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Hydrotreating Pyrolytic Lignin to Produce a Refinery Feedstock

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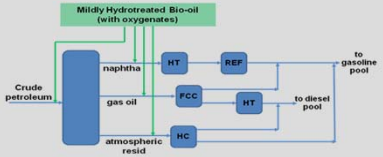
Bio-oil Co-Feeding Scenario

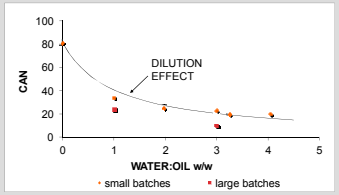


Co-processing bio-oil in a petroleum refinery is an attractive option to decrease the cost of upgrading pyrolysis oil to transportation fuels. However, the oil would need to fulfill several criteria, among others

1. *the acidity of the bio-oil must be reduced from the typical TAN (total acid number) value of over 100 to about 15 if bio-oil is blended in ratio 1:8*
2. *the bio-oil must be miscible with hydrocarbons*
3. *the bio-oil must be highly volatile so that it is amenable to fractional distillation*

The lignin fraction of pyrolysis oil has a lower oxygen and acid content than whole bio-oil and could give better properties than the whole oil. We produced pyrolytic lignin by adding water to pyrolysis oil, and hydrotreated the pyrolytic lignin fractions with the goal of producing bio-oil that fulfills the above criteria.

Water-Separated Pyrolytic Lignin



Acid number of lignins separated with various amounts of water. Acidity decreases with increased dilution and improved stirring of large batches

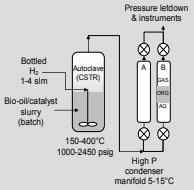
Composition of Water-Precipitated Organic Fractions on a Wet Basis

Run	H_2O: Oil	C	H	N	S	O	Ash	Water	Volatiles
	w/w	% w/w	% w/w	% w/w	% w/w	% w/w	% w/w	% w/w	% w/w
-,3,-	3:1	57.80	6.74	0.13	0.03	35.91	<0.05	17.2	55.6
-,1,-	1:1	59.41	6.58	0.12	0.01	34.57	<0.05	10.8	62.6

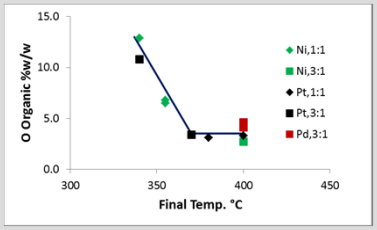
Catalysts Employed

Catalyst	Composition	Manufacturer	Pretreatment
Ni	Ni-Mo/γ-Al_2O_3, 5% NiO, 25% MoO_3	Grace Davison	Milled, screened to 35-57 μm, presulfided
Pt	5% Pt on char	Johnson Matthey	Heated to final operating T in H_2
Pd	5% Pd on activated C	Johnson Matthey	Heated to final operating T in H_2

Semi-Batch Autoclave

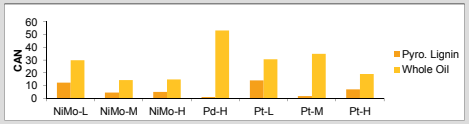


Oxygen Content



Oxygen content for total organic product with all catalysts <5% at higher temperature/pressure

Less Acid Than Whole Oil



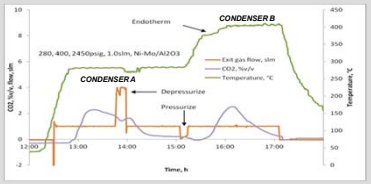
Acid number of hydrogenated products from pyrolytic lignin much lower than that of products from whole oil at similar conditions

Carbon Distribution

Run cat,fd,T	Org C Yield %w/w	Aqueous C Yield %w/w	Coke C Yield %w/w	Gas C Yield %w/w	CO_2 C Yield %w/w	CO C Yield %w/w	CH_4 C Yield %w/w	Other Gas C Yield %w/w
Ni,1,L	62.9	5.1	1.1	2.6	1.8	0.2	0.7	0.0
Ni,1,M	69.4	1.7	1.5	5.1	1.6	0.1	3.2	0.3
Ni,1,M	78.3	1.9	1.3	5.9	1.3	0.2	3.5	0.9
Ni,3,H	66.9	2.3	1.0	4.1	1.0	0.1	2.6	0.4
Pt,3,L	63.3	3.2	4.4	5.7	2.8	0.6	1.9	0.3
Pt,3,M	57.4	3.5	4.4	7.1	3.5	0.4	2.8	0.3
Pt,1,M	66.2	4.0	3.8	11.5	5.7	0.6	4.6	0.5
Pt,1,H	67.4	2.7	3.4	6.6	3.7	0.3	1.6	1.0
Pd,3,H	62.1	3.4	3.5	7.2	1.5	1.0	4.0	0.7
Pd,3,H	68.0	3.2	2.3	6.7	1.4	1.0	3.8	0.6

Platinum yields higher coke and CO_2
Palladium yields higher methane

2-Stage Hydrotreating

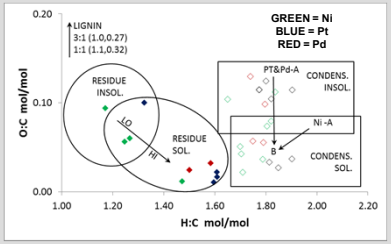


Experimental Conditions

Run* cat.,feed, T	Catalyst	Feed	H_2 flow slm	Pressure psig	Stabil. temp. ° C	Final temp. ° C	Mass Balance %
Ni,1,L	Ni-Mo/Al_2O_3	1:1	1	1000	150	340	93
Ni,1,M	Ni-Mo/Al_2O_3	1:1	1	2450	280	355	80
Ni,1,M	Ni-Mo/Al_2O_3	1:1	1	2450	280	355	94
Ni,3,H	Ni-Mo/Al_2O_3	3:1	1	2450	280	400	91
Pt,3,L	Pt/char	3:1	1	1000	150	340	96
Pt,3,M	Pt/char	3:1	1	2450	280	370	91
Pt,1,M	Pt/char	1:1	1	2450	295	380	100
Pt,1,H	Pt/char	1:1	1	2450	280	400	89
Pd,3,H	Pd/C	3:1	1	2450	280	400	89
Pd,3,H	Pd/C	3:1	1	2450	280	400	99

*Run designation is catalyst, feed, final temperature, e.g., Ni=Ni-Mo/Al_2O_3, 1=water: oil during oil separation =1:1, L =low temperature (340° C)

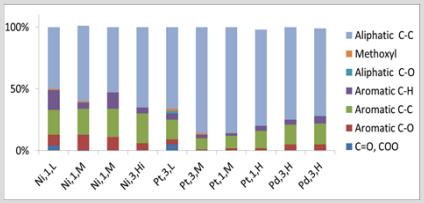
Miscibility in Hydrocarbons



Hydrodeoxygenation is greater at higher temperature/pressure and with precious metal catalysts, giving better miscibility

Functional Groups

Analysis of residue samples remaining in reactor at end of experiment



C^{13} NMR shows high conversion to aliphatics with residual phenolics

Peak	RT	%Area no solvent	Library ID Pt,1,H	Quality
13	11.482	1.66	trans-Decalin, 2-methyl-	97
2	2.915		Methylene Chloride	96
7	9.386	1.72	1H-Indene, octahydro-, cis-	96
10	10.564	2.96	Naphthalene, decahydro-, trans-	96
22	13.832	1.33	Naphthalene, 1,2,3,4-tetrahydro-6-methyl-	96
34	15.567	2.07	Naphthalene, 1,2,3,4-tetrahydro-5,7-dimethyl-	96
3	6.425	1.53	Cyclohexane, ethyl-	94
5	8.262	4.45	Cyclohexane, propyl-	94
9	10.105	1.73	Cyclohexane, butyl-	94
14	11.754	1.99	Naphthalene, decahydro-2-methyl-	94
26	14.225	3.76	Naphthalene, 1,2,3,4-tetrahydro-5-methyl-	93
28	14.570	2.59	Naphthalene, 1,2,3,4-tetrahydro-2,7-dimethyl-	92
29	14.678	2.60	1H-Indene, 2,3-dihydro-1,1,5-trimethyl-	92
15	12.098	1.61	1H-Indene, 2,3-dihydro-5-methyl-	91
27	14.388	1.89	1,1'-Bicyclohexyl	91
33	15.500	2.06	Benzocyclodecene, tetradecahydro-	90
4	7.452	1.53	1-Ethyl-4-methylcyclohexane	87
6	9.235	2.37	Cyclohexane, 1-methyl-2-propyl-	87
19	12.715	3.93	Cyclopentylcyclohexane	87
1	2.685		Acetone	86
20	13.349	3.35	Cyclohexane, (4-methylpentyl)-	83
23	13.953	1.35	Cyclohexane, (cyclopentylmethyl)-	81
37	16.860	4.07	Cyclohexane, (3-cyclopentylpropyl)	80

GC/MS Spectrum shows predominantly 1&2-ring cyclo-aliphatic and cyclo-aliphatic-aromatic

Conclusions

The hydrotreating of pyrolytic lignin was studied over NiMo, Pt and Pd catalysts. 55% conversion of the carbon in the biomass pyrolysis lignin to a low-oxygen (<5%), low-acid, volatile, hydrocarbon-miscible liquid product can be achieved. This was possible with all three catalysts at the most severe condition (400° C, 2450 psig) and with platinum at somewhat less severe conditions.

The results suggest that hydrotreating of the organic fraction (pyrolytic lignin) is a technically feasible strategy for producing a refinery intermediate, and oil with better properties (lower O and lower TAN) than for hydrotreating of the whole oil can be produced at equivalent conditions.

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