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Characterization of Hydrotreated Fast Pyrolysis Liquids

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This paper focuses on analytical methods to determine the composition of hydrotreated fast pyrolysis liquids. With this information, it is possible to gain insights in the chemical transformations taking place during catalytic hydrotreatment (hydrogenation and/or hydrodeoxygenation, HDO) of pyrolysis liquids. Three different samples, produced at different hydrotreatment severity levels (defined by temperature and residence time) using Ru/C as the catalyst, were analyzed in detail. The composition of the products was determined by solvent fractionation followed by detailed analysis of the various fractions by gas chromatography/mass selective detector (GC/MSD), capillary electrophoresis (CE), and NMR (¹H NMR, ¹³C NMR, and ³¹P NMR). The decrease in the carbohydrate fraction was easily followed by the Brix method after solvent fractionation.

Introduction

The objective of catalytic upgrading of pyrolysis liquids is to improve their product properties and to extend the application range. For instance, the EU BIOCOUP project concerns the conversion of pyrolysis liquids into a product suitable for cofeeding in conventional oil refineries.¹ The difference in properties between highly polar pyrolysis liquid and a typical aliphatic fluid catalytic cracking (FCC) feed is significant and poses a real challenge. Oxygen in pyrolysis liquids is bound to various compounds in the liquid,⁴ and full removal of oxygen would lead to very low product yields. Hence, the discovery of the lowest oxygen level of the product that still qualifies as an FCC feed is of utmost importance. In a recent paper, it was concluded that oils with oxygen contents as high as 17–28 wt % (dry basis) could be used for coprocessing in conventional FCC processing units (Mercader et al.⁵). However, it is envisaged that not only the oxygen content alone but also the type of oxygen containing compounds determines the suitability of the product as a refinery feed.

Catalytic hydrotreatment with heterogeneous catalysts at elevated temperatures (up to 500 °C) and pressures (up to 300 bar) has been identified as a very promising option to improve

the properties of pyrolysis liquids and make them suitable as a refinery feed. Results from the BIOCOUP project on the hydroprocessing of pyrolysis liquids have been presented recently.² A two-stage hydrotreatment process, initially proposed by Elliott et al.³ is employed. However, there is a need for detailed information on the chemical composition of these hydrotreated oils. With this information, the chemical transformations taking place during the hydrotreatment process can be monitored and may provide insights in desired chemical transformations to improve properties and optimize the use of the product oils for cofeeding in refineries.

The objective of this paper is to provide and discuss analytical methods suitable for the characterization of upgraded fast pyrolysis liquids. The focus is on providing analytical protocols to determine the composition of the products at a molecular level. The products are very complex in nature and contain hundreds of compounds belonging to a variety of organic compound classes. This poses a real challenge. To reduce complexity, a solvent fractionation method was applied as the first step in the analytical protocol. This method (Figure 1) originally developed for crude fast pyrolysis liquids⁶ leads to a number of fractions with chemical components of similar solubility characteristics. It has been used successfully for the characterization of pyrolysis liquids and to determine changes in composition during storage. A shorter and faster method has been developed more recently.⁷ We will show that solvent extraction in combination with other techniques (¹H-, ¹³C-, ³¹P NMR, gas chromatography/mass selective detector (GC/MSD)) is a very useful approach to gain insights in the composition of upgraded pyrolysis liquids.

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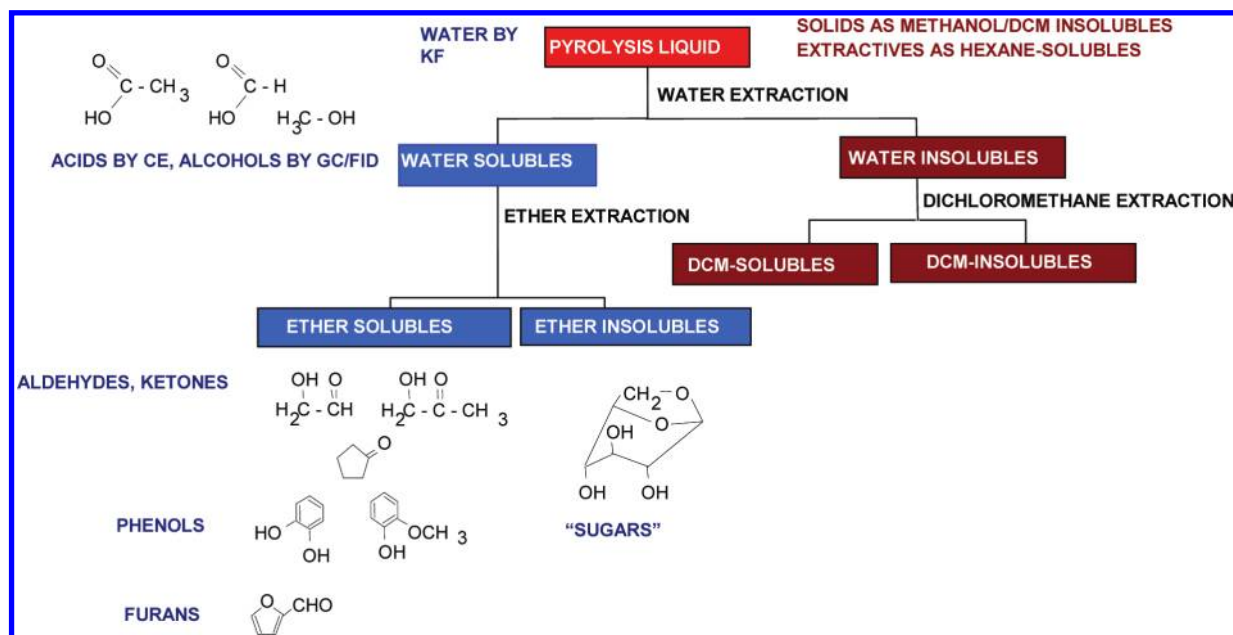


Figure 1. Solvent fractionation scheme for fast-pyrolysis liquid.

Experimental Section

Pyrolysis Liquid. Pyrolysis liquid from forestry residue was produced⁸ in VTT's transport bed reactor Process Development Unit (PDU). The pyrolysis temperature was approximately 500 °C, and the residence time for pyrolysis vapors was approximately 0.5–2 s. The main part of the char particles and the heat transfer sand was removed by cyclones from a hot stream of product gases and vapors before entering liquid scrubbers. The product vapors were condensed in liquid scrubbers, where the product liquid was used as a cooling agent. The amount of raw material and product liquid was measured by weighing. The product yields (on a dry basis) from forest residue varied depending on the feedstock properties (volatiles, ash): 45–60 wt % organic liquids, 12–14 wt % product water (chemically dissolved in organic liquids), 20 wt % char, and 10–14 wt % noncondensable gases. The separation of the top phase (11 wt % of the total liquid product) from the forest residue product liquid was performed at 35 °C within 24 h by the standard method described earlier.⁹ The bottom phase was used for the hydrotreatment experiments.

Hydrotreatment Experiments. The catalytic hydrotreatment reactions were carried out in a continuous setup consisting of four packed bed reactors in series.² The temperature in each reactor can be varied independently and was in these experiments between 175 and 400 °C. Ru/C in pelletized form was used as the catalyst. The weight hourly space velocity (WHSV, in kilograms of oil/hour per kilogram of catalyst) were typically between 2.5 and 7.13 h⁻¹. The experiments were performed at a fixed hydrogen pressure of 200 bar. An overview of the experiments is given in Table 1. The experiments were classified according to process severity and labeled as stabilization, mild hydrotreatment, and second stage hydrotreatment. In stabilization the aim is mainly to change reactive functional groups into more stable ones. In mild hydrotreatment low temperatures and low hydrogen consumption are used. Second stage hydrotreatment uses the oily product from mild hydrotreatment, which will be treated at higher temperatures and hydrogen pressures. The

feed of the latter experiment was the organic phase from the mild hydrotreatment reaction. Oils derived from three selected experiments were used for detailed analyses.

Elemental Analyses and Water Content. The elemental composition (carbon, hydrogen, and nitrogen) was determined using an Elementar VARIOMAX 785-500, according to the ASTM D 5291 method. The water content of the pyrolysis liquids was analyzed by Karl Fischer (KF) titration according to ASTM E 203-96.

Solvent Fractionation. Liquid products were characterized using a solvent fractionation scheme. The following fractions are obtained by this procedure: a water-insoluble (WIS) fraction, which was further divided into a DCM (dichloromethane)-soluble (low-molecular-mass, LMM lignin, extractives present in this fraction) and a DCM-insoluble (high-molecular-mass, HMM lignin) fraction and a water-soluble (WS) fraction, which was further extracted into an ether soluble (ES) and ether insoluble (EIS, "sugars") fraction. The "sugars" in the water-soluble (WS) fraction were analyzed by the Brix method⁷ using an Anton Paar DMA4500 density/specific gravity/concentration meter. The Brix method has been developed and found out to be suitable for pyrolysis liquids.⁷ The solvent fractionation scheme developed for pyrolysis liquids was re-evaluated for hydrotreatment by characterizing the fractions by gas chromatography/flame ionization detector (GC/FID) and GC/MSD.

Capillary Electrophoresis. The organic acids in the water-soluble (WS) fraction were analyzed by capillary electrophoresis (CE). In the method, anions were separated from each other in narrow capillary pipes with the aid of an external electric field. The equipment used at VTT was a Waters capillary ion analyzer, model CIA 4100, data transfer SAT/IN module, empower TM 2 program. The reactants were sodium acetate, sodium formate, sodium, sodium glycolate chemicals, anhydrous monobasic sodium phosphate, anhydrous dibasic sodium phosphate, 100 mM of tetradecyltrimethyl ammonium hydroxide (OTMOH) solution, 0.25 N NaOH solution (for pH control of the electrolyte), and ion-exchanged water. The equipment is calibrated for acetic acid, formic acid, and glycolic acid at least by three-point calibrating through zero point. The calibration solutions were produced from the Na salt of the acids. The sample was prepared as follows: weigh about 2 g of pyrolysis oil directly into the graduated 100 mL flask, add about 50 mL of distilled water, and let the sample stay in the shaker overnight. Further dilutions can be prepared from this sample if needed.

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Table 1. Overview of Experiments

code VTT	material	T (°C)	WHSV (h ⁻¹)
PR08-36-1	stabilization	175–175–175–175	7.13
PR08-36-2	mild hydrotreatment ^a	175–225–350–400	5.6
PR08-36-3	second stage hydrotreatment ^b	350–375–400–400	2.5

^a Separate aqueous phase formed during reaction. ^b Separate aqueous phase formed during reaction but not analyzed.



Figure 2. Visual appearance of crude pyrolysis liquid and hydrotreated products. The feed for the second stage hydrotreatment was the oil phase of the mild hydrotreatment.

GC/MSD. Qualitative determination of individual compounds in the product liquids was performed by GC/MSD (HP 5970 controlled by an HP 9000 series Pascal ChemStation computer). The column was a HP Ultra 1 (cross-linked methyl siloxane), 50 m, 0.32 mm, 0.52 μ m. The oven temperature program was initial temperature 100 °C, hold 0, ramp 4 °C/min, final temperature 300 °C, hold 20 min. For the injector, the split ratio was 15:1, heater 250 °C, injection volume 1 μ L. To analyze catechols, extractives, and anhydrosugars, a silylation procedure is required. Silylation was performed by dissolving the samples (10 mg) in potassium hydroxide (KOH) dried pyridine (0.5 mL) and adding bis(trimethylsilyl)-trifluoroacetamide (0.5 mL) and trimethyl-chlorosilan (10 drops) prior to analyses.

¹H NMR and ¹³C NMR Analyses. ¹H NMR and ¹³C NMR analyses were performed on nonphase separated oils (crude pyrolysis liquid and stabilization product) and the organic phase of the phase-separated products (mild and second hydrotreatment products). The spectra were recorded on a Varian AS400 (¹H NMR) or Varian VXR-300 (¹³C NMR). The samples were dissolved in CDCl₃, dried over MgSO₄ to remove residual water in the samples, and filtered. For ¹H NMR spectra, 64 repetitions and a 1 s relaxation delay was applied. For the ¹³C NMR spectra, a relaxation delay of 4 s was applied. Separate experiments with a longer relaxation delay (12 s) gave similar integration results, indicating that a 4 s relaxation delay is sufficient to avoid peak saturation. There were 10 000–12 000 repetitions applied.

CDCl₃ (99.8 atom % D) was purchased from Sigma Aldrich (Missouri). Dried MgSO₄ (99%) was obtained from Boom BV (Meppel, The Netherlands).

³¹P NMR Analyses. The water-insoluble fraction of the liquid products was characterized by ³¹P-NMR. Sample preparation:¹⁰ the sample was accurately weighted (~40 mg) and dissolved in 0.300 mL of *N,N*-dimethylformamide (DMF) in a 10 mL vial. After full dissolution (1–5 h), 0.200 mL of Py-*d*₅, 0.400 mL (0.025 M) of an internal standard solution (endo-*N*-hydroxy-5-norbornene-2,3-dicarboximide, e-HNDI, 0.01 mmol) in Py/CDCl₃ (1.6/1, v/v) and 0.050 mL of a Cr(acac)₃ solution (11.4 mg/1 mL) in Py/CDCl₃ (1.6/1, v/v) were added. Next, 0.200 or 0.300 mL of a phosphitylation reagent 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane

(P.R.(II)) was added. Finally, 0.250 mL of CDCl₃ was added to the solution, resulting in a light brown to black solution.

The NMR solution (Py/CDCl₃), internal standard, and Cr based relaxation reagent were prepared for the same Py/CDCl₃ NMR solvent beforehand, as bigger stock solutions and the required amount of reagents were pipetted to NMR tubes using Finn-pipettes. Phosphitylation reagent [P.R.(II)] (97%) was used as it was. Freshly prepared samples were measured with ³¹P NMR, at room temperature, immediately after preparation. The amount of phosphitylation reagent 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane [P.R.(II)] was 2–3 times higher than usual because the samples contained water. Commercially available reagents were used without further purification, and all of the solvents were HPLC grade.

Chemical shifts are reported relative to a sharp signal (132.2 ppm) from the reaction between water and P.R.(II). Spectra were measured using a 90 °C pulse and an inverse-gated decoupling sequence. The following NMR parameters were used: nt = 512, d1 = 5 s, and lb = 2.

Results and Discussion

The catalytic hydrotreatment studies were carried out using Ru/C as the catalyst in a dedicated continuous setup.² Processing information of relevance for the current paper is given below.

Liquid Yields and Visual Appearance of Products. The visual appearance (Figure 2) of the products after the catalytic hydrotreatment with Ru/C is a clear function of the process severity. The product from the stabilization experiment (Table 1) was isolated as a dark brown viscous homogeneous liquid, whereas a clear phase separation into an organic and aqueous phase was observed for the mild and second stage hydrotreatment experiments. Figure 2 shows that the density of the oily phase, after the second stage hydrotreatment, is lower than the aqueous phase. The density of the organic phase apparently depends on the process severity, as shown in Table 2. All oil phases were analyzed in detail. The aqueous phase of the mild hydrotreatment was also analyzed; the aqueous phase of the second stage hydrotreatment was not.

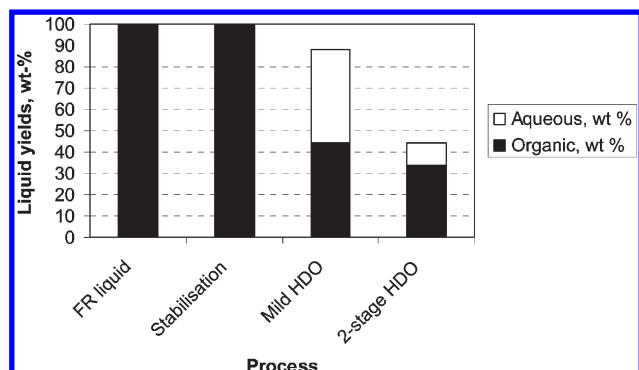
The liquid yields of the products are given in Figure 3. Losses are due to the formation of solids and gases.^{3,11}

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Table 2. Elemental Composition of the Organic Products^a

	water wt %	density kg/dm ³	elemental analysis, wt % dry basis				mol/mol, dry basis	
			C	H	N	O (diff.)	H/C	O/C
pyrolysis liquid	24.4	1.20	55.3	6.6	0.2	38	1.42	0.51
stabilization	28.4	1.17	56.7	7.5	0.6	35	1.57	0.47
mild HDO	6.4	1.10	71.3	8.3	0.6	20	1.39	0.21
2-stage HDO	6.0	1.03	75.6	9.6	0.7	14	1.51	0.14

^a Sample codes and process data in Table 1.**Figure 3.** Yields of organics and aqueous products (wt % of forest residue (FR) pyrolysis liquid). The processing data are in Table 1.

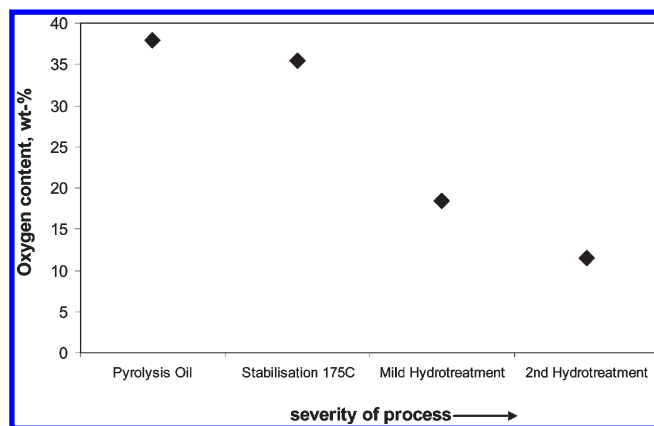
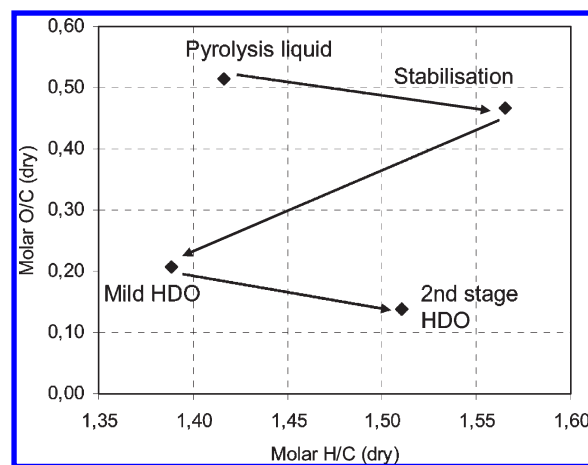
Elemental Composition. The water content and elemental composition of the feed and oily products are shown in Table 2. The oxygen content of the original pyrolysis liquid feed is highest for all products; for the hydrotreated products it is a clear function of the temperature and processing time. The lowest values are observed for the second stage hydro-treatment product. Thus, the oxygen content of the product is a measure for the process severity. At higher severity (higher temperature and/or lower WHSV), the oxygen content is reduced considerably (Figure 4).

A Van Krevelen diagram (Figure 5) shows that the H/C ratio increases from 1.42 to 1.57 in the stabilization step, an indication that hydrogenation of components in the pyrolysis liquid takes place to a significant extent. Upon mild hydro-treatment, the H/C ratio is lower than the original pyrolysis liquid. This is likely due to the formation of considerable amounts of organic products with a low H/C ratio by dehydration/polymerization reactions.² In the second stage hydro-treatment, the H/C ratio increases considerably, a clear indication that hydrogenation of reactive components in the mild hydrotreatment product takes place to a large extent.

The hydrogen uptake during the stabilization step is typically about 100 nL/kg. This corresponds to an increase in less than 1 wt % and is within the experimental error. These values were measured experimentally.² Figure 4 and Table 3 show that there is a decrease in the oxygen content on a dry basis and an increase in the water content. Thus, water is formed and also reactive components like aldehydes, ketones and C=C double bonds are reduced by hydrogen. The latter is clearly shown in Table 5, which shows a reduction among other total carbonyl and aromatics content.

Chemical Composition of Liquid Products Using a Solvent Extraction Scheme. The chemical composition of the upgraded products as determined by a solvent fractionation scheme is shown in Figure 6. Clear differences in composition were observed for the various hydrotreated products.

When comparing the stabilized oil with the original pyrolysis liquid, the amount of water and HMM lignin (including

**Figure 4.** Oxygen content as an indication of process severity. The processing data are given in Table 1.**Figure 5.** Van Krevelen diagram of the hydrotreated oils compared with the feed liquid.

polymeric products) is considerably higher and this is at the expense of the ether soluble and “sugar” fraction. Apparently, components in the ether soluble and “sugar” fraction are hydrogenated (see Figure 5) and also converted to higher molecular weight components and water.

In the mild hydrotreatment step, two product phases are formed, an aqueous and organic phase. Both were subjected to the solvent extraction scheme and the results are also given in Figure 6. Also, in the figure an additional column is added abbreviated as mild HDO-total, which is the sum of the aqueous and organic fraction. The major conclusions are that (i) the “sugar” fraction is mainly converted in the mild hydrotreatment step and (ii) the aqueous layer contains considerable amounts of organic components, mainly belonging to the ether soluble fraction.

The solvent extraction data for the mild and second stage hydrotreatment steps are rather similar, and the solvent

Table 3. Acid Composition of Hydrotreated Products^a

	amount wt % of feed	water wt %	acids, wt %				total whole liquid product	total wt % of pyrolysis liquid
			acetic	formic	glycolic	total		
pyrolysis liquid	100	24.4	5.6	0.9	0.2	6.8	6.8	6.8
stabilization	99.7	28.4	5.8	0.5	0.6	6.9	6.9	6.9
mild HDO-oil	44.5	6.4	3.4	0.0	0.0	3.4	3.8	3.3
mild HDO-aqueous	43.4	69.6	4.2	0.0	0.0	4.2		
2-stage HDO-oil	33.8	6.0	2.5	0.0	0.0	2.5		0.84
2-stage HDO-aqueous	6.5							

^a Processing data are given in Table 1.**Table 4. ¹H-NMR Analysis of Oil Products¹⁵**

chemical shift region (ppm)	type of protons	pyrolysis liquid (% H)	stabilization (% H)	mild hydrotreatment (% H)	second stage hydrotreatment (% H)
10.0–8.0	—CHO, —COOH, downfield ArH	5.33	1.32	0.00	0.00
8.0–6.8	ArH, HC=C (conjugated)	11.71	10.26	9.75	9.23
6.8–6.4	HC=C (nonconjugated)	5.95	5.33	7.84	6.36
6.4–4.2	=CHO, ArOH, HC=C (nonconjugated)	22.09	17.98	6.59	3.72
4.2–3.0	CH ₃ O—, —CH ₂ O—, =CHO	19.07	20.21	15.60	9.41
3.0–2.2	CH ₃ CO=, CH ₃ —Ar, —CH ₂ Ar	8.66	10.14	13.62	15.85
2.2–1.6	—CH ₂ —, aliphatic OH	14.69	14.25	16.64	17.33
1.6–0.0	—CH ₃ , —CH ₂ —	14.59	20.5	29.97	38.10
	aliphatics/ aromatics ^a	1.72	3.00	4.78	6.01

^a The aliphatic area was taken as the area in the region δ 2.2–0.00 ppm, while the aromatic area was taken as the area in the region δ 8.0–6.4 ppm.**Table 5. ¹³C-NMR Analyses^{15, 16}**

chemical shift region (ppm)	carbon assignments	pyrolysis liquid (% C)	stabilization (% C)	mild hydrotreatment (% C)	second stage hydrotreatment (% C)
215–163	total carbonyl	12.07	7.46	3.74	0.94
215–180	carbonyl (ketones + aldehydes)	2.42	1.09	0.22	0.14
180–163	carbonyl (ester + carboxylic acids)	9.65	6.37	3.51	0.80
163–100	total aromatics	47.18	30.87	35.85	22.06
163–125	general aromatics	25.79	13.27	17.43	15.41
125–112	aromatics (guaicyl)	10.50	6.61	11.07	6.55
112–100	aromatics (syringyl)	10.88	10.99	7.35	0.10
110–84	carbohydrate	2.06	0.14	0.00	0.00
84–54	methoxy/hydroxy	38.69	21.43	7.15	2.00
54–1	alkyl carbons (total)	38.96	40.10	53.27	75.00
54–36	long/branched aliphatics	1.70	7.00	11.36	25.16
36–1	short aliphatics	37.26	33.10	41.91	49.84
	total aliphatics/ total aromatics ^a	0.83	1.30	1.49	3.40

^a The area of total aliphatics was taken as the area in the region δ 54–1 ppm, while the area of total aromatics was taken as the area in the region δ 163–100 ppm.

extraction procedure does not provide additional information on the various reactions taking place.

The capillary electrophoresis method was developed for pyrolysis liquid samples both at VTT and at RUG. The results were compared with a standard sample which contained 4 wt % acetic acid, 2 wt % formic acid, and 3.5 wt % glycolic acid. The results were as follows: acetic acid 3.86 (VTT) and 3.95 wt % (RUG), formic acid 1.97 (VTT) and 1.65 wt % (RUG), and for glycolic acid 3.53 (VTT) and 3.52 wt % (RUG).

The amount and composition of the organic acids in the various products is shown in Table 3. The acid fraction mainly consists of acetic acid. Formic-, glycolic-, propionic-, and lactic acid are also present, though in low concentrations. Similar results have been reported by others.^{12–14} The total amount of acetic acid before and after the stabilization step is essentially similar. This implies that acetic acid is not

converted at these relatively mild conditions, which is in line with the literature.¹⁷ The amount of formic acid is lowered in the stabilization step. Formic acid is known to be decomposed by Ru/C catalysts at mild conditions.¹⁷

A significant decrease in the acid content was observed after mild hydrotreatment however. Apparently also acetic acid is converted at these conditions, in agreement with work from Elliot on the catalytic hydrotreatment of aqueous acetic acid solutions with Ru/C.¹⁹ In these model studies in batch, the acetic acid conversion was about 90% after a 4 h batch

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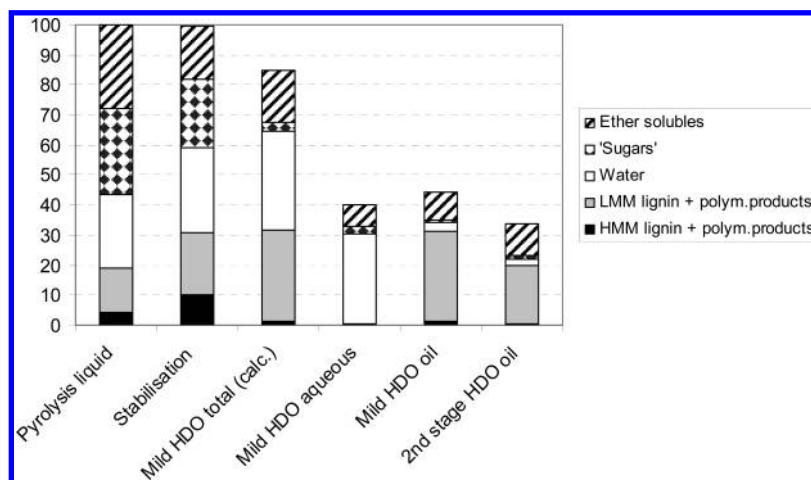


Figure 6. Chemical composition of samples based on a solvent fractionation scheme. The processing data are given in Table 1.

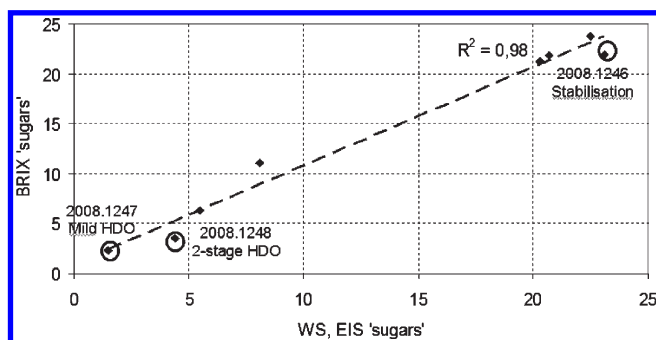


Figure 7. Change in “sugars” in hydrotreatment products^{6,7} (“sugars” in oil and aqueous fractions combined). WS = water-solubles, EIS = ether-insolubles. The figure also includes samples other than those provided in this study. The suitability of the Brix method to pyrolysis liquids has been described in an earlier paper.⁷

time at 250 °C. Also of interest is the observation that acetic acid distributes between the organic and aqueous phase and is not solely present in the aqueous phase. In the second stage hydrotreatment, a further minor decrease in the acetic acid content was observed.

Aqueous phases from phase separated pyrolysis liquids are typically more challenging to characterize than organic phases because the presence of high amounts of water excludes several analytical tools. Solvent fractionation gives a picture of the overall composition (Figure 6). An alternative procedure to determine the “sugar” fraction in the aqueous phase is the Brix method.⁷ The Brix values for the water-soluble fractions of the hydrotreatment products were determined, and the results are compiled in Figure 7. In this figure, the “sugars” determined as ether-insolubles (EIS)⁶ of the water-soluble (WS) fraction by the solvent fractionation method are plotted against “sugars” as determined by Brix from the water-soluble fraction. A good correlation is obtained, thus the Brix method is a good alternative to determine the “sugar” fraction in aqueous phases. The “sugar” fraction in the stabilized oil is highest. Hydrotreatment at higher severity leads to a reduction in the “sugars” fraction.

GC/MSD analyses. Solvent extraction schemes give information on the amounts of groups of organic components with rather similar solubility characteristics. GC/MSD was applied to gain insights in the composition of the various fractions of the hydrotreated products.

The results for the product obtained after the stabilization step is given in Figure 8. Special attention is given to the “sugar” and the water-insolubles (combined HMM-LMM lignin fraction). The “sugar” fraction consists of low-molecular weight diols and hydroxyl-acids and, as expected, a wide range of monomeric “sugars”. In the stabilization step, no major reduction in the “sugars” fraction was observed (Figure 8). However, the composition is different from that of crude pyrolysis liquid. For instance, diols are absent in crude pyrolysis liquids and are likely formed in the stabilization step by hydrogenation of (hydroxy)-aldehydes (Figure 8).

The water-insoluble (WIS) fraction contains considerable amounts of low-molecular weight phenolic components like catechols, guaicol, and syringols. Most of this fraction cannot be analyzed by GC/MSD, but the main changes can be followed by using the solvent fractionation. An increase in the WIS and its HMM lignin fraction was observed after stabilization. This was not only due to the formation of polymerization products but also due to a change in solubility compared with the original pyrolysis liquid. In the crude pyrolysis liquid, the WIS fraction consisted mainly of degraded lignin, extractives, and small amounts of syringols and catechols.

A significant change in “sugars” took place during mild hydrotreatment, partly due to the formation of higher alcohols. The diols formed during stabilization disappeared. A high temperature during mild hydrotreatment caused hydrogenation of carbonyl compounds. The separation of the water fraction that occurred in mild hydrotreatment may have contributed to the removal of the carbonyl compounds from the hydrotreatment products.

The water-insoluble fraction of the organic product after the mild hydrotreatment step was also analyzed by GC/MSD. In mild hydrotreatment, the WIS increased due to a change in solubility compared with the original pyrolysis liquid. A clear change in the proportion of phenolics took place (Figure 9). Compared with the feed, the proportion of phenols and catechols increased and the amount of syringols decreased.

The composition of the HMM fraction of the second stage hydrotreated product is given in Figure 10. The high temperature during the second stage hydrotreatment caused further hydrogenation of the aldehydes and ketones, resulting in a very low carbonyl concentration (Table 6) in the

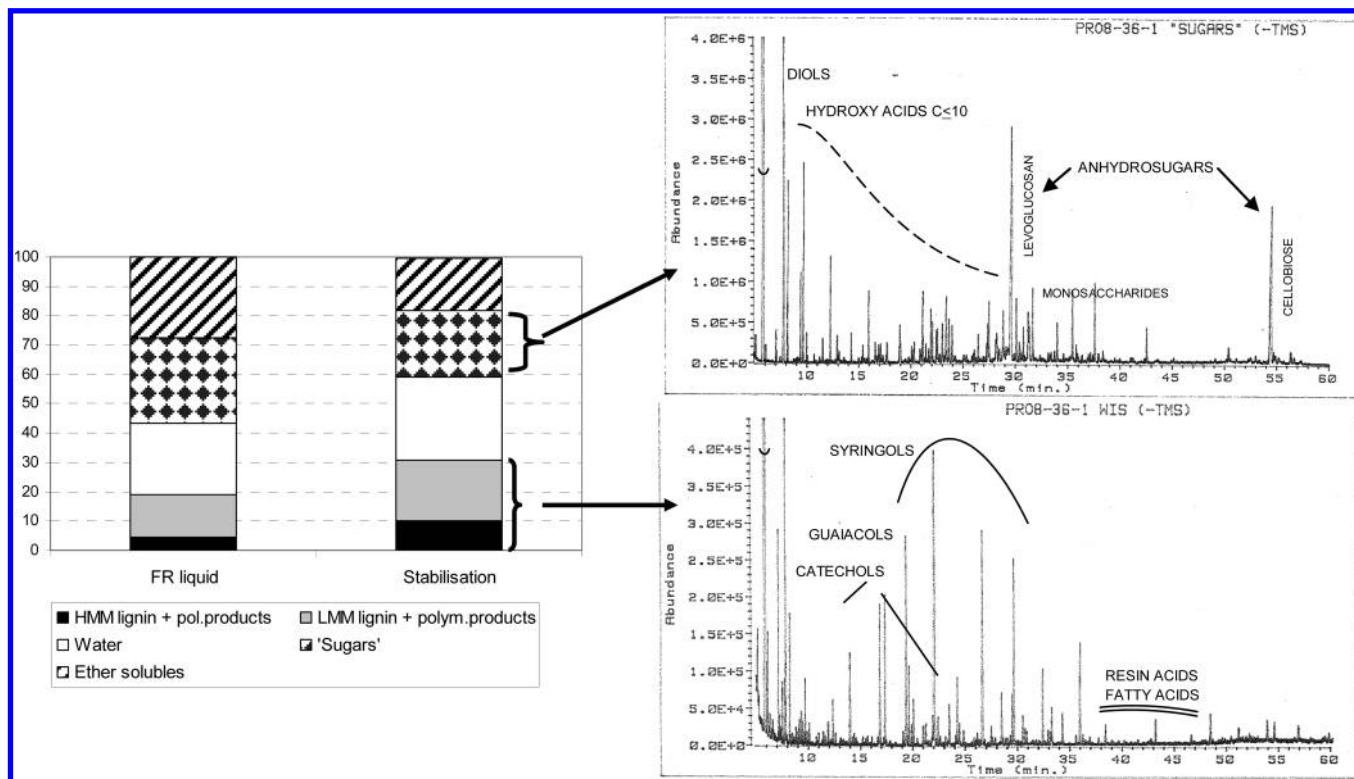


Figure 8. Molecular composition of selected fractions of the stabilization product.

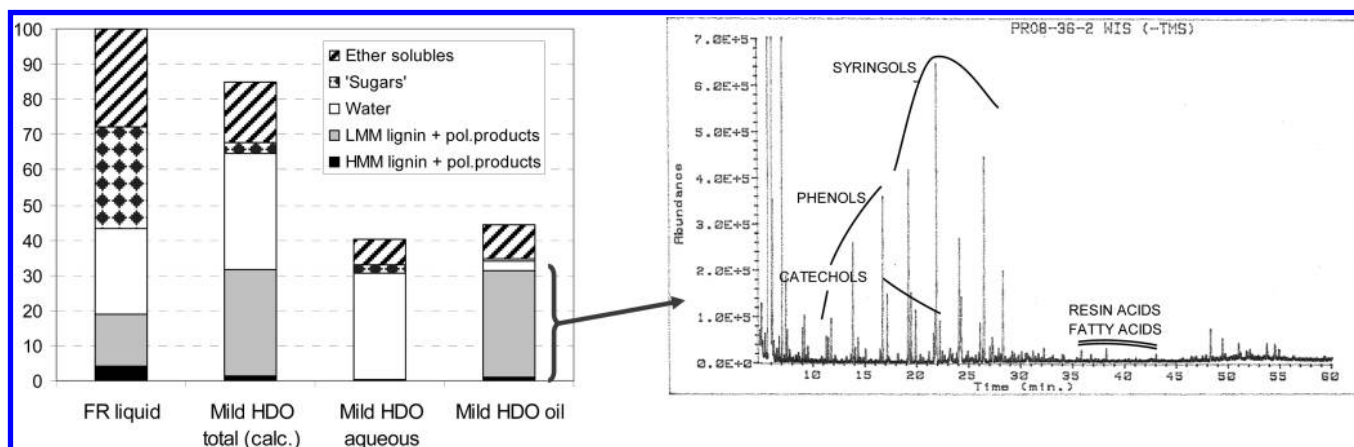


Figure 9. Chemical composition of fractions of the mild hydrotreatment product. GC/MSD was done for the water-insoluble fraction of mild HDO oil.

product. An additional separation of the aqueous phase occurred in the second stage hydrotreatment.

After the second stage hydrotreatment, the syringols have almost disappeared and a significant amount of phenols and catechols formed. In addition, there is indication for the formation of benzene derivatives and PAH (polyaromatic hydrocarbon) compounds. Extractives (fatty acids) are present as traces.

NMR Studies. ^1H -NMR and ^{13}C -NMR. The changes in the molecular composition as a function of the severity of the catalytic hydrotreatment reaction were also analyzed by ^1H - and ^{13}C -NMR of the organic phase of the upgraded products. To semiquantify the changes in the oil, the ^1H -NMR spectra were divided into regions characteristic of certain chemical groups and the regions were integrated according to a method suggested by Ingram¹⁵ and Mullen.¹⁶

The integration results, after normalization, are given in Table 4.

The disappearance of resonances in the region δ 10.0–8.0 ppm indicates that during the hydrotreatment reactions, the aldehydes are hydrogenated rapidly in line with model studies at similar conditions and with Ru/C.^{17,18} The aromatics regions (δ 8–6.8 ppm and δ 6.8–6.4 ppm), when summed, showed a slight decrease after hydrotreatment. There is also some overlap with olefinic carbons in these regions. The region (δ 6.4–4.2), representing methoxy groups (i.e., in methoxyphenols), phenolic OH, and many of the hydrogen atoms in the carbohydrate-like molecules, decreased slightly after stabilization but more significantly after mild hydrotreatment and the second stage hydrotreatment. The region (δ 4.2–3.0 ppm) that represents the protons on the carbon atoms next to the aliphatic alcohol or

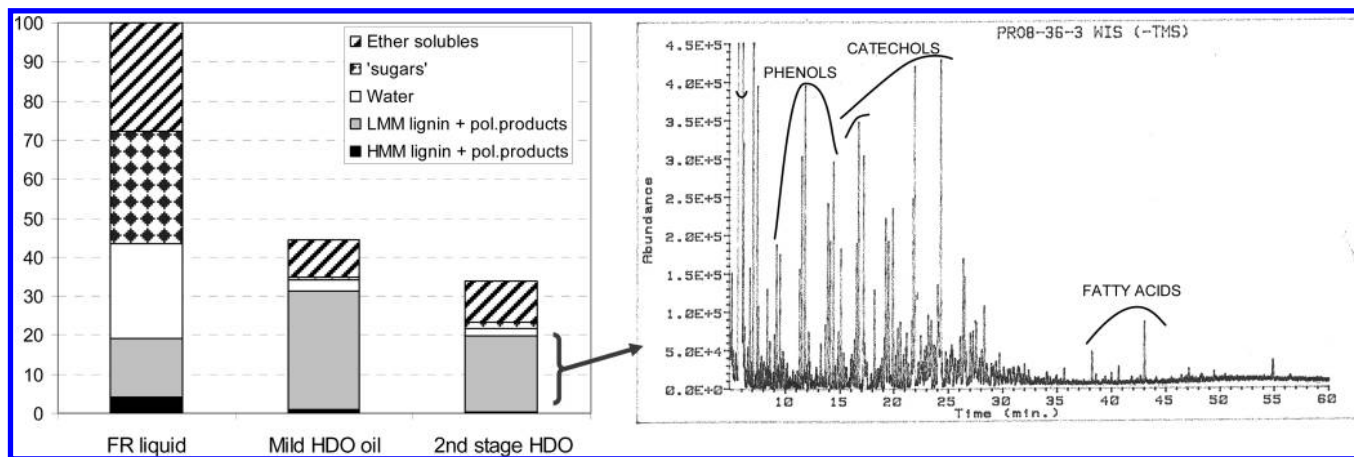


Figure 10. Molecular composition of the LMM fraction of the second stage hydrotreatment product.

Table 6. ^{31}P -NMR Analyses^a

sample	aliphatic OH	aromatic OH	S + C	G	Ca	H	carboxylic acid	total OH	H ₂ O
(1) pyrolysis liquid	1.42	6.53	3.51	1.26	1.15	0.61	0.13	8.08	0.66
(2) stabilization	1.50	3.23	1.90	0.60	0.44	0.28	0.36	5.08	6.91
(3) mild hydrotreatment	0.28	3.90	1.49	0.49	1.18	0.74	0.42	4.60	3.43
(4) second stage hydrotreatment	0.40	2.81	0.84	0.23	0.88	0.85	0.31	3.51	11.60

^a Amounts of different hydroxyl group species (mmol/g) in water-insoluble fractions 1–4. S + C = syringyl + condensed phenolic units, G = guaiacyl phenolic units, Ca = catechols, and H = *p*-hydroxyphenyl phenolic units.

ether, the methoxy group, or a methylene group that joins two aromatic rings decreased as the process became more severe. The decrease in the area representing the methoxy groups indicates that less of the methoxyphenols were present after hydrotreatment. As the area of the aromatics did not change significantly, it indicates the detachment of methoxy groups from the aromatics. The region (δ 3.0–2.2 ppm) representing protons located α to ketones, aldehydes, or carboxyl groups and benzylic protons and the region (δ 2.2–0 ppm) representing protons attached to aliphatic carbons increased as the process became more severe.

A parameter aliphatics to aromatics ratio was added to give an indication of the quality of the product. Aliphatic is a desired compound, as it gives products with good physical properties (low viscosity, can be evaporated at high temperature, and thus produces less coke). The increase in the aliphatics to aromatics ratios after hydrotreatment shows that the hydrotreatment resulted in products with better physical properties than the pyrolysis liquid.

The carbon assignments and integration (after normalization) for the ^{13}C NMR spectra are given in Table 5. The number of carbon atoms in the carbonyl groups (ketones, aldehydes, ester, and carboxylic acids) decreased at higher process severity. The decrease in the concentration of the carbonyl groups after stabilization occurred solely due to hydrogenation. Mild hydrotreatment and two-stage hydrotreatment hydrogenated the carbonyl even further, resulting in a very low carbonyl concentration in the product of the two-stage hydrotreatment. The separation of the water fraction that occurred during mild and two-stage hydrotreatment may also have contributed to the removal of the carbonyl compounds from the hydrotreatment products.

The percentage of total aromatics (δ 163–100 ppm) decreased after a stabilization experiment but then increased after mild hydrotreatment. This was probably due to the occurrence of phase separation. This implies that the aromatics components were less soluble in the aqueous phase

and thus became more concentrated after the removal of water from the hydrotreatment products. This was also seen in the solvent fractionation and GC/FID of WIS and from the ^{31}P NMR. After a two-stage hydrotreatment experiment, the content of aromatic components decreased significantly. The decrease in the amount of syringyl moieties (δ 112–100 ppm) at higher severity is also confirmed by GC/FID and ^{31}P NMR (see later). The area decrease in peaks at δ 84–54 ppm represents the detachment of methoxy ($-\text{OCH}_3$) and hydroxy ($-\text{OH}$) groups during hydrotreatment. The detachment of the hydroxyl groups is better explained by the ^{31}P NMR, as this method can separate the aliphatic and aromatics OH. The percentage of alkyl carbons (aliphatics, δ 54–1 ppm) in the stabilization product is similar to that of the pyrolysis liquid and increases significantly after the mild and two-stage hydrotreatment experiments.

The aliphatic to aromatic ratios were also calculated in a similar way to the analysis of the ^1H NMR spectra. Similar trends, e.g., an increase in the aliphatic to aromatic ratio at higher process severity, were observed, although the exact numerical values were different. This could be due to an extensive overlap of regions in the ^1H NMR spectra.

^{31}P NMR Spectra. The water-insoluble fraction of pyrolysis liquid and its upgraded products were characterized in order to get information on chemical changes in this fraction. The sample pretreatment is described in the Experimental Section. Samples 1 (pyrolysis liquid) and 2 (stabilization), in particular, contained many sharp peaks in the spectra, which most probably originated from small molecular weight compounds. The water-insoluble fractions of the upgraded products were characterized by ^{31}P NMR (Table 6).

On the basis of ^{31}P NMR (Table 6), the amount of guaiacyl, phenolic, syringyl, and condensed phenolic units decreased when the process severity increased. The catechols and hydroxyphenol units decreased in the stabilization step but increased during mild hydrotreatment. The increase in catechols was also clearly seen by GC/FID, and the decrease

Table 7

method	main information obtained
KF water titration	water content, water balance
CHN analyzer	elemental balances, H/C, O/C
solvent fractionation	changes in product groups
Brix by density meter	change in “sugars”
CE	amount of volatile acids (acetic, formic, glycolic, lactic)
¹ H-NMR	hydrogenation of carbonyls and acids, detachment of methoxyl groups from aromatics
¹³ C-NMR	hydrogenation of carbonyls and acids, change in phenolics, change in aromatics
³¹ P-NMR	change in phenolics
GC/MSD, GC/FID	change in CC-eluted compounds
GC/MSD, GC/FID with derivatization	catechols

in syringyls was observed by ¹³C NMR after mild and second stage hydrotreatment.

Conclusions

We have shown that the characterization of hydrotreated pyrolysis liquid samples with a protocol consisting of a solvent extraction scheme followed by characterization of the fractions with a variety of techniques is a very powerful method. The approach was successfully applied to characterize the oil fractions of three hydrotreated products produced at different process severity. With this information available, it is also possible to draw conclusions with respect to the complex chemistry taking place during the catalytic hydrotreatment process.

The “sugars” disappeared with increasing severity of hydrotreatment. CE is an accurate method for acid analyses. During stabilization, there was no change in acids. The hydrogenation of acids took place in mild hydrotreatment due to the high temperature applied.

Qualitative GC/MSD gives information on changes in GC-eluted compounds. In stabilization, the aldehydes and some “sugars” were hydrogenated into alcohols, which were seen as an increase in the diols. The diols disappeared with increasing severity of hydrotreatment. Quantitative GC/MSD provides information on the change in GC-eluted compounds. However, the amount of identified compounds is below 25 wt % of the

sample. In addition, the analysis should also be conducted for a derivatized sample in order to follow changes in catechols.

NMR is a useful tool for creating information on the reactions taking place during hydrotreatment, e.g., changes in carbonyl compounds, phenolics, and carbohydrates. The hydrogenation of aldehydes was clearly seen by both ¹H NMR and ¹³C NMR. ¹H NMR also indicated the detachment of methoxyl groups from the aromatics. The increase in aliphatics/aromatics ratios after hydrotreatment shows that the hydrotreatment resulted in products with better physical properties than the pyrolysis liquid. ¹³C NMR and ³¹P NMR are useful tools for following up changes in phenolics. The research has also shown that the well know Brix method can be used to determine the “sugar” content in various fractions. A good correlation was found for the direct determination of “sugar” content by Brix and an indirect method using solvent extraction.

By combination of various methods, a clearer picture of the composition of whole liquids can be obtained. A summary of proposed analytical methods to follow the changes in hydrotreatment is presented in Table 7.

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