PYROLYSIS BIO-OIL UPGRADING TO RENEWABLE FUELS

Final Report

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16. Abstract

This study aims to upgrade woody biomass pyrolysis bio-oil into transportation fuels by catalytic hydrodeoxygenation (HDO) using nanospring (NS) supported catalyst via the following research objectives: (1) develop nanospring-based catalysts (nanocatalyst) and (2) evaluate the nanocatalysts for the hydrogenation of pyrolysis bio-oil into liquid fuels.

We developed protocols for HDO treatment of bio-oil and model compounds and product evaluation using commercial Ni and Ru based catalysts initially. We successfully synthesized Ni decorated NS catalysts (Ni-NS), in small amounts (mg level) and characterized the catalysts. It was shown that the Ni-NS catalyst had to be reduced (activated) before use. The Ni based catalysts were able to hydrodeoxygenate the model compounds and bio-oil and conversion was Ni content and temperature dependent. Low conversions using the Ni-NS catalysts were obtained, but only very small amounts of catalyst were used. Further work is required to scale up the Ni-NS catalyst production, increase Ni loading on NSs, and modify the reactor for future work in bio-oil upgrading.

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EXECUTIVE SUMMARY

This study aims to upgrade pyrolysis oil into transportation fuels by catalytic hydrodeoxygenation (HDO). Catalysts with high activity and selectivity are thereby highly desired in the upgrading process. Nickel (Ni) and ruthenium (Ru) supported on silica and alumina were introduced in this study as catalysts for bio-oil HDO. Besides, silica nanosprings (NS) were successfully synthesized and decorated with Ni nanoparticles and the catalyst characterized. The catalytic behaviors of all the catalysts were first tested on model compounds, guaiacol and vanillin, for pyrolysis bio-oil. Conversion rate was shown to be temperature dependent. The Ni-NS was shown to partially deoxygenate guaiacol to hydrocarbons even at extremely low Ni contents relative to starting material (1:1000). The Ni-NS have the potential to upgrade pyrolysis bio-oil but larger quantities of Ni-NS are required. HDO trials on bio-oil show that a 2 step process is required to minimize coke formation. Results from bio-oil catalytic hydrogenation revealed that mainly furans, ketones, and aldehydes in water soluble bio-oil were reduced to their corresponding alcohol. Furthermore, the organic bio-oil fraction was successfully hydrocracked into small aromatic compounds which can easily be upgraded to hydrocarbons. Further work is required to scale up the Ni-NS catalyst production (from mg to g), increase Ni loading on NS, and modify the reactor for subsequent work on using Ni-NS catalysts for bio-oil upgrading.

DESCRIPTION OF PROBLEM

In order to reduce the greenhouse gas (GHG) emissions, biomass derived fuels have become an alternative to fossil fuels. Wood and agricultural biomass are a readily available renewable resource. Fast pyrolysis is a process that can convert the woody biomass to a crude bio-oil (pyrolysis oil) which contains anhydro-sugars, alcohols, ketones, aldehydes, carboxylic acids, phenols and water [1,2]. Nevertheless, some of these compounds contribute to bio-oil shelf life instability and difficulty in refining. Catalytic hydrodeoxygenation (HDO), and hydrogenation, of the bio-oil can upgrade the bio-oil into stable hydrocarbons which can be refined into various fuel grades (gasoline, jet fuel and diesel). Therefore, developing new catalysts with enhanced performance and lowering costs for upgrading bio-oils is required.

Although many catalysts have been developed for different purposes, there are still rare ones that can effectively favor the deoxygenation reactions. Conventional hydrotreating catalyst like Co(Ni)MoS have been proposed for years due to their active hydrodesulfanation (HDS) and HDO capabilities, however, it was proved that they cannot deoxygenate the bio-oil as effectively as they do on petroleum oil [3,4]. Moreover, this kind of sulfur containing catalyst is not suitable for producing green fuels from bio-oil. Therefore, this study aims to develop a green heterogeneous catalyst for bio-oil HDO. Nickel (Ni) and ruthenium (Ru) based catalysts thereby were selected due to their high catalysis activity. Besides, the porosity, or pore shape of the catalyst support, can also have a great effect on catalytic properties. Silica nanospring (NS), a novel catalyst support, was synthesized and further decorated with Ni or Ru particles in this study. Two main targets of this research are 1) developing a good routine that can successfully deoxygenate bio-oil; 2) testing the catalytic properties of NS based catalyst during hydrotreating bio-oil.

APPROACH AND METHODOLOGY

A commercial nickel (Ni/SiO$_2$-Al$_2$O$_3$, 66% Ni loading, Acros Organics) and ruthenium (Ru/Al$_2$O$_3$, 5% Ru loading, Acros Organics) catalysts were introduced first in the study for establishing HDO experimental protocols on bio-oil. In addition, due to the complexity of bio-oil, it's difficult to study the catalytic behaviors of NS catalyst during hydrotreatment. Therefore, guaiacol and vanillin were selected as bio-oil model compounds for studying the specific catalytic properties including activity and selectivity.

1 Catalyst Preparation and Characterization

1.1 Nanospring Catalyst

To assess the reducibility of Ru and Ni supported on NS, H$_2$ temperature programmed reduction (H$_2$-TPR) was performed on free standing NS catalysts decorated with the two metals. Silica NS were grown on a variety of supports depending upon the application. For Co-NS based catalyst, they were grown on Si wafer (111) p-type. For Ru-NS and Ni-NS based catalysts, they were either grown on aluminum foil as the final free standing catalyst which can easily be scrapped off, or on stainless steel wire mesh (200 x 200 mesh, type 316). Cobalt (III) acetylacetonate, ruthenium acetylacetonate and nickel carbonate were used as precursors, and preparation followed the procedures of Luo et al. [5]. The successful bio-oil upgrading using commercial catalysts with high Ni loading prompted us to increase the Ni loading of the Ni nanocatalysts. The conventional and NS based catalysts were reduced (activated) by passing H$_2$ (10 mL min^{-1}) respectively at 350 and 500°C.

1.2 Ni-ZSM5 Catalyst

Zeolite supported Ni catalyst (Ni-ZSM5) was synthesized by the incipient wetness impregnation method. CH$_4$Ni$_3$O$_7$ (2.0 g) was dissolved in H$_2$O (10.0 g) with the addition of cHCl (1 mL) and the aqueous solution slowly dropped onto H-ZSM5 (4.67g) upon continuous stirring. After 3 hours, the catalyst was dried at 102˚C for 12 hours, air-calcined at 400˚C for 4 hours, and H$_2$ reduced (40 mL/min) at 450˚C for 4 hours.

2 Catalytic Hydrotreatment on Guaiacol and Vanillin

A stirred 300 mL batch reactor (Parr model 4564) was set up to accommodate reaction temperatures of 250°C and pressures of 3000 psi. The bio-oil (40 mL) together with the catalyst (1 g for Ni/SiO$_2$-Al$_2$O$_3$, H-ZSM5 and Ni-ZSM5 and 70 mg for Ni-NS with 20% Ni loading) was introduced into the reactor, closed, flushed with H$_2$ and then pressurized with H$_2$ to 250 psi (maximum pressure for the regulator used). The reaction mixture was heated to 250°C and stirred for 4 hours. The reaction was then quenched by placing the reactor in an ice-water bath. The reaction products were analyzed by GC-MS.

3 Bio-oil Hydrotreatment by Ni/SiO$_2$-Al$_2$O$_3$

3.1 Phase Separation

Bio-oil was produced via the fast pyrolysis of pine at 500˚C. The bio-oil was mixed with deionized water at the weight ratio of 1:1. After 1 hour ultrasonication, the water soluble phase separated as the top layer while water insoluble (organic) phase was the bottom layer. The organic water insoluble phase, which is about 15% of the original bio-oil, was then collected for further hydrocracking to produce low molecular aromatics. The water soluble phase was hydrogenated in a two-stage process.

3.2 2-Stage Hydrotreatment of the Water Soluble Phase

All hydrogenation reactions were carried out in a Parr reactor equipped with a stirrer and controller. The feedstock and catalyst weight ratio during hydrogenation was 30:1. Mild hydrogenation was firstly applied at temperature of 150˚C and pressure of 300 psi. This mild hydrogenation lasted for 9 hours during which additional H$_2$ was added every 3 hours. The 2nd-stage hydrogenation was performed at 250˚C and 300 psi for a further 9 hours. Furthermore, additional H$_2$ was added to the reactor for every 3 hours to prevent coke formation. The hydrogenated liquid products were then analyzed by GC-MS. Gases in the reactor were vented into a Tedlar PVF (300 × 300 mm^2) gas-sampling bag for GC-TCD analysis.

3.3 Water Insoluble Hydrocracking for Aromatics

Mixing ethanol with the water insoluble bio-oil at a weight ratio of 4:1 (EtOH:Bio-oil) until the bio-oil fully solubilized. The mixture was then transferred into the Parr reactor with Ni/ZSM-5

for hydrocracking reaction at 250˚C and 300 psi of hydrogen. The vessel was stirred for 4 hours at 600 rpm and then cooled in an ice-water bath. Liquid products after reaction were analyzed by ESI-MS.

3.4 Analytical Techniques

Condensed liquid products were analyzed by gas chromatography-mass spectrometry (GC-MS, Focus-ISQ, ThermoScientific). Separation was achieved on an RTx-5ms (30 m × 0.25 mm) with a temperature program of 40 to 290°C at 5°C min^{-1}. 1,2,4-Trichlorobenzene was used as an internal standard. Compounds were identified by their mass spectra, library mass spectral matching (NIST 2008) and retention times of known standards. Gaseous products taken from the sampling bag by a syringe were analyzed by gas chromatography-thermal conductivity detector (GC-TCD, GOWMAC, Series 350) equipped with a HaySep DB stainless steel packed column (9.1 m × 3 mm).

Non-volatile compounds were analyzed by electrospray ionization mass spectrometry (ESI-MS). Positive ion ESI-MS (m/z 100–2000) was performed on an LCQDeca (ThermoQuest) instrument. Samples were dissolved in MeOH (1 mg mL^{-1}) and introduced into the ESI source at 10 μL min^{-1}. The ion source and capillary voltages were 4.48 kV and 47 V, respectively; temperature: 275°C.

Field emission scanning electron microscopy (SEM) studies were performed using a Leo Supra 35 SEM equipped with an X-ray energy dispersive spectrometer (EDS). Morphologies were characterized by transmission electron microscopy (TEM, Jeol JEM-2010 TEM, 200kV). Sample specimens for TEM tests were prepared by dispersion of the catalysts in ethanol and the suspension dropped onto a copper grid.

X-ray photoelectron spectroscopy (XPS) measurements were performed in a custom built ultra-high vacuum system using the Mg Kα line (1253.6 eV) and kinetic energy of the photoelectrons was measured with a hemispherical analyzer with a net resolution of 300 meV.

H_2-temperature programmed reduction (H_2-TPR) spectra of the catalysts were recorded using a Micromeritics AutoChem II 2920 Chemisorption Analyzer, equipped with a thermal conductivity detector (TCD). Sample (50 mg) was loaded in a U-shape quartz reactor and first

purged in a flow of He (50 mL min^{-1}) at 250°C for 1 hour to remove water, cooled to 50°C, then a 10% H_2 in Ar (50 mL min^{-1}) was purged and heated to 800°C at 10°C min^{-1}.

FINDINGS

1 Nanospring Catalyst Characterization

1.1 Co-NS Catalyst

In situ reduction consisted of timed exposures of the sample to 1 x 10^{-6} Torr of H_2 at 385°C, and then allowing the sample to cool to room temperature and the chamber to pump down. XPS spectra were acquired after each exposure. XPS quantitative analysis of the unreduced Co-NS catalyst yielded 70% Co^{3+} (octahedral) and 30% Co^{2+} (tetrahedral), at binding energies of 779.7 eV and 782 eV respectively, which is consistent with the Co_3O_4 spinel phase of cobalt. The reduction proceeds through the following scheme:
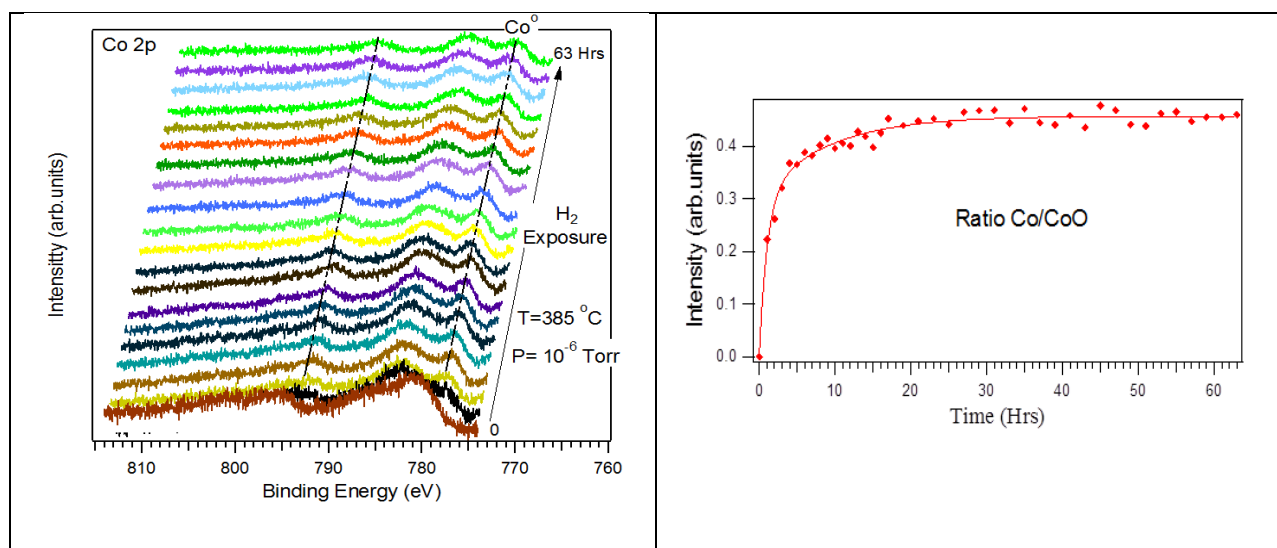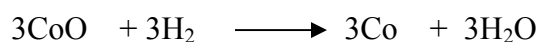
$$Co_3O_4 + H_2 \longrightarrow 3CoO + H_2O$$

$$3CoO + 3H_2 \longrightarrow 3Co + 3H_2O$$

Figure 1: (Left) XPS Co 2p core level states of Co-NS and (Right) ratio Co^0/CoO during H_2 reduction.

As the reduction time increases CoO (~783 eV) and Co0 (778 eV) are gradually formed (Fig.1). The two-step reduction is consistent with H_2-TPR results [5]. The information gained with XPS findings are the description of the reduction states of the Co-NS catalyst during activation. The coexistence of the three oxidation states of Co during reduction also tells us that the two reduction steps are simultaneous. As the sample becomes more metallic, the Co0 shoulder

increases while the CoO peak decreases (Fig. 2). At 385°C and 1 x 10^{-6} Torr of H$_2$, the reduction saturates after ~20 hours at the rate of 41.4%. These results confirmed the incomplete reduction of Co-NS catalyst during our previous Fischer-Tropsch synthesis and bio-oil upgrading experiments and the need for higher activation temperature (603°C) according to H$_2$-TPR [5].
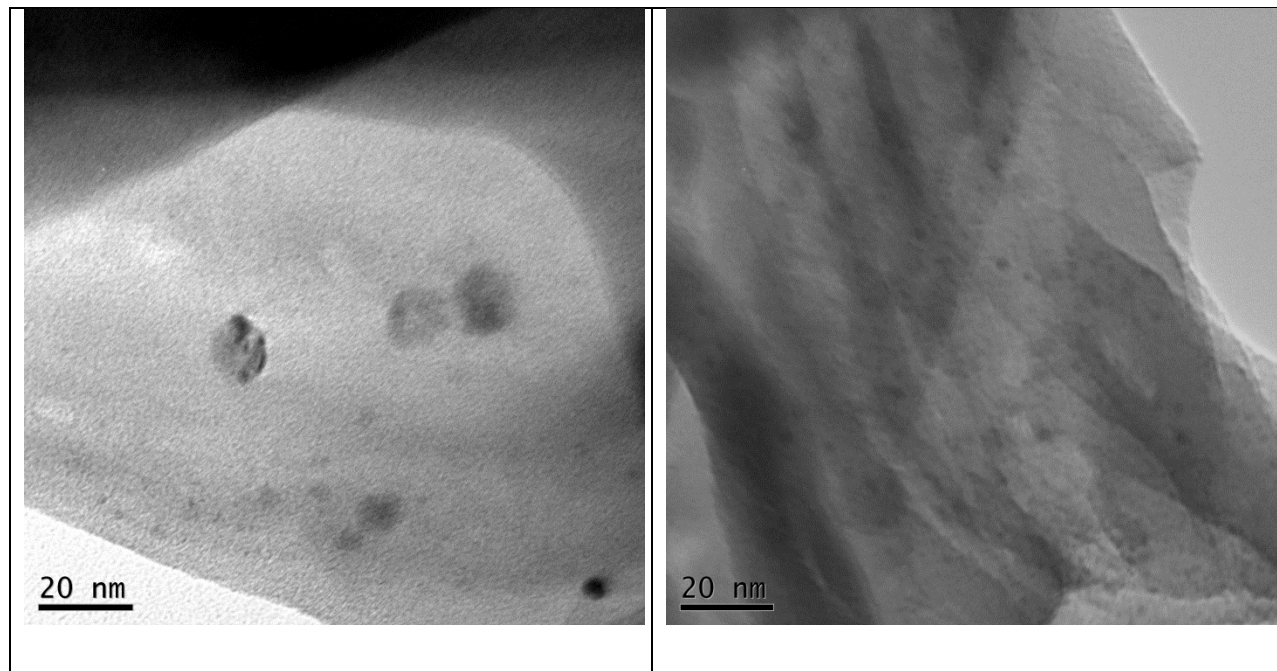

Figure 2: TEM micrographs of (Left) the starting Co-NS catalyst and (Right) reduced catalyst.

TEM micrographs of the fresh and the reduced catalysts show how the Co particle size decreases by more than 50% upon reduction, proving that there is no coalescence or sintering of Co during the process.

1.2 Ni-NS and Ru-NS Catalysts

The Ni-NS and Ru-NS catalysts were prepared on stainless steel mesh (for hydrogenation studies) and on aluminum foil (for catalyst characterization studies). The H$_2$-TPR analyses (Fig. 3) of the two catalysts were performed to determine the temperature when the metal fully reduces. Both nanocatalysts were shown to reduce around 450°C and therefore an activation temperature of 500°C was employed.

Preliminary work with the Ni commercial catalyst showed that the high Ni content (66%) was desirable for bio-oil upgrading. The metal loading on the Ni-NS catalysts was determined by SEM-EDS analysis. The composition is given in Table 1, and the EDS spectrum is shown in Fig. 4 (top). A Ni content slightly greater than 20% was obtained. Based on these results a double treatment of the NS with nickel carbonate was employed and this approach increased the Ni loading to about 30%. A small amount of C and Cl was detected in the sample and is possibly due to contaminants from the air and solvent used. XPS analysis showed that the surface region of the NS is composed of Si, O, Ni, and some C impurities. Fig. 4 (bottom) shows a XPS spectrum of unreduced Ni-NS showing Ni 2p core levels states. The binding energy is typical of that of Ni in NiO, which means that the fresh catalyst needs to be reduced (activated) prior to use.
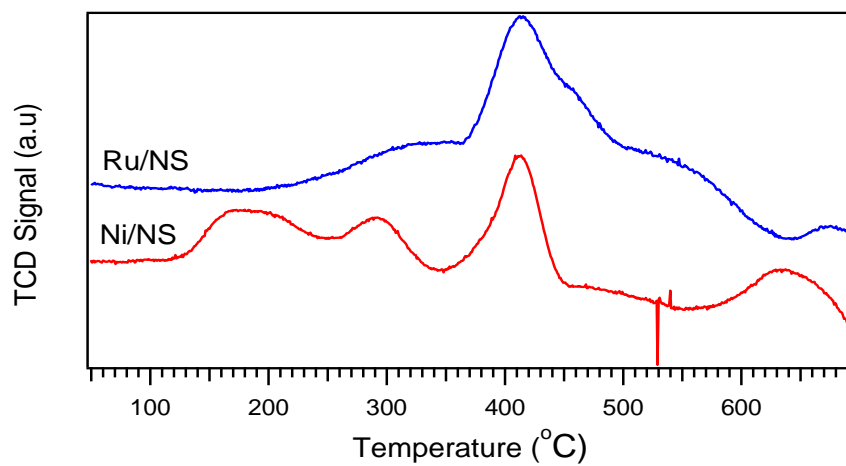

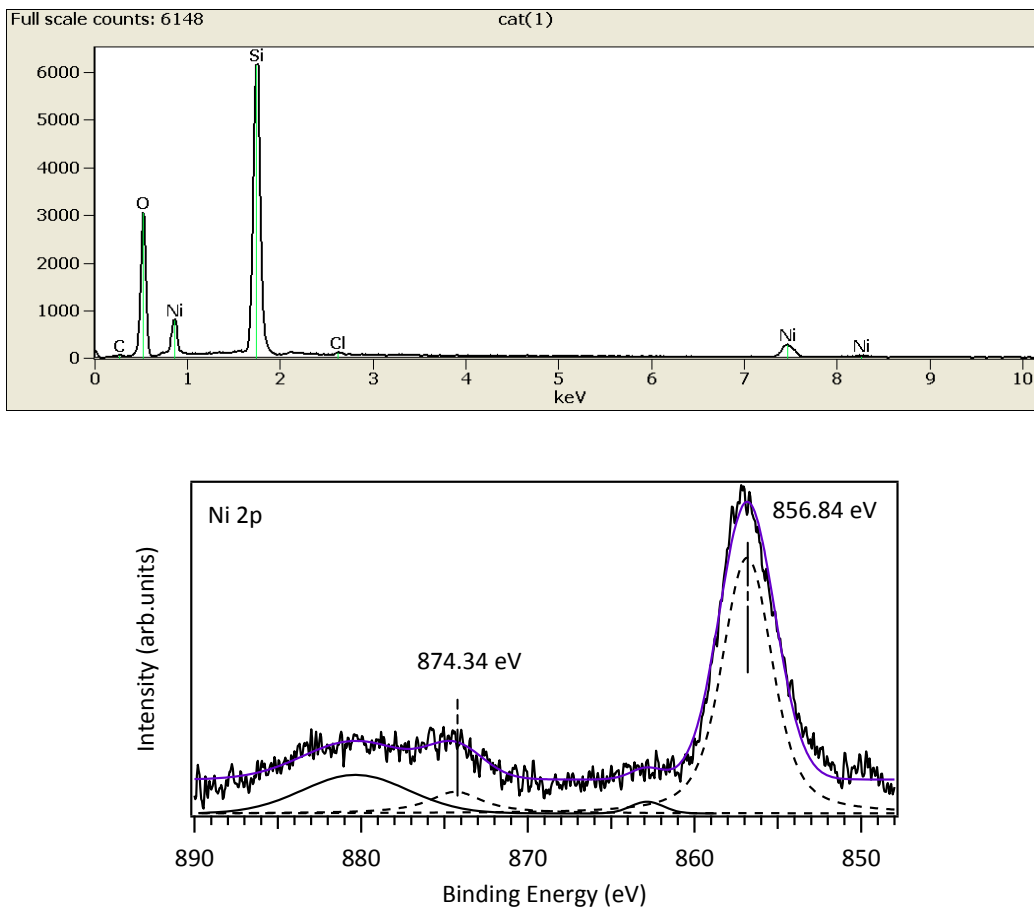**Figure 3: H$_2$-TPR profiles for Ru-NS and Ni-NS catalysts.**

Figure 4: (top) EDS spectrum for the Ni-NS catalyst and (bottom) XPS spectrum of unreduced Ni-NS showing Ni 2p core level states.

Table 1: EDS Compositional Analysis of the Ni-NS Catalyst

Element Line	Net Counts	Net Counts Error		Weight %	Weight % Error	Atom %	Atom % Error
C K	234	+/-	26	1.60	+/-0.178	3.11	+/-0.346
O K	18534	+/-	148	38.95	+/-0.311	56.92	+/-0.455
Si K	55651	+/-	296	37.27	+/-0.198	31.03	+/-0.165
Si L	0		0	---	---	---	---
Cl K	454	+/-	51	0.40	+/-0.045	0.26	+/-0.030
Cl L	145	+/-	16	---	---	---	---
Ni K	4453	+/-	154	21.77	+/-0.753	8.67	+/-0.300
Ni L	6640	+/-	125	---	---	---	---
Total				100.00		100.00	

2 Catalytic Hydrotreatment (or HDO) on Guaiacol and Vanillin

Pyrolysis bio-oil is a complex mixture of sugar, lipid and phenolic derived compounds. Therefore examining functional groups of compounds and monitoring these changes upon upgrading is a way to examine the hydrogenation reaction. Methoxyls ($-OCH_3$), phenol hydroxyls (Ar-OH) and aldehydes (-C=O) are three main oxygen-containing functional groups in bio-oil. Feasible routines to deoxygenate these groups are demethoxylation, dehydration and hydrogenation, respectively. To simplify the system and to examine the effect of catalyst on select functional groups model compounds were used. Therefore, guaiacol and vanillin were selected for preliminary evaluation of the catalysts and to monitor the catalytic reactions.

2.1 Guaiacol Hydrotreatment/HDO

Reactions were carried out using a H_2 pressure of 250 psi (gas regulator pressure limit). Products from guaiacol hydrogenation catalyzed by Ni and Ru catalysts were characterized by GC-MS as shown in Figs. 5-11. The corresponding amounts of those deoxygenation (completely and partially) products were subsequently quantified by GC-MS peak area percentage as shown in Table 2. Fig. 5 is a chromatogram of guaiacol. Hydrogenations below 250˚C gave a conversion rate of guaiacol with Ru/Al_2O_3 catalyst at 14.7%. There were only minor amounts of phenol and cyclohexanol (hydrogenation products) produced which indicated demethoxylation and subsequent hydrogenation occurred on guaiacol at this condition. Under the same hydrotreating condition, using $Ni/SiO_2-Al_2O_3$, however, effectively converted guaiacol into hydrocarbons like benzene and cyclohexene, as shown in Fig. 7. The conversion rate in this case was 64.1%. Furthermore, more phenol, cyclohexanol and cyclohexanone were produced with $Ni/SiO_2-Al_2O_3$ catalysis than from Ru/Al_2O_3. The results revealed that the demethoxylation, hydrogenation and dehydration all took place on guaiacol with the $Ni/SiO_2-Al_2O_3$ catalyst which gave a deeper deoxygenation than Ru/Al_2O_3.

In order to test whether temperature has a positive effect on hydrocarbon yield, another hydrogenation of guaiacol catalyzed by $Ni/SiO_2-Al_2O_3$ at 300˚C was carried out. The results show that the guaiacol conversion rate increased to 79.2%. Besides, a higher conversion to hydrocarbons, including benzene (11.2%) and cyclohexene (4.5%), was obtained at higher temperature (Fig. 8).

The main products of guaiacol hydrogenation with the Ni-NS catalyst were phenol and cyclohexanol (Fig. 9). This experiment supported our original idea that the NS catalyst can also partially deoxygenated guaiacol like the commercial Ni catalyst (guaiacol/Ni = 23:1) although only a small amount of hydrocarbons were produced. The low yield of hydrocarbons probably resulted from low overall Ni content (guaiacol/Ni = 1000:1) which was based on the low amount of NS catalyst (0.07 g) used relative to the commercial. Given that the Ni content was extremely low this still shows that the Ni-NS catalyst is promising and needs further optimization. Furthermore, by increasing the H_2 pressure to at least 750 psi, based on other studies, would no doubt improve conversion and future studies are aimed at this.

For comparative purposes, H-ZSM5 was trialed as a catalyst. Since H-ZSM5 has been reported as a strong heterogeneous acid catalyst which favors the dehydration reaction, pure H-ZSM5 and Ni-ZSM5 (20% Ni loading) were separately tested for catalytic behaviors during guaiacol hydrogenation at 300°C. The GC-MS chromatograms of the experiments are respectively shown in Figs. 10 and 11. Pure H-ZSM5 only favored isomerization reactions of guaiacol but no deoxygenation occurred. However, once Ni was incorporated hydrocarbon products, like benzene, were produced at the conversion rate of 9.8% which was comparable to the commercial Ni/SiO_2-Al_2O_3 catalyst. This interesting phenomenon also confirmed that Ni is the prime reactive site for deoxygenating reactions.

In summary, these results have shown that Ni based catalysts can convert guaiacol into hydrocarbons and the yields of these hydrocarbons increase with temperature. Furthermore, the Ni decorated NS catalyst can deoxygenate guaiacol although hydrocarbons yield was low and this may be attributed to the low Ni loading and small amount of catalyst used.
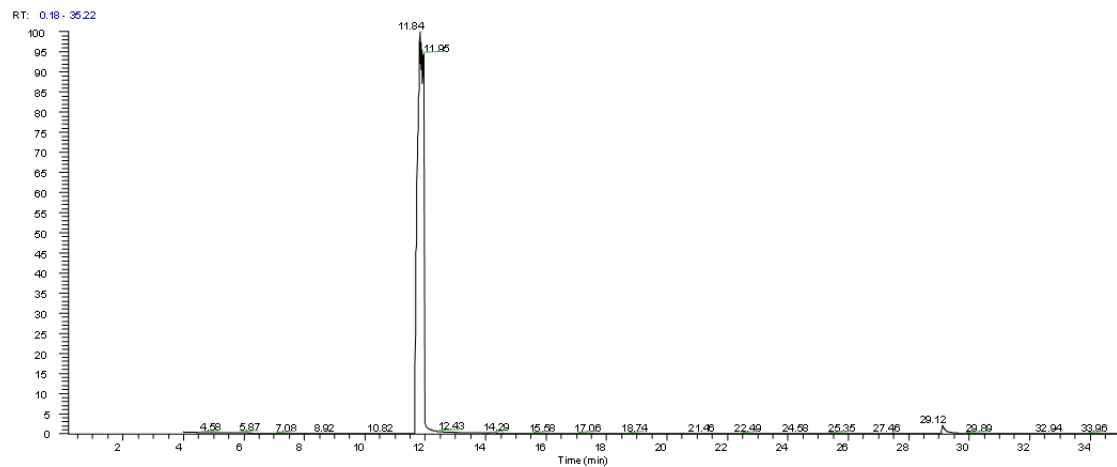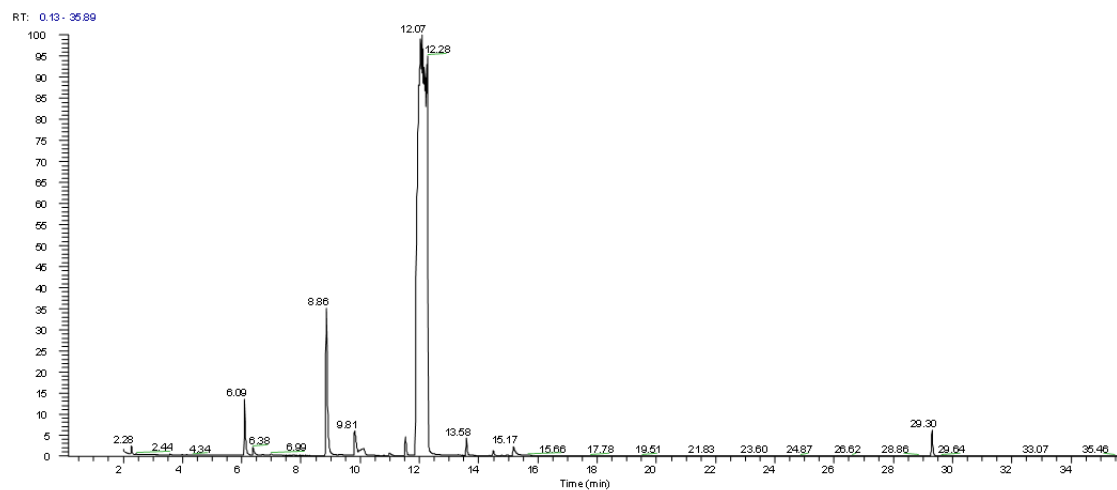
Figure 5: GCMS chromatogram of guaiacol.

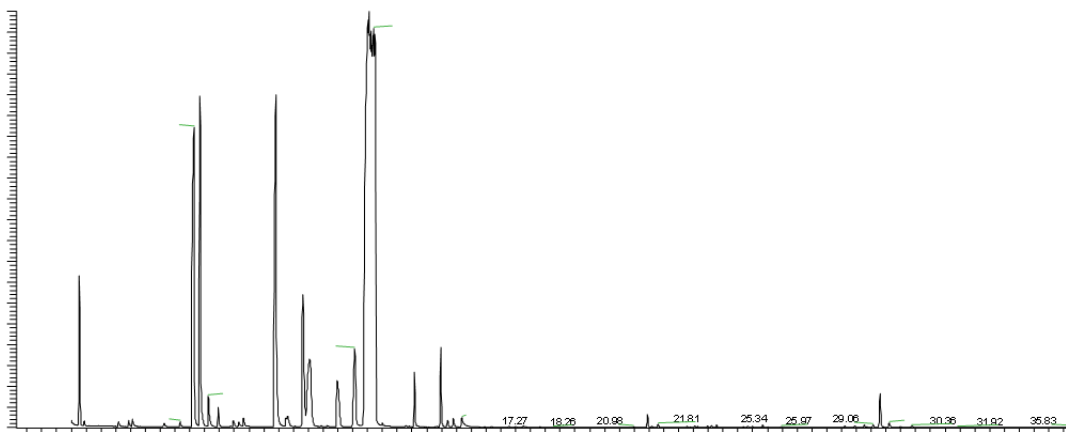**Figure 6: GCMS chromatogram of Ru/Al$_2$O$_3$ catalyzed guaiacol products at 250˚C.**

Figure 7: GCMS chromatogram of Ni/SiO$_2$-Al$_2$O$_3$ catalyzed guaiacol products at 250°C.

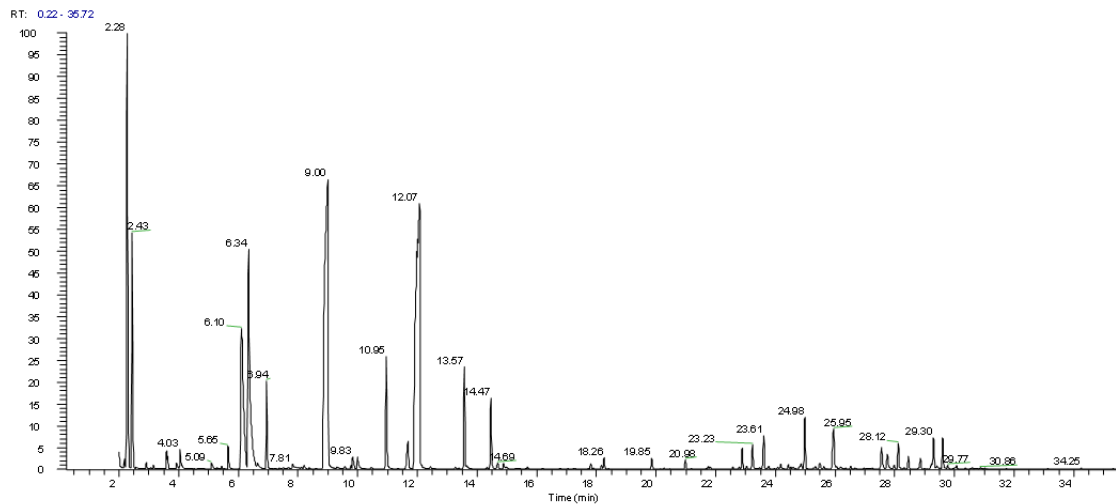**Figure 8: GCMS chromatogram of Ni/SiO$_2$-Al$_2$O$_3$ catalyzed guaiacol products at 300°C.**
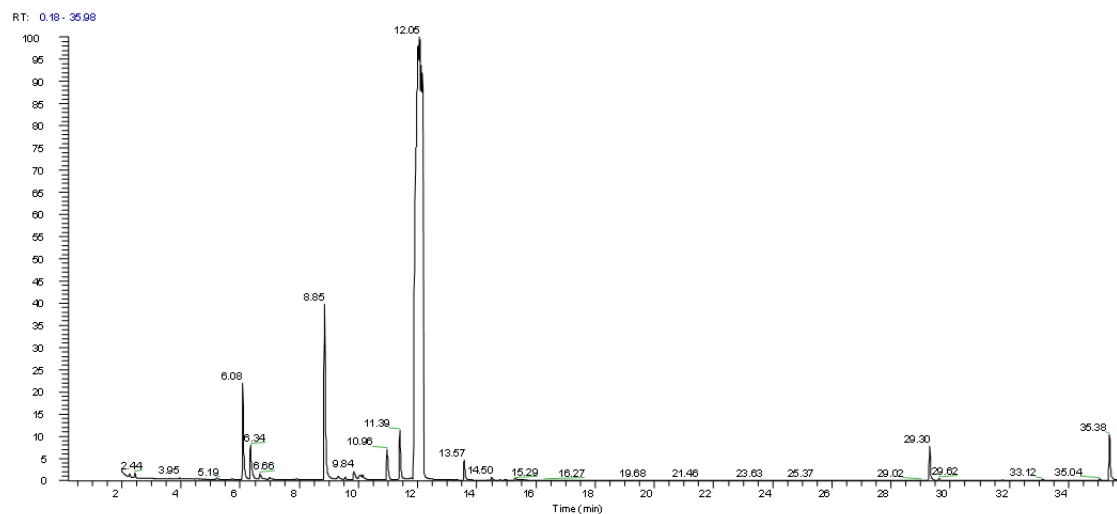
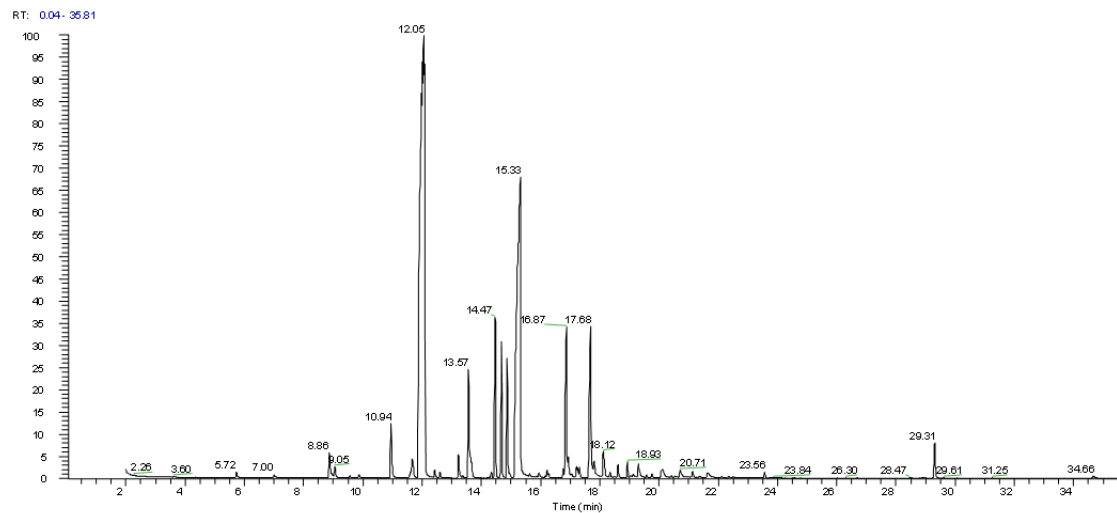**Figure 9: GCMS chromatogram of Ni-NS catalyzed guaiacol products at 300˚C.**

Figure 10: GCMS chromatogram of H-ZSM5 catalyzed guaiacol products at 300˚C.
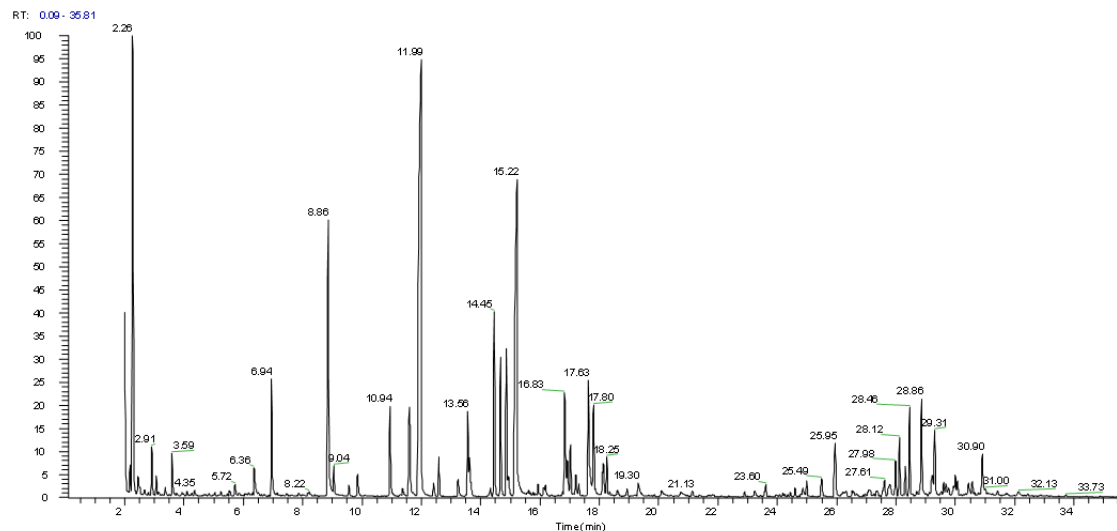
Figure 11: GCMS chromatogram of Ni-ZSM5 catalyzed guaiacol products at 300˚C.

Table 2: GC-MS Peak Area Percentage of Deoxygenation Products from Guaiacol Hydrotreatment

	Untreated	250˚C (%)		300˚C (%)			
		Ru/Al$_2$O$_3$	Ni/SiO$_2$-Al$_2$O$_3$	Ni/SiO$_2$-Al$_2$O$_3$	Ni-NS	H-ZSM5	Ni-ZSM5
Guaiacol	98.0	85.3	35.9	20.8	78.3	41.1	18.0
Benzene		0.15	1.9	11.2			9.8
Cyclohexane				4.5	0.11		
Cyclohexanol		1.6	9.1	7.5	2.8		
Cyclohexanone		0.3	5.7	8.6	1.3		0.7
Anisole							1.9
Phenol		5.8	9.8	20.5	6.8	0.7	5.6
Cresol					1.3		4.0
Other hydrocarbons							2.5

2.2 Vanillin Hydrotreatment

Methoxyl and phenol can be successfully removed using a Ni catalyst. Therefore vanillin was used to examine the effect of the hydrogenation on the aldehyde (C=O) functional group together with methoxyl and phenol. Fig. 12. shows the chromatogram of products from vanillin hydrogenation catalyzed by Ni/SiO$_2$-Al$_2$O$_3$ at 250˚C. Analysis of the GCMS data indicated that

almost all of the vanillin was converted into guaiacol (24.1%), cresol (21.3%), phenol (4.3%), cyclohexanol (1.9%), benzene (1.3%) and cyclohexane (0.7%). These results again show that $Ni/SiO_2-Al_2O_3$ can completely reduce the -C=O into -C-O or –C-C- via hydrogenation below 250˚C.
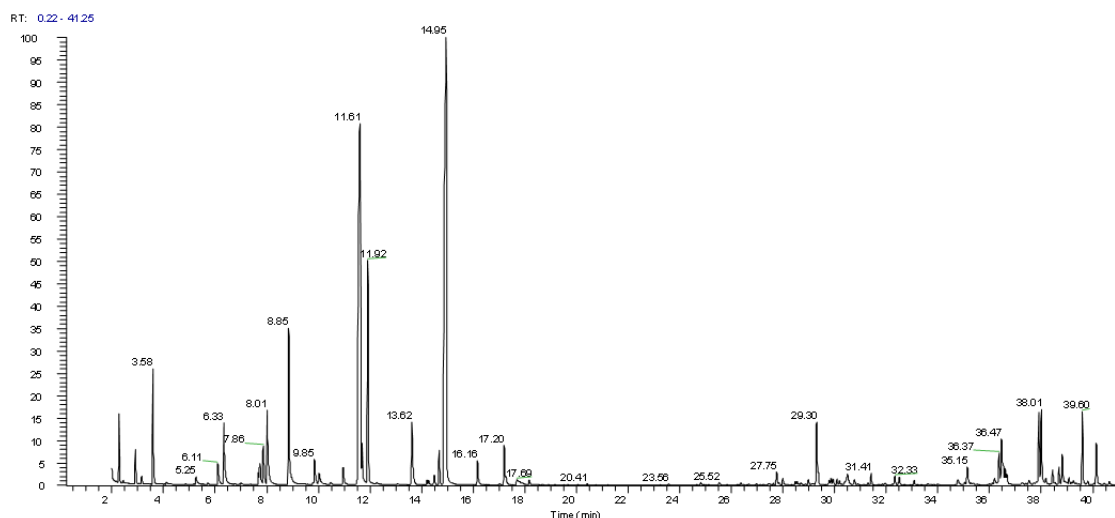

Figure 12: GCMS chromatogram of Ni/SiO$_2$-Al$_2$O$_3$ catalyzed vanillin products at 250˚C.

3 Bio-oil Hydrotreatment by Ni/SiO$_2$-Al$_2$O$_3$

3.1 2-stage Hydrotreatment of the Bio-oil Water Soluble Fraction

A 2-stage hydrotreatment process was investigated to upgrade the bio-oil in order to minimize coke formation on the catalyst. The premise was to perform a mild 1st stage hydrogenation to reduce the easily convertible compounds and suppress polymerization reactions (stabilize). The second stage was to fully reduce the stabilized mixture to hydrocarbons. Fig. 13 shows a GCMS chromatogram of the bio-oil water soluble fraction before and after catalytic hydrogenation. The composition of the bio-oil before and after hydrogenation is given in Table 3.

Butanol, furanol and pentone were the main products formed by Ni catalyzed hydrogenation (Table 3). These compounds were probably produced from furans and levoglucosan hydrogenolysis however, phenolics in bio-oil were hardly deoxygenated. Under these conditions, the water soluble phase of bio-oil can be hydrogenated into a stable alcohol mixture. But the hydroxyl group can hardly be removed which means the dehydration merely occurred.
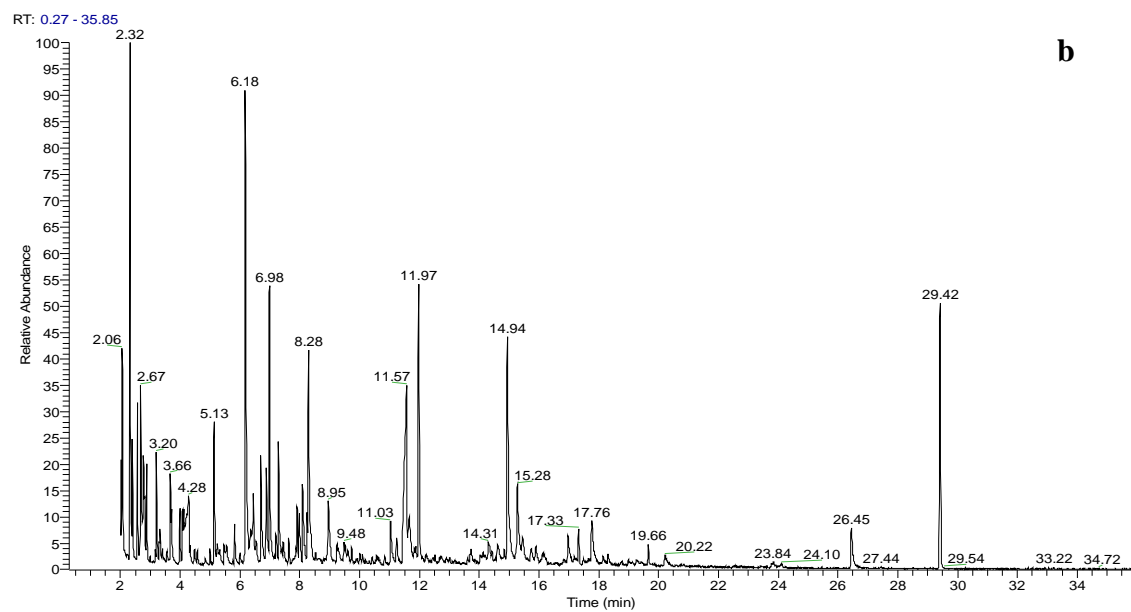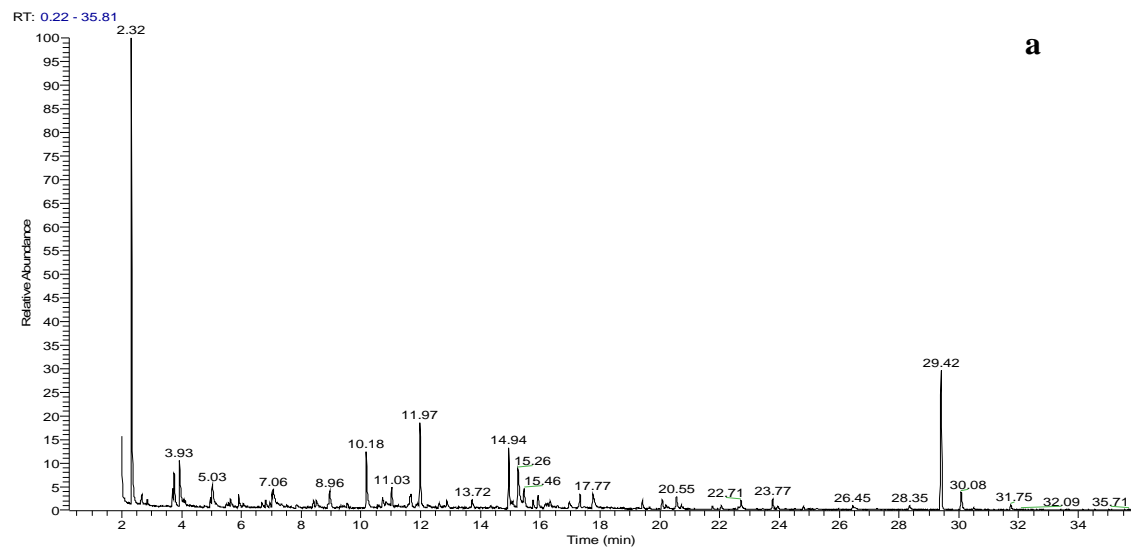
Figure 13: GC-MS on bio-oil aqueous phase before (a) and after (b) catalytic hydrogenation.

Table 3: Identified Compounds from Water Soluble Bio-oil before and after Hydrogenation

Retention time (min)	Identified compounds	Area % of peaks in GC-MS		MW
		Before hydrogenation	After hydrogenation	
2.06	tetrahydrofuran		1.84	72
2.32	1-butanol		5.54	74
2.32	acetol	11.68		74
2.56	2-pentanone		1.21	86
2.67	3-pentanone		2.29	86
2.77	tetrahydropyran		2.34	86
3.20	2-methyl-1-butanone		1.23	88
3.66	1-hydroxy-2-butanone	1.2		88
3.66	1-pentanol		1.59	88
3.72	1,2-ethanediol-monoacetate	2.74		104
3.91	butanedial	2.74		86
4.28	butanoic acid		2.56	88
4.98	2,5-dimethyl-furan	3.14		96
5.13	2-methyl-cyclopentanone		1.81	98
6.18	tetrahydro-2-methyl-2-furanol		6.59	102
6.45	hexanoic acid		2.01	116
6.69	cyclopentane-methanol		1.57	100
6.87	(5-methyltertahydro-2-furanyl)-methanol		1.31	116
6.98	4-hydroxy-butanoic acid		3.66	104
7.01	2-(5H)-furanone	3.7		84
8.28	tetrahydropyran-2-carbinol		4.22	116
8.37	5-methyl-2-furaldehyde	1.55		110
8.93	phenol	1.35	1.78	94
10.19	2-hydroxy-3-methyl-2-cyclopenten-1-one	4.24		112
11.02	2-methyl-phenol	1.23		108
11.57	butyric anhydride		5.91	158
11.64	4-methyl-phenol	1.39		108
11.97	guaiacol	5.09	4.08	124
14.94	4-methyl-guaiacol	4.22	4.46	138
15.24	1,2-benzenediol	4.94	1.89	110
17.73	4-methyl-1,2-benzenediol	2.49	1.36	124
20.54	vanillin	1.26		152
22.70	4-hydroxy-3-methoxy-acetophenone	1.14		166

3.2 Hydrogenation of the Bio-oil Organic Phase (Water Insoluble)

The bio-oil organic phase contains oligomeric compounds that cannot be analyzed by GCMS. Therefore we analyzed these fractions by ESI-MS which can cover the molar mass range of 100 to 2000 g/mol.

Fig. 14a. clearly shows the molar mass distribution of the organic soluble bio-oil fraction with a main cluster ranging from m/z 365-1304 which were assigned to oligomeric compounds. Upon hydrogenation (Ni-ZSM5), this peak cluster almost completely disappeared (Fig. 14b). This result indicated that the bio-oil water insoluble organic phase can be completely converted into small aromatics under the applied hydrocracking conditions. These small aromatic products can thus be further upgraded into hydrocarbons with a second hydrogenation step.
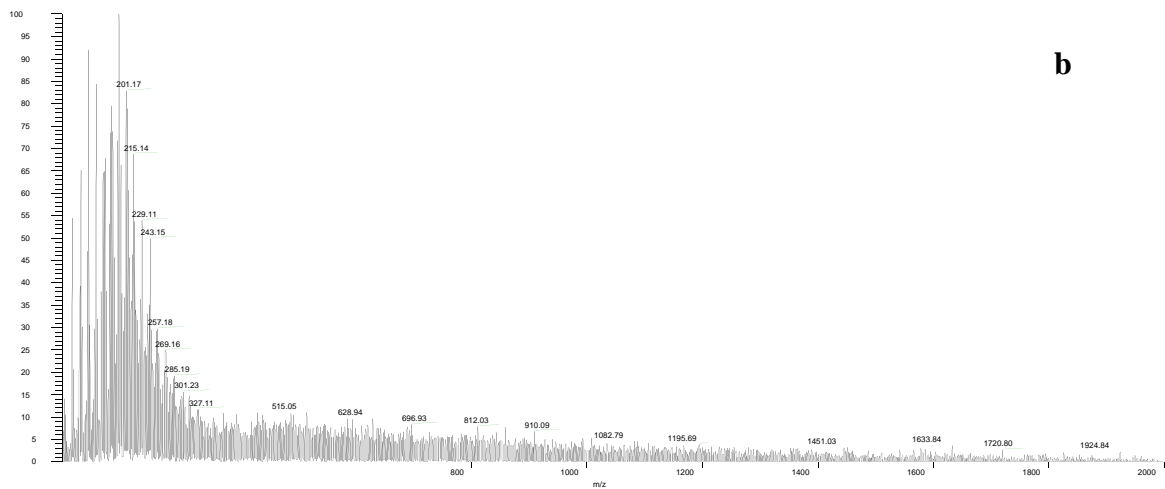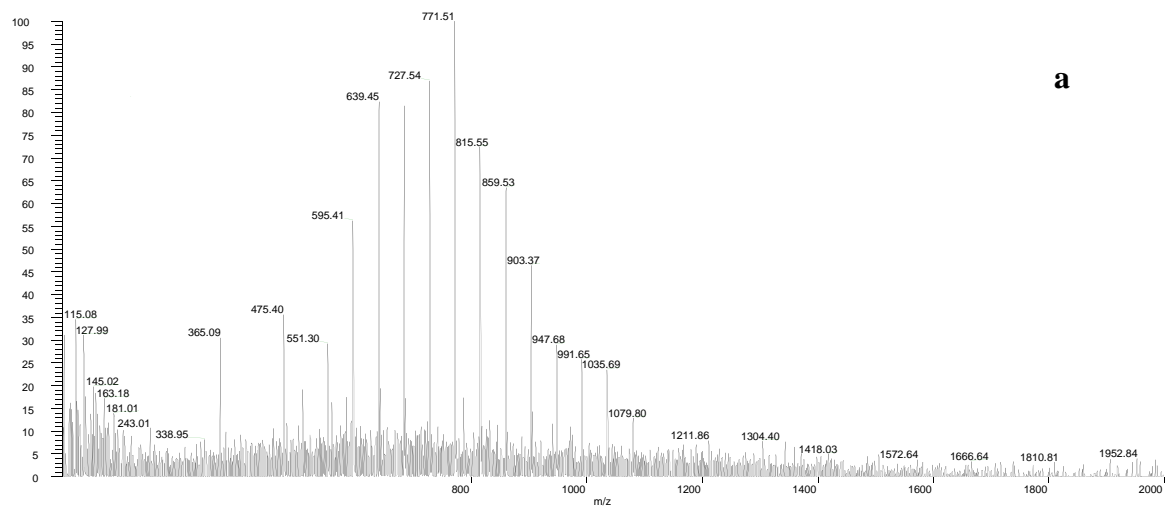
Figure 14: ESI-MS of the bio-oil water insoluble organic fraction before (a) and after hydrogenation with Ni-ZSM5 at 300°C (b).

CONCLUSIONS

XPS was successfully used to monitor the oxidation states of Co-NS during reduction (activation). A two-step reduction process was required in order to improve catalyst activation.

Ni based catalysts were able to convert guaiacol, vanillin, and pyrolysis bio-oil into hydrocarbons. A two-step hydrogenation process prevented coke formation. The organic bio-oil fraction could be effectively hydrocracked into smaller compounds for a subsequent second hydrogenation step. It is believed that using higher H_2 pressure greater conversions could be obtained.

Ni and Ru decorated NS were successfully prepared and characterized. The Ni-NS catalyst deoxygenated guaiacol and was shown to work to a limited extent, even with an extremely low Ni content of the catalyst relative to starting material. The Ni-NS have the potential to upgrade pyrolysis bio-oil. But further work is required to scale up the NS catalyst production, increase Ni loading on NS, and modify the reactor for subsequent work on using Ni-NS catalysts for bio-oil upgrading.

RECOMMENDATIONS

Based on our findings, Ni based catalysts work well for converting pyrolysis bio-oil into hydrocarbons. We have successfully prepared Ni-NS but at low levels for this proof of concept study. We have developed a range of tools to characterize the catalysts and assess its activation. The Ni-NS catalyst gave low conversions of guaiacol (model compound) to products, but the starting material/Ni ratio was 1000:1 which proved to be an effective catalyst. The next steps are to increase the Ni loading on Ni-NS catalysts and increase Ni-NS catalyst production for ongoing studies. We have found an issue with the current reactor setup which was low H_2 pressure (250 psi) and plan to increase to 750-1000 psi to drive the hydrogenation/HDO reactions, improve conversion yields and minimize coke formation.

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APPENDIX

The following are presentations that resulted from this research:

- Presentation 1: Yinglei Han, Armando G. McDonald, Dan Mottern (2013) Characterization of bio-oil produced from woody biomass fast pyrolysis. Western Forestry Graduate Research Symposium 2013, Oregon State University, Corvallis, OR, April 22-23, 2013.

- Poster 1: Alex Kengne, David McIlroy, Armando McDonald (2013) XPS study of a Fischer-Tropsch cobalt catalyst supported on silica nanosprings during reduction", presented at the 2013 symposium of the Pacific Northwest of the AVS (American Vacuum Society) held in Troutdale, Oregon, September 19 – 20, 2013.

- Poster 2: Alex Kengne, David McIlroy, Armando McDonald (2013) XPS study of a Fischer-Tropsch cobalt catalyst supported on silica nanosprings during reduction, presented at the University of Idaho during the 9th annual College of Science Student Research Exposition, November 8, 2013.

- Poster 3: Alex Kengne, David McIlroy, Armando McDonald (2013) "Reforming of sygas into higher order alkanes using a Fischer-Tropsch cobalt catalyst supported on silica nanosprings", was presented at the 2013 MRS (Materials Research Society) fall meeting, December 1 – 6, 2013, Boston, Massachusetts.