Hydrodeoxygenation of Beech Wood Bio-Oil over Nickel catalyst

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BIO ECONOMY RESEARCH BADEN-WÜRTTEMBERG

Research Area Lignocellulose

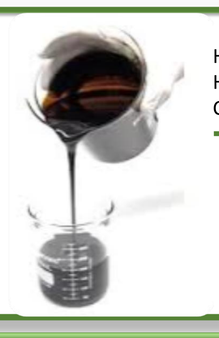
Motivation

- Investigate the Hydrotreatment of beech wood bio-oil composed by a light and a heavy phase over a nickel catalyst at different pressure and temperature conditions.

Bio-oil from biomass

~500°C, N_2 atmosphere, ambient pressure

Thermochemical conversion Fast Pyrolysis



High Temperature (~175 - 380°C)
High Pressure (35-300 bar of H_2)
Catalyst

Hydrodeoxygenation (HDO)

Fuel and chemicals

Bio-oil:

Beech Wood bio-oil → Light Phase (59 wt.%) / Heavy Phase (41 wt.%)

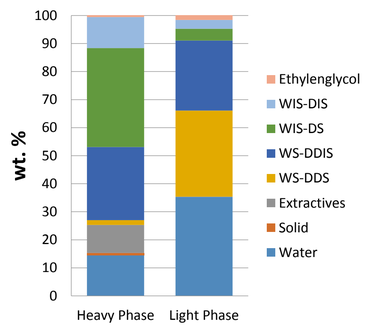


Figure 1. Solvent extraction of beech wood LP and HP

WIS-DIS: Solids, aging products and High Molecular Weight Lignin.
WIS-DS: Aging products and Low Molecular Weight Lignin.
WS-DDIS: Water, sugars, additives, hydroxyacids.
WS-DDS: Aldehydes, ketones, furans, lignin monomers and volatile acids.
DS: Dicloromethane Solubles
DIS: Dicloromethane Insolubles
DDIS: Dicloromethane diethylether Insolubles
DDS: Dicloromethane, Diethylether Solubles

Table 1. Physicochemical properties beech wood LP and HP

	Light Phase	Heavy Phase
pH	2,7	3,0
Density (g/cm³)	1,17	1,19
Metals (wt.%)	0,03	0,04
Elemental Composition (wt. %)		
	Wet basis / **Dry basis**	**Wet basis** / **Dry basis**
C	34,3 / 53,01	54,3 / 63,51
H	8,3 / 6,77	7,5 / 6,89
O	57,3 / 40,19	38,2 / 29,59
N	<0,2 / <0,2	<0,2 / <0,2
S	0,02 / 0,01	0,01 / 0,01
HHV (MJ/Kg)	14,1 / 22,33	23,1 / 27,23

Hydrodeoxygenation

Catalyst:

Table 2. Metal content of the catalyst

Metal content (wt. %)						BET area (m^2/g)	Average crystalline size (nm)
Al	Cr	Fe	Mg	Ni	Zn		
0,94	12,80	0,41	0,58	60,80	0,45	93,88	4,4

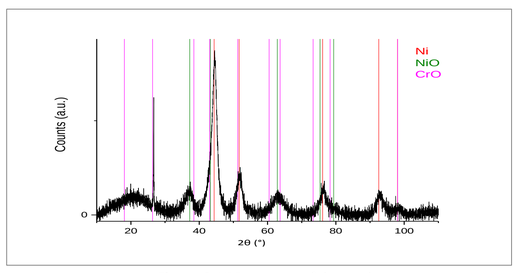


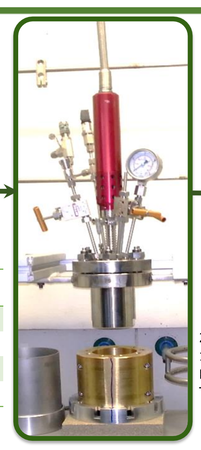
Figure 2. XRD patterns of the catalyst

Table 3. EDX surface composition analysis

Element	C K	O K	Al K	Mg K	Si K	Ca K	Cr K	Fe K	Co K	Ni K
Weight %	12,51	28,09	0,78	0,28	10,02	0,09	8,45	0,26	0,27	39,26
Atom %	25,79	43,5	0,71	0,29	8,84	0,06	4,03	0,11	0,11	16,56

Reactions:

50 g Bio-oil
2,5 g catalyst

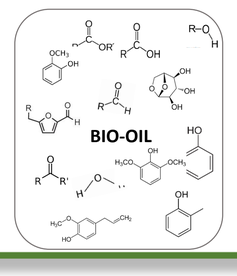


200 ml autoclave
1000 rpm (magnetically coupled stirrer)
Reaction time: 4h
Temperature ramp: 6 °C /min

Table 4. Experiment conditions

Temperature (°C)	Pressure (bar)
225	80
175	80
225	100
175	100

→ **Gaseous Products**
→ **Light Phase**
→ **Upgraded Bio-oil**
→ **Solids**



H_2, catalyst, ↑temperature → **UPGRADED PRODUCTS**

- **Decarboxylation:** R-COOH + H_2 → R-H + CO_2
- **Hydrogenation:** R_1-CH=CH-R_2 + H_2 → R_1-CH_2-CH_2-R_2
- **Hydrodeoxygenation (hydrogenolysis and dehydration):** CH_2-CH_2-CH_2-CH_2-CH_2-CH-OH + H_2 → C_6H_{12} + H_2O
- **Hydrocracking:** R_1C-CH_2-CH_2-R_2 + H_2 → R_1CH_3 + H_3CR_2
- **Cracking:** R_1-CH_2-CH_2-CH_2-CH_2-R_2 → R1-CH_2-CH_3 + CH_2=CH_2-R_2

Results

Mass balance

Table 5. Mass balance after upgrading reactions

	Light Phase (wt.%)		Heavy Phase (wt.%)		Solid (wt.%)		Gas (wt.%)		Loss (wt.%)	
225 °C; 80 bar	51,15	±0,79	39,46	±2,56	0,71	±0,06	1,13	±0,01	7,53	±1,71
175 °C; 80 bar	50,33	±0,19	40,59	±1,80	0,55	±0,06	0,72	±0,03	7,81	±2,02
225 °C; 100 bar	52,54	±1,43	38,95	±2,23	0,55	±0,04	0,72	±0,04	6,27	±0,80
175 °C; 100 bar	48,1	±5,34	42,42	±4,57	0,76	±0,06	0,64	±0,01	8,06	±0,87

H_2 uptake

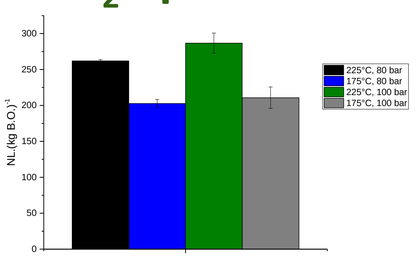


Figure 3. Hydrogen consumption during upgrading reactions

Gas products

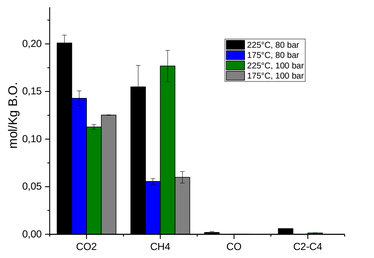


Figure 4. Gas products obtained after upgrading reactions

Metal leaching: light phase

Table 6. Metal content in the light phase after upgrading reactions

	Cr (ppm)	Ni (ppm)
225 °C; 80 bar	90,0	39,0
175 °C; 80 bar	362,0±3,9	752,0±160,7
225 °C; 100 bar	63,5±14,7	257,0±37,2
175 °C; 100 bar	357,5±83,3	650,0±17,6

Liquid Products: Light and heavy phases

Table 7. Elemental analysis, calorific value and water content upgraded fractions

		C (wt.%)		H (wt.%)		N (wt.%)		S (wt.%)		O (wt.%)		HHV (MJ/Kg)		water content (wt.%)
		Wet basis	dry basis	wet basis	dry basis	wet basis	dry basis	wet basis	dry basis	Wet basis	Dry basis	wet basis	dry basis	
Feed	LP	34,3	53,01	8,3	6,77	<0,2	<0,2	0,02	0,03	40,19	40,19	14,1	22,33	35,3
	HP	54,3	63,51	7,5	6,89	<0,2	<0,2	0,01	0,01	38,2	29,59	23,1	27,23	14,5
175 °C,	LP	27,99±0,02	49,54±0,31	9,43±0,14	8,14±0,25	<0,3	<0,3	<0,02	<0,02	62,58±0,16	42,32±0,06	12,61±0,06	22,51±0,17	43,5±0,40
80 bar	HP	58,30±0,39	65,43±0,16	8,05±0,09	7,67±0,09	<0,3	<0,3	<0,02	<0,02	33,65±0,29	26,75±0,21	26,15±0,14	29,13±0,10	10,89±0,38
225 °C,	LP	25,50±0,09	49,71±0,28	9,4±0,68	7,78±1,35	<0,02	<0,02	<0,02	<0,02	65,10±0,76	42,52±1,11	11,81±0,078	22,94±1,61	48,45±0,49
80 bar	HP	59,05±2,06	65,10±1,72	8,15±0,10	7,73±0,13	<0,3	<0,3	<0,02	<0,02	32,80±2,16	27,12±1,85	26,25±1,01	29,03±0,95	10,9±0,78
175 °C,	LP	28,13±0,07	49,80±0,21	9,29±0,18	7,9±0,35	<0,3	<0,3	<0,02	<0,02	62,57±0,25	42,30±014	12,73±0,01	22,32±0,35	43,49±0,40
100 bar	HP	54,85±6,34	60,90±4,34	7,9±0,29	7,58±0,51	<0,3	<0,3	<0,02	<0,02	34,57±1,71	28,69±3,69	23,07±2,86	26,85±6,08	11,12±0,0
225 °C,	LP	25,87±0,09	49,82±0,15	9,84±0,24	8,7±0,51	<0,3	<0,3	<0,02	<0,02	64,28±0,15	41,47±0,66	11,95±0,15	23,36±0,72	48,12±0,42
100 bar	HP	59,25±0,49	66,76±0,04	8,75±0,29	8,6±0,35	<0,3	<0,3	<0,02	<0,02	32,0±0,78	24,59±0,09	27,01±0,18	30,79±0,46	11,25±0,67

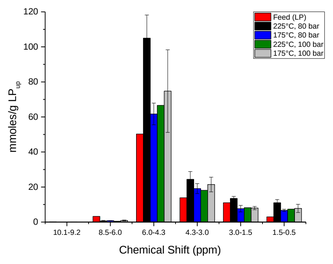


Figure 5. ^{1}H-NMR spectra integration of upgraded LPs.

1.5-0.5 ppm: alkanes
3.0-1.5 ppm: α proton to unsaturated, acid carboxylic or keto-groups
4.3-3.0 ppm: alcohols, ethers

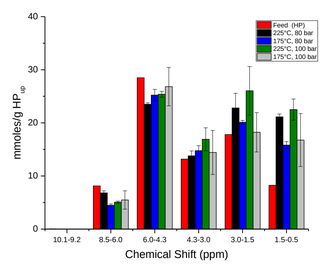


Figure 6. ^{1}H-NMR spectra integration of upgraded HPs.

6.0-4.3: water, carbohydrates, O-H exchanging group
8.5-6.0 ppm ((hetero) aromatics,

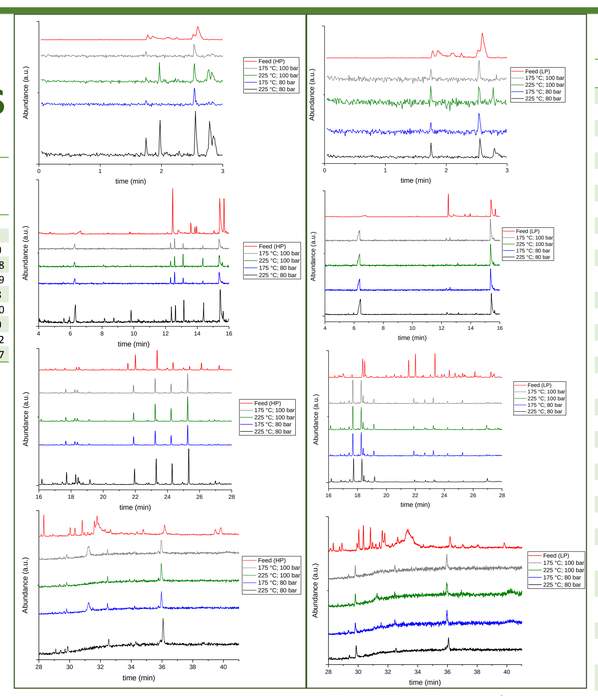


Figure 7. Chromatogram of upgraded HPs. The main peaks identified are correlated with data given in Table 8.

Figure 8. Chromatogram of upgraded HPs. The main peaks identified are correlated with data given in Table 8.

Table 8. Compounds identified by GC-MS

R.T. (min)	Compound
1.98	Cyclopentane, methyl-
2.79	1-Propene, 2-methoxy-
9.84	Cyclopentanone, 2-methyl-
12.37	Cyclopentanol
12.45	2- Propanone, 1-hydroxy-
12.63	2-Hexen-1-ol, (E)
13.61	2-Cyclopenten-1-one
13.86	2-Cyclopenten-1-one, 2-methyl-
14.40	Cyclohexanol
15.46	Acetic Acid
15.70	Furfural
16.19	2-Furanol, tetrahydro-2-methyl-[a]
17.48	2,3-Butanediol[a]
17.73	Propylene Glycol
18.29	1,2-Ethanediol
18.45	1,2-Ethanediol, monoacetate
19.19	1,2-Butanediol
21.54	2-Cyclopenten-1-one, 2-hydroxy-3-methyl-
21.96	Phenol, 2-methoxy-
22.71	1,4-Butanediol[a]
23.31	Phenol, 2-methoxy-4-methyl-
23.40	1,2-Cyclohexanediol
23.96	Phenol, 2-methyl-
24.01	Phenol
24.29	Phenol, 4-ethyl-2-methoxy-
25.33	Phenol, 2-methoxy-4-propyl
26.12	Eugenol
27.22	Phenol, 2-methoxy-3-(1-propenyl)-,(E)-
28.32	Phenol, 2-methoxy-3-(1-propenyl)-
30.04	2-Furancarboxaldehydes,5-(hydroxymethyl)-
30.82	Vanillin
31.61	Ethanone, 1-(3-hydroxy-4-methoxyphenyl)-
36.08	Benzeneacetic acid, 4-hydroxy-3-methoxy
39.83	4-Hydroxy-2-methoxycinnamaldehyde

[a]: Compounds observed only in the LP.

Conclusion

- The catalyst was active for all conditions evaluated, especially at 225 °C and 100 bar;
- The higher the hydrogen consumption, the higher the deoxygenation degree;
- Compounds such as ketones and furfural were not observed after upgrading;
- Further experiments will be performed at higher temperatures and pressure in order to evaluated the hydrodeoxygenation at harsh conditions.

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