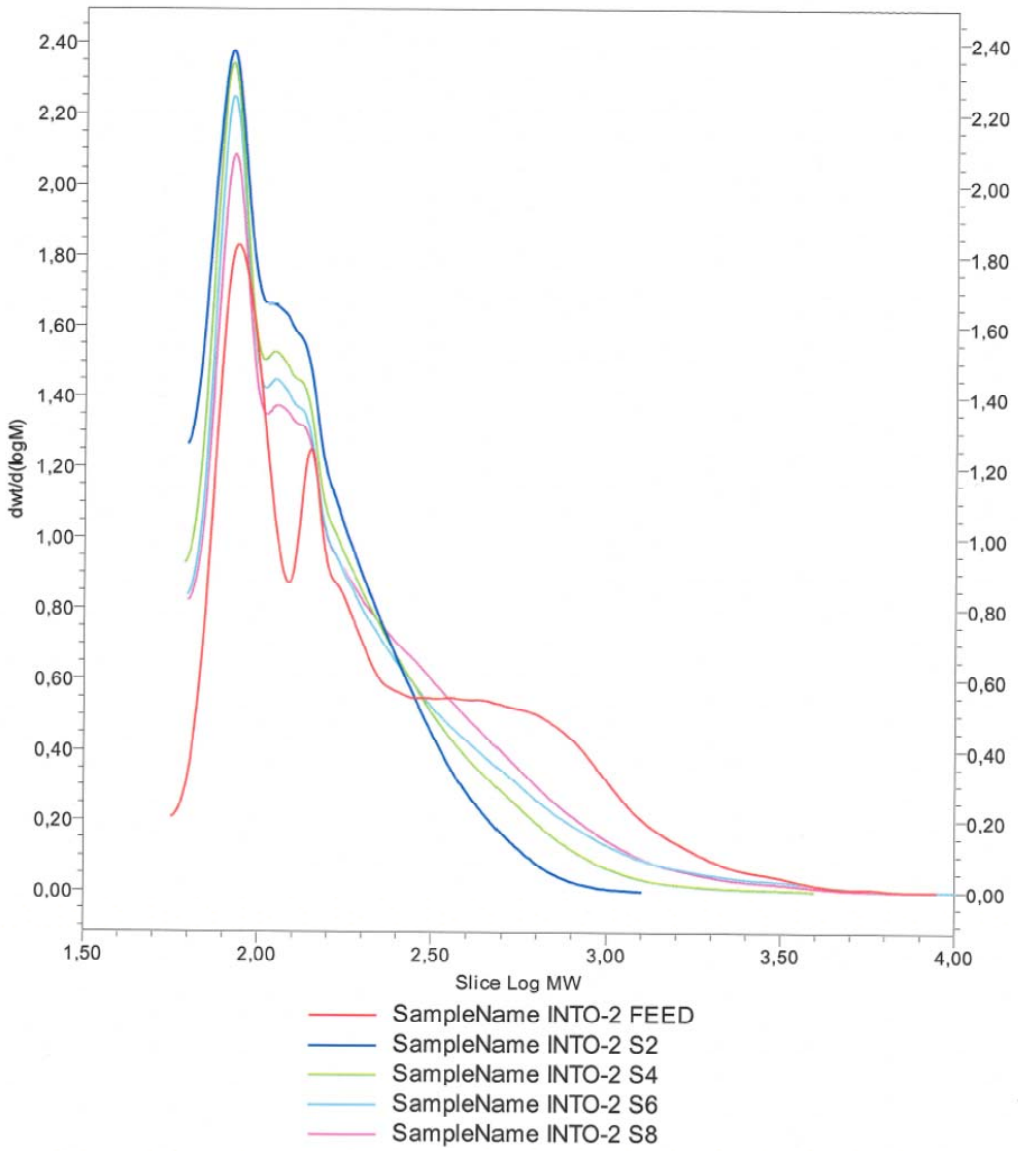
	Label	SampleName	Mn	Mw	MP	Polydispersity
1	03394661	INTO 1 FEED	163	392	82	2,4
2	03394662	INTO 1 S5	135	224	83	1,7
3	03395965	INTO 1 S10	141	239	83	1,7
4	03397784	INTO 1 S12	139	238	74	1,7
5	03397785	INTO 1 S13	144	263	75	1,8

Report Method: BIOBOOST_MWD_MULTI

19.1.2015

Project Name: LIGNIINI

APPENDIX 5. GPC chromatograms for oil products with Catalyst A in INTO-2 test run.



GPC Results

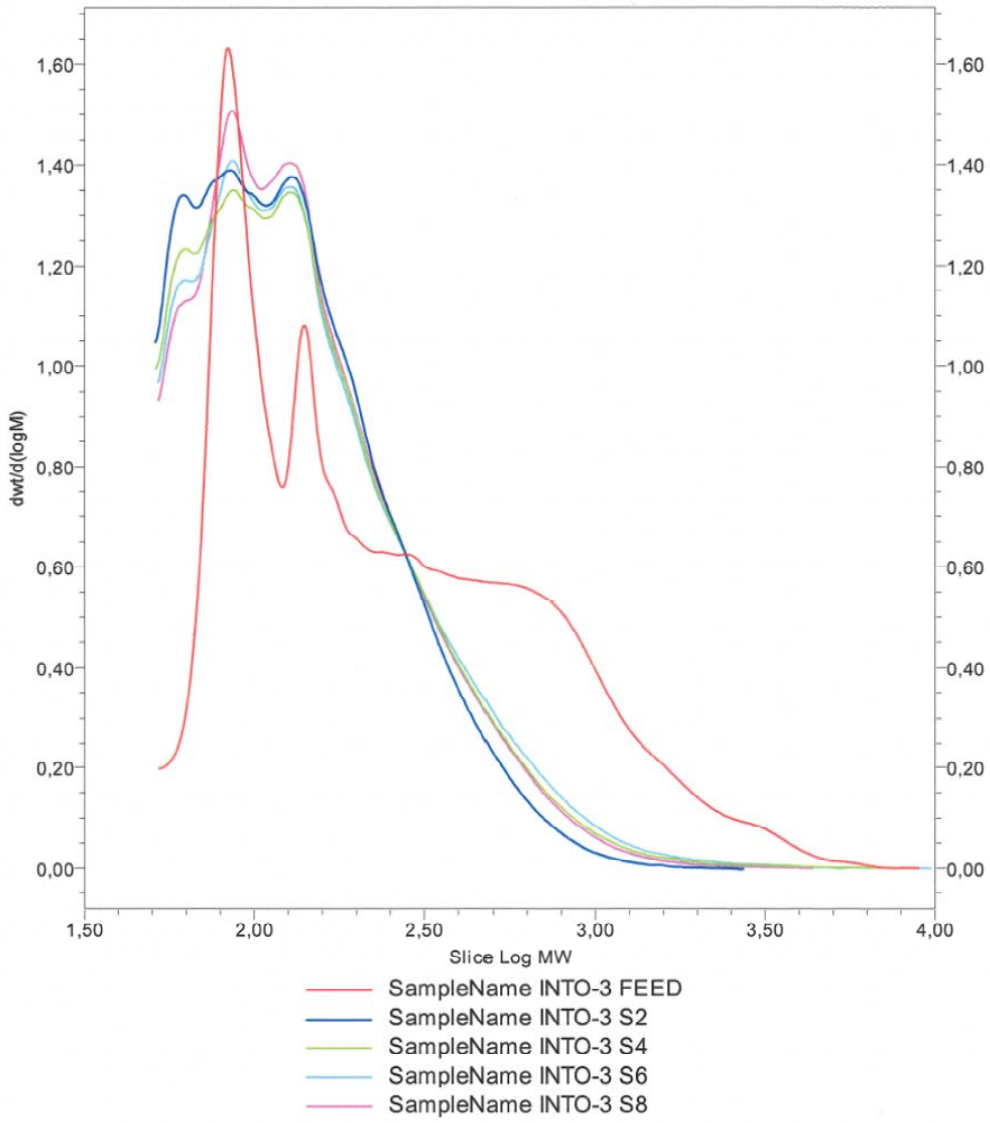
	Label	SampleName	Mn	Mw	MP	Polydispersity
1	03459203	INTO-2 FEED	152	349	86	2,3
2	03464646	INTO-2 S2	116	153	83	1,3
3	03464649	INTO-2 S4	122	190	83	1,5
4	03467105	INTO-2 S6	131	255	83	1,9
5	03467103	INTO-2 S8	136	254	84	1,9

Report Method: BIOBOOST_MWD_MULTI

19.1.2015

Project Name: LIGNIINI

APPENDIX 6. GPC chromatograms for oil products with Catalyst B in INTO-3 test run.



GPC Results

	Label	SampleName	Mn	Mw	MP	Polydispersity
1	03530050	INTO-3 FEED	165	433	83	2,6
2	03530049	INTO-3 S2	112	168	61	1,5
3	03530048	INTO-3 S4	116	195	84	1,7
4	03530047	INTO-3 S6	119	206	85	1,7
5	03530046	INTO-3 S8	118	188	85	1,6

Report Method: BIOBOOST_MWD_MULTI

30.12.2014

Project Name: LIGNIINI

APPENDIX 7. GC-MS results for oil products from batch reactor test run (Test 4).

The main components identified by GC-MS in the liquid oil phase of hydrotreated CP oil are shown in Table 8.1 and some examples of the structures are shown in Figure 8.1. These compounds were also present in the catalytic pyrolysis oil. Due to experimental set up the majority of the lighter compounds was entrained in the exit flow stream of the hydrogen gas and are not included with these analyses.

Table 8.1. Main groups of compounds in the oil product obtained in hydrotreatment of CP oil (Test 4).

Compound group	Alkyl ligand(s)	Total carbon number
Alkylbenzenes	C1 -C7	C7 - C13
Indanes	None or C1 - C3	C10 - C12
Naphthalenes	None or C1 - C3	C11 - C13
Phenols	None or C1 - C4	C6 - C10
Indanols	None or C1	C9 - C10
Benzofurans	None or C1 - C2	C8 - C10

Compared to the CP oil used as feed, the composition was less complex after hydro-treatment. In the reaction conditions used, both hydrogenation and hydrodeoxygenation reactions took place: aliphatic C=C double bonds were hydrogenated (including methylene-, vinyl- and allyl-groups attached to aromatic rings) and keto-, formyl-, hydroxyl- and alkoxy-groups were hydrodeoxygenated. These reactions were seen as diminished amounts of styrenes, indenes, aliphatic O-compounds (especially cycloketones), benzenediols, indenols, naphthols and aromatic O-compounds with methoxygroups (see examples of components in Figure 8.2). The reaction conditions used were not yet severe enough to give complete oxygen removal, leaving phenolic compounds and benzofurans in the product. The reactivity of oxygenated groups followed the order proposed in literature. No aliphatic hydrocarbons were observed in the oil phase.

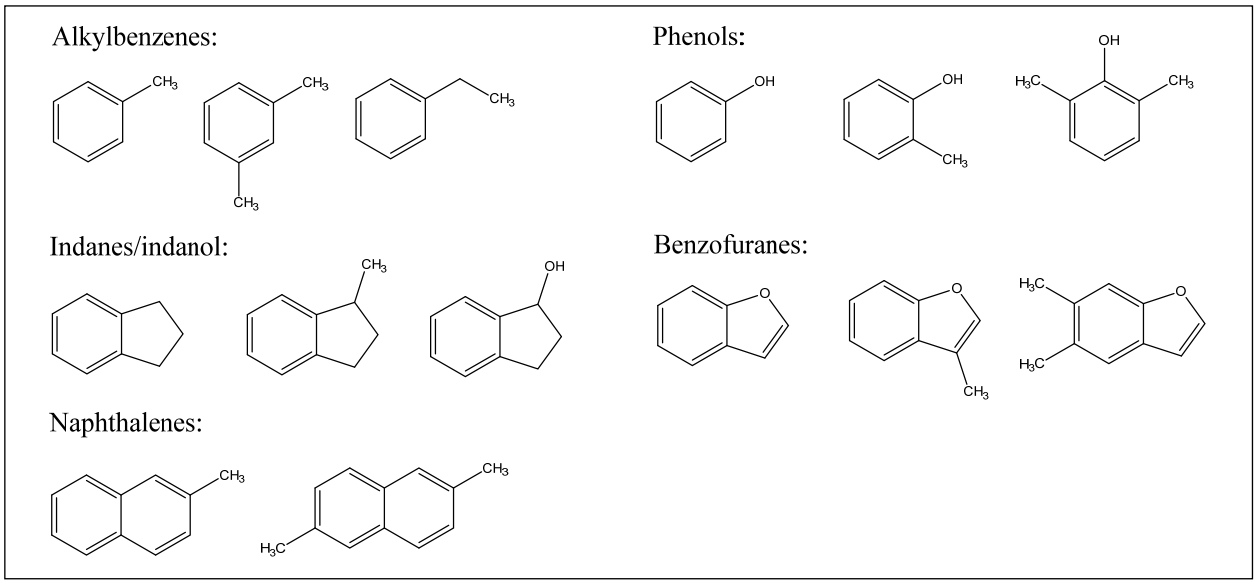


Figure 7.1. Representatives of components in oil phase of hydrotreated CP oil (Test 4).

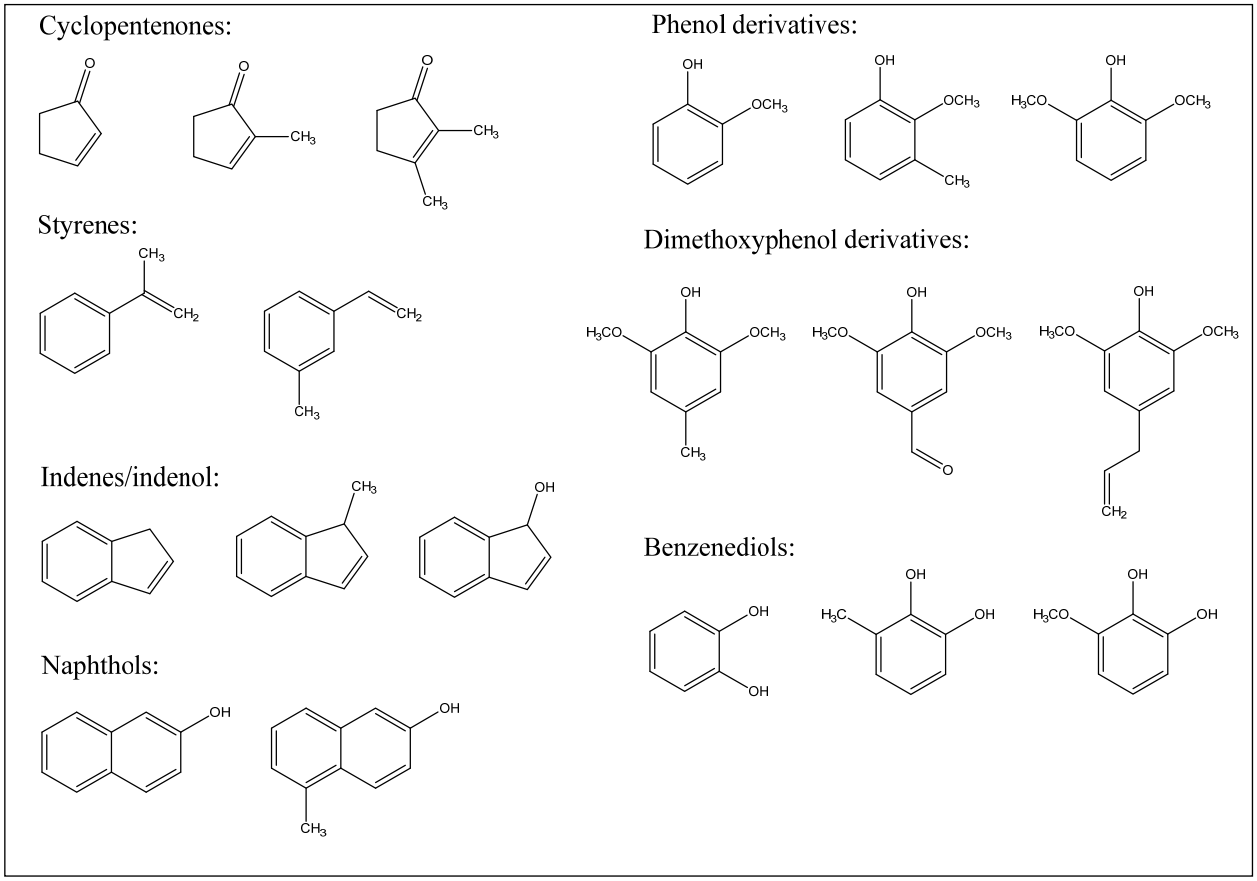


Figure 7.2. Representatives of components with functional groups being hydrogenated and hydrodeoxygenated during hydrotreatment.

APPENDIX 8. Acids in aqueous phases from screening test run in INTO-1 determined by HPLC.

Acids by HPLC method NM547			03432549	03432548	03432547	03432546	03432545
			INTO-1 Sample 13	INTO-1 Sample 12	INTO-1 Sample 10	INTO-1 Sample 8	INTO-1 Sample 5
			pH ~9	pH ~8	pH ~7	pH ~4	pH ~5
			15.6.2014	14.6.2014	13.6.2014	12.6.2014	11.6.2014
Formic	C1:0	mg/kg	31	37	73	80	160
Acetic	C2:0	mg/kg	240	700	5640	22500	10300
Propionic	C3:0	mg/kg	52	150	1240	3380	1280
Butanoic	C4:0	mg/kg	130	360	3980	3220	1260
2-Methylpropanoic	iso-C4:0	mg/kg	2	7	110	150	69
Pentanoic	C5:0	mg/kg	6	17	210	110	60
Methylbutanoic	iso-C5:0	mg/kg	6	15	220	100	67
Hexanoic	C6:0	mg/kg	1	4	60	15	8
2-Hydroxypropanoic	C3:0-OH	mg/kg					
Butanedioic	C4:0-di	mg/kg					
Oxoethanoic	C2:0-ALDO	mg/kg					
Hydroxyethanoic	C2:0-OH	mg/kg					
2-Oxopropanoic	C3:0-KETO	mg/kg	2	3	11	9	
Propanedioic	C3:0-di	mg/kg			9		
cis-Butenedioic	cis-C4:1-di	mg/kg					
trans-Butenedioic	trans-C4:1-di	mg/kg					
Hydroxybutanedioic	C4:0-OH-di	mg/kg					
Methylene butanedioic	C5:1-di	mg/kg					
Pentanedioic	C5:0-di	mg/kg			10	30	20
Oxopentanedioic	C5:0-KETO-di	mg/kg					
Glucuronic	C6-uronic	mg/kg					
Galacturonic	C6-uronic	mg/kg					
Total amount of acids			**470**	**1293**	**11563**	**29594**	**13224**

APPENDIX 9. Acids in aqueous phases formed with Catalyst A in INTO-2 test run determined by HPLC.

Acids by HPLC method NM547			03467104	03467102	03467106	03467100	03464769	03464648	03464650
			INTO-2 Sample 8	**INTO-2 Sample 7**	**INTO-2 Sample 6**	**INTO-2 Sample 5**	**INTO-2 Sample 4**	**INTO-2 Sample 3**	**INTO-2 Sample 2**
			yellow ish	reddish		reddish	almost colourless, clear; pH ~8	pH ~8	light colour (muddy) pH ~8
			20.9.2014	19.9.2014	19.9.2014	22.9.2014	18.9.2014	18.9.2014	17.9.2014
Formic	C1:0	mg/kg	29	37	34	42	52	89	137
Acetic	C2:0	mg/kg	160	340	450	490	52	294	170
Propionic	C3:0	mg/kg	37	74	97	101	106	59	30
Butanoic	C4:0	mg/kg	15	35	36	40	37	26	16
2-Methylpropanoic	iso-C4:0	mg/kg	6	14	16	17	18	10	5
Pentanoic	C5:0	mg/kg	8	19	22	21	22	12	6
Methylbutanoic	iso-C5:0	mg/kg	10	21	25	24	27	14	7
Hexanoic	C6:0	mg/kg	16	34	36	34	35	20	12
2-Hydroxypropanoic	C3:0-OH	mg/kg	<1	<1	<1	<1	<1	<1	<1
Butanedioic	C4:0-di	mg/kg	<1	<1	<1	<1	<1	<1	<1
Oxoethanoic	C2:0-ALDO	mg/kg	<1			<1	<1	<1	<1
Hydroxyethanoic	C2:0-OH	mg/kg	<1		<1	<1	<1	<1	<1
2-Oxopropanoic	C3:0-KETO	mg/kg	<1	<1	<1	<1	<1	<1	<1
Propanedioic	C3:0-di	mg/kg	<1	<1	<1	<1	<1	<1	<1
cis-Butenedioic	cis-C4:1-di	mg/kg	<1	<1	<1	<1	<1	<1	<1
trans-Butenedioic	trans-C4:1-di	mg/kg	<1	<1	<1	<1	<1	<1	<1
Hydroxybutanedioic	C4:0-OH-di	mg/kg	<1	<1	<1	<1	<1	<1	<1
Methylene butanedioic	C5:1-di	mg/kg	<1	<1	<1	<1	<1	<1	<1
Pentanedioic	C5:0-di	mg/kg	<1	<1	<1	<1	<1	<1	<1
Oxopentanedioic	C5:0-KETO-di	mg/kg	<1	<1	<1	<1	<1	<1	<1
Glucuronic	C6-uronic	mg/kg	<1	<1	<1	<1	<1	<1	<1
Galacturonic	C6-uronic	mg/kg	<1	<1	<1	<1	<1	<1	<1
Total amount of acids			**281**	**574**	**716**	**769**	**349**	**524**	**383**

APPENDIX 10. Acids in aqueous phases formed with Catalyst B in INTO-3 test run determined by HPLC.

Acids by HPLC method NM547			03530052	03530051	03530045
			INTO-3 Sample 6	INTO-3 Sample 2	INTO-3 Feed
			pH 8	pH 7	
			9.12.2014	6.12.2014	22.10.14
Formic	C1:0	mg/kg	29	100	4700
Acetic	C2:0	mg/kg	110	2800	44000
Propionic	C3:0	mg/kg	18	460	3000
Butanoic	C4:0	mg/kg	7	140	180
2-Methylpropanoic	iso-C4:0	mg/kg	2	35	45
Pentanoic	C5:0	mg/kg	2	56	6
Methylbutanoic	iso-C5:0	mg/kg	2	34	3
Hexanoic	C6:0	mg/kg	2	38	4
2-Hydroxypropanoic	C3:0-OH	mg/kg	<1	3	290
Butanedioic	C4:0-di	mg/kg	2	15	1200
Oxoethanoic	C2:0-ALDO	mg/kg	<1	<1	<1
Hydroxyethanoic	C2:0-OH	mg/kg	<1	7	2100
2-Oxopropanoic	C3:0-KETO	mg/kg	<1	<1	270
Propanedioic	C3:0-di	mg/kg	7	17	290
cis-Butenedioic	cis-C4:1-di	mg/kg	<1	2	13
trans-Butenedioic	trans-C4:1-di	mg/kg	<1	<1	<1
Hydroxybutanedioic	C4:0-OH-di	mg/kg	2	5	<1
Methylene butanedioic	C5:1-di	mg/kg	<1	<1	<1
Pentanedioic	C5:0-di	mg/kg	1	17	2400
Oxopentanedioic	C5:0-KETO-di	mg/kg	<1	<1	<1
Glucuronic	C6-uronic	mg/kg	<1	<1	<1
Galacturonic	C6-uronic	mg/kg	<1	1	<1
Total amount of acids			**184**	**3730**	**58501**

APPENDIX 11. Composition of gas phases from screening test runs in INTO-1 by GC-MS.

SAMPLE		INTO-1	S 6		S 8		S 10	
OiLi			03394007		03395255		03395937	
Composition								
		Hydrogen	43,85	mol-%	94,72	mol-%	98,13	mol-%
		Carbon dioxide	9,61	mol-%	0,21	mol-%	0,30	mol-%
		Carbon monoxide	0,17	mol-%	0,04	mol-%	0,00	mol-%
		Hydrocarbons	46,37	mol-%	5,02	mol-%	1,57	mol-%
			100		100		100	
Composition without hydrogen								
		Carbon dioxide	20,70	p-%	4,22	p-%	16,00	p-%
		Carbon monoxide	0,24	p-%	0,55	p-%	0,00	p-%
		Hydrocarbons	79,06	p-%	95,22	p-%	84,00	p-%
			100		100		100	
Most abundant hydrocarbon components:								
NRO	MW	COMPONENT						
1	16,04	Methane	16,65	p-%	11,99	p-%	8,88	p-%
3	30,07	Ethane	7,92	p-%	8,80	p-%	6,01	p-%
5	44,09	Propane	8,91	p-%	7,44	p-%	5,59	p-%
14	58,12	n- Butane	36,88	p-%	48,58	p-%	43,19	p-%
16	56,10	trans-2-Butene	1,89	p-%	1,72	p-%	1,66	p-%
19	56,10	cis-2-butene	0,77	p-%	0,48	p-%	0,47	p-%
25	72,15	iso-Pentane	0,77	p-%	1,18	p-%	0,97	p-%
32	72,15	n-Pentane	1,21	p-%	0,00	p-%	1,74	p-%
48	70,13	Cyclopentane	1,45	p-%	4,20	p-%	2,70	p-%
63	86,17	n-Hexane	0,13	p-%	0,57	p-%	0,35	p-%
77	84,16	Methyl-cyclopentane	0,56	p-%	3,25	p-%	1,60	p-%
104	84,16	Cyclohexane	0,37	p-%	3,25	p-%	2,02	p-%
147	98,18	Methyl-cyclohexane	0,10	p-%	1,23	p-%	1,75	p-%
			77,62		92,70		76,95	

APPENDIX 12. Composition of gas phases formed with Catalyst A in INTO-2 test run by GC-MS.

SAMPLE		INTO-2	S2		S 4		S 6	
OiLi			03463920		03463919		03465294	
Composition								
		Hydrogen	95,15	mol-%	94,22	mol-%	95,07	mol-%
		Carbon dioxide	0,20	mol-%	0,30	mol-%	0,29	mol-%
		Carbon monoxide	0,06	mol-%	0,08	mol-%	0,07	mol-%
		Hydrocarbons	4,58	mol-%	5,41	mol-%	4,57	mol-%
			100		100		100	
Composition without hydrogen								
		Carbon dioxide	5,06	p-%	5,50	p-%	6,49	p-%
		Carbon monoxide	0,97	p-%	0,89	p-%	0,93	p-%
		Hydrocarbons	93,97	p-%	93,61	p-%	92,58	p-%
			100		100		100	
Most abundant hydrocarbon components:								
NRO	MW	COMPONENT						
1	16,04	Methane	19,65	p-%	15,55	p-%	15,98	p-%
3	30,07	Ethane	11,95	p-%	9,60	p-%	9,77	p-%
5	44,09	Propane	12,06	p-%	11,50	p-%	11,84	p-%
10	58,12	iso-Butane	0,77	p-%	0,70	p-%	0,71	p-%
14	58,12	n- Butane	9,31	p-%	8,85	p-%	9,08	p-%
25	72,15	iso-Pentane	2,06	p-%	2,07	p-%	2,10	p-%
32	72,15	n-Pentane	2,95	p-%	2,99	p-%	2,86	p-%
48	70,13	Cyclopentane	7,29	p-%	7,77	p-%	7,64	p-%
53	86,17	2-Methyl-pentane	0,71	p-%	0,71	p-%	0,79	p-%
63	86,17	n-Hexane	0,99	p-%	1,04	p-%	0,93	p-%
77	84,16	Methyl-cyclopentane	4,86	p-%	5,58	p-%	5,36	p-%
93	78,11	Benzene	0,55	p-%	0,67	p-%	0,63	p-%
104	84,16	Cyclohexane	7,73	p-%	8,59	p-%	7,97	p-%
146	98,18	1-cis-2-Dimethyl-cyclopentane	0,92	p-%	1,29	p-%	1,15	p-%
147	98,18	Methyl-cyclohexane	3,90	p-%	5,48	p-%	4,89	p-%
174	92,13	Toluene	0,83	p-%	1,90	p-%	1,75	p-%
207	112,21	C8H16-Naphthene	0,45	p-%	0,72	p-%	0,62	p-%
236	112,21	Ethyl-cyclohexane		p-%	0,72	p-%	0,64	p-%
258	106,16	para-Xylene		p-%	0,69	p-%	0,65	p-%
			86,97		86,42		85,37	

APPENDIX 13. Composition of gas phases formed with Catalyst B in INTO-3 test run by GC-MS.

SAMPLE		INTO-3	S4		S8	
OiLi			03519631		03521240	
Composition						
		Hydrogen	94,53	mol-%	95,17	mol-%
		Carbon dioxide	0,30	mol-%	0,26	mol-%
		Carbon monoxide	0,06	mol-%	0,05	mol-%
		Hydrocarbons	5,10	mol-%	4,52	mol-%
			100		100	
Composition without hydrogen						
		Carbon dioxide	5,98	p-%	5,54	p-%
		Carbon monoxide	0,78	p-%	0,70	p-%
		Hydrocarbons	93,24	p-%	93,76	p-%
			100		100	
Most abundant hydrocarbon components:						
NRO	MW	COMPONENT				
1	16,04	Methane	14,70	p-%	13,47	p-%
3	30,07	Ethane	12,25	p-%	11,70	p-%
5	44,09	Propane	11,36	p-%	11,37	p-%
10	58,12	iso-Butane	0,73	p-%	0,76	p-%
14	58,12	n- Butane	8,38	p-%	8,75	p-%
25	72,15	iso-Pentane	2,04	p-%	2,15	p-%
32	72,15	n-Pentane	4,37	p-%	4,57	p-%
48	70,13	Cyclopentane	6,49	p-%	6,80	p-%
53	86,17	2-Methyl-pentane	0,68	p-%	0,69	p-%
58	86,17	3-Methyl-pentane	0,52	p-%	0,53	p-%
63	86,17	n-Hexane	1,75	p-%	1,80	p-%
77	84,16	Methyl-cyclopentane	4,46	p-%	4,67	p-%
93	78,11	Benzene	0,61	p-%	0,72	p-%
104	84,16	Cyclohexane	9,90	p-%	10,12	p-%
147	98,18	Methyl-cyclohexane	7,32	p-%	7,51	p-%
174	92,13	Toluene	1,20	p-%	1,43	p-%
207	112,21	C8H16-Naphthene	0,56	p-%	0,38	p-%
236	112,21	Ethyl-cyclohexane	0,80	p-%	0,87	p-%
			88,11		88,27	