UPGRADING BIOMASS PYROLYSIS BIO-OIL TO RENEWABLE FUELS

Final Report





Armando McDonald and David McIlroy

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| Fast pyrolysis is a process that can convert woody biomass to a crude bio-oil (pyrolysis oil). However, some of these compounds contribute to bio-oil shelf life instability and difficulty in refining. Catalytic hydrodeoxygenation (HDO) of the bio-oil can upgrade the bio-oil into transportation fuels. Therefore, nickel (Ni) and ruthenium (Ru) catalysts supporting a novel nanomaterial, silica nanospring (NS) showed the best performance for HDO of phenol. In terms of bio-oil hydrotreatment, the bio-oil was fractionated by phase separation by addition of water to obtain a water-insoluble (WIS) and water-soluble (WS) fractions from the bio-oil. The WS of bio-oil can be upgraded into cycloalkanes of 30% wt. and alcohols of 18% wt. over Ni-NS and Ni(65%)/SiO ₂ -Al ₂ O ₃ catalyst. The WIS of bio-oil had been effectively cracked in methanol over Ni(65%)/SiO ₂ -Al ₂ O ₃ catalyst. A further step of HDO on the cracked oil had successfully deoxygenated the phenolics into cycloalkanes. All the produced alkanes and alcohols can be directly used as drop-in transportation fuels. Future work will focus on upscaling the process to a small pilot operation to fully assess these catalysts for producing biofuels. | | | | | |
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EXECUTIVE SUMMARY

Utilization of lignocellulosic biomass for renewable biofuels production is highly desirable for meeting transportation fuel needs. Among several conversion technologies, fast pyrolysis is considered the most promising due to a high yield liquid bio-oil readily produced at a relatively low cost. However, the bio-oil requires catalytic upgrading by hydrodeoxygenation (HDO) to deoxygenate the bio-oil components to green hydrocarbon fuels. This study aims to develop novel nanostructured catalysts with high activity and selectivity, metal decorated nanosprings (NS), for HDO treatment of bio-oil. Therefore, nickel (Ni) and ruthenium (Ru) decorated on a NS support were evaluated as HDO catalysts for phenol (a bio-oil model compound) upgrading and compared to conventional silica and alumina supports. HDO treatment of Douglas-fir bio-oil directly resulted in considerable coke formation and poor yields obtained. Therefore a strategy of bio-oil cleanup was required to minimize coke formation during HDO treatment. The bio-oil was fractionated by phase separation to obtain water-insoluble (WIS) and water-soluble (WS) fractions. The WS bio-oil fraction was readily HDO upgraded to cycloalkanes and alcohols with no coke formation. The WIS bio-oil fraction, comprising mainly of lignin oligomers, needed a hydrocracking step to reduce its molar mass and minimize coke formation prior to an HDO treatment. All the produced alkanes and alcohols can be directly used as drop-in transportation fuels. The NS based catalysts had lower Ni or Ru loadings and performed better than the conventionally supported catalysts. Future work will focus on (i) improving the NS based catalysts and (ii) upscaling the process to a small pilot operation to fully assess these catalysts for producing biofuels.

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]. For example, more than 3 million tons/yr of woody biomass is available in the Pacific Northwest alone and this can theoretically produce 5 million barrels/yr of pyrolysis bio-oils [3]. Mobile pyrolysis units can utilize biomass through conversion to bio-oil, reducing transport volumes by >70%, which can increase supply chain efficiencies and decrease transport costs by 30%. Therefore, there is a need to produce renewable fuels regionally in an efficient manner from underutilized biomass sources. Bio-oil cannot be used directly as a transportation fuel and requires catalytic upgrading by hydrodeoxygenation (HDO) into stable hydrocarbons which can be refined into various fuel grades (gasoline, jet fuel and diesel) [4].

The creation of new, highly efficient, catalysts (such as nanospring based catalysts) for upgrading crude bio-oil to drop-in fuels will be a significant step forward in reaching this goal. This will benefit the nation's energy security and independence by displacing petroleum imports. In addition, using biofuels will reduce the carbon footprint of transportation. The proposed project will have a large impact on the nation's economy, transportation and environment. The objective of this study was to develop an effective method for HDO of pyrolysis bio-oil. The bio-oil was fully characterized and fractionated by phase separation by addition of water to obtain water-insoluble (WIS) and water-soluble (WS) fractions from the bio-oil. Subsequently, the two separate fractions were investigated for their suitability for HDO treatment. The hydrocarbons products were characterized and discussed in term of the potential application as transportation fuels.

APPROACH AND METHODOLOGY

Catalyst Preparation

All the catalysts used in this study were prepared by using the wetness impregnation method [5]. NiCl₂· $6H_2O$ and RuCl₃· $6H_2O$ were used as Ni and Ru precursors, respectively. The applied catalyst supports were silica gel (40-63 μ m (#1) and 210-500 μ m (#2), Fisher Chemical), alumina (Υ -Al₂O₃, 74-177 μ m, Fisher Chemical) and silica nanosprings (NS). Chemical vapor deposition (CVD) method was applied for synthesizing NS onto an aluminum foil substrate using flow furnace technique [6]. After the NS mats were formed, they were easily peeled off from the foil to give free standing NS. The desire amounts of precursors were dissolved in water (100 mg/mL for 20% Ni, 400 mg/mL for 50% Ni, 15 mg/mL for 5% Ru) in a flask (10 mL) and then the silica and alumina gel support (1 g) were introduced to the solution and the mixture was ultrasonicated for 4 hours at room temperature. For NS (200 mg), the metal precursors were dissolved in ethanol (10 mL, 25 mg/mL for 20% Ni, 100 mg/mL for 50% Ni, 3 mg/mL for 5% Ru, 6.4 mg/mL for 10% Ru, 14.3 mg/mL for 20% Ru) due to the NS hydrophobicity and again the mixture ultrasonicated. The solvent was then evaporated at room temperature and the samples were dried overnight at 104°C. The dried catalysts were ground in a mortar and pestle and then calcined in air for 4 hours (450°C for Ni catalysts and 350°C for Ru catalysts). The calcined catalyst materials were reduced in a tubular quartz reactor (10 mm $\emptyset \times 300$ mm) by heating from room temperature to desired temperature (400°C for Ni catalysts and 300°C for Ru catalysts) under a H_2 flow (60 mL/min). This reduction step was maintained for 4 hours. After cooling to room temperature, the reduced sample was transferred to the reactor for HDO.

Bio-oil Production and Fractionation

The pyrolysis bio-oil was produced by conventional pyrolysis of Douglas-fir sawdust (20 kg h^{-1} , <5 mm) in a 100 mm diameter auger pyrolyzer (mobile in-house ½ ton d^{-1} Advanced BioRefinery Inc (ABRI) pyrolysis unit) at 450-500°C. The pyrolysis vapors were trapped using a series of five tube-shell condensers. The bio-oil was collected over a 2 hour operational period once the pyrolysis was at steady state, and then combined, thoroughly mixed, and stored in a freezer at -20°C. Yield of bio-oil was 50% based on original wood dry

weight basis. Bio-oil (20 g, batches) was fractionated by dispersing the bio-oil in water (40 ml), sonicating for 30 min, and then centrifuged at 3000 rpm for 60 min. Once separation was achieved, gravimetric yields of the top aqueous water soluble (WS) layer and bottom water insoluble (WIS) layer were $79.1\pm 0.8\%$ and $21.9\pm 0.5\%$, respectively.

Hydrogenation on Bio-oil WS and WIS Fractions

The top aqueous WS layer was then utilized for subsequent hydrogenation (HYD) using a commercial Ni/SiO₂-Al₂O₃ (65% Ni loading, Alfa Aesar) or Ni(20%)-NS catalyst. The hydrogenation reaction was performed with a stirred 300 mL batch reactor (Parr model 4564). The bio-oil WS fraction (30 g) and the catalyst (1.5 g) were introduced into the reactor, closed, flushed with H₂ and then pressurized with H₂ to 2.8 MPa (400 psi). The reaction mixture was heated to 300°C and stirred at 500 rpm for 12 hours.

The water-insoluble (WIS) bio-oil bottom layer (10 g) was dispersed in methanol (20 g) and hydrocracked at 200°C using a Ni(65%)/SiO₂-Al₂O₃ (Alfa Aesar) catalyst with 600 psi of H₂ pressure for 10 hours. The catalyst to WIS bio-oil weight ratio was 1:20. The hydro-cracked WIS oil fraction was concentrated using a rotary evaporator to remove methanol. The WIS cracked oil was then mixed with n-hexane as solvent for HDO by using Ni/SiO₂-Al₂O₃ or Ni(20%)-NS catalyst at 250°C and 4.1 MPa (600 psi) of H₂ pressure for 10 hours.

Product Characterization by GC-MS

GC-MS (FOCUS-ISQ, ThermoScientific) was used to characterize the volatile components in the bio-oil fractions (1.0 mg of bio-oil sample was solubilized in 1 mL of CH_2Cl_2 containing anthrancene (0.05 mg mL⁻¹) as internal standard), where the separation was achieved using a RTx-5MS capillary column (30 m × 0.25 mm Ø, Restek) using a temperature program of 40°C (hold for 2 min) to 250°C (10 min) at 5°C min⁻¹. Compounds were identified using known standards, mass spectral library matching (National Institute of Standards and Technology (NIST) 2008), and by their mass spectra. The HDO reaction over each catalyst was carried out twice and the corresponding calculated values were the average for both reactions. Conversion and selectivity (degree of deoxygenation, DOD) were calculated on the basis of the number of carbon moles defined as follows:

TranLIVE

$$Conversion = \left(1 - \frac{\text{Moles of residual phenol}}{\text{Moles of initial phenol}}\right) \times 100\%$$
$$DOD = \left(1 - \frac{\text{Oxygen content in the final organic compounds}}{\text{Total oxygen content in the initial phenol}}\right) \times 100\%$$

The bio-oil WS layer was characterized by HPLC using a Rezex ROA organic acid column (7.8 × 30 cm, Phenomenex) and a Waters HPLC (Waters, Milford, MA) equipped with a differential refractive index detector (ERC-5710, ERMA), on elution with 0.005 N aqueous sulfuric acid (0.5 mL min-1) at 65°C. In addition, the non-volatile compounds in the bio-oil were analyzed by ESI-MS. Bio-oil samples (1 mg) were dissolved in methanol containing 1% acetic acid (1 mL) and directly analyzed in both positive and negative ion electrospray ionization-mass spectrometry (ESI-MS, m/z 90-2000) on a Finnigan LCQ-Deca instrument (Thermoquest, San Jose, CA) at a flow rate of 10 μ L/min. Data analysis was based on the calculation of number average molar mass (M_n) as M_n= Σ MiNi/ Σ Ni and weight average molar mass (M_w) as M_w= Σ Mi²Ni/ Σ MiNi with Mi as m/z and Ni as intensity of ions [7].

FINDINGS; CONCLUSIONS; RECOMMENDATIONS

Compositions of Bio-oil Identified by GC-MS and ESI-MS

Bio-oils are very complex mixtures of different chemical species derived from depolymerization and fragmentation of biomass main components, covering a wide range of molecular weights [1,7,8]. The bio-oil obtained from Douglas-fir fast pyrolysis in this study was characterized by GC-MS and products listed in Table 1. It should be noted that there is a high proportion of oxygenated compounds in the pyrolysis oil. These oxygen-containing groups were mainly composed by carboxylic acid, ester, aldehydes and ketones, aliphatic and aromatic alcohols, phenols, and methoxylated phenols. In addition, compounds with carbon double bonds were also identified, such as vinyl-guaiacol and propenyl-guaiacols, that are reactive and can easily polymerize at room temperature. In terms of the amount of compounds in the bio-oil, acetic acid (2.4%), furfural (4.7%), cresol (3.4%), phenols (6.4%), guaracols (19%) and oxygenated acids (7.6%) represented the major components of the pyrolysis bio-oil. The phenolic compounds were derived from lignin pyrolysis. Furan derivatives were derived from hemicellulose and cellulose pyrolysis. However, no levoglucosan was detected in the bio-oil by GC-MS, which is generated from cellulose pyrolysis. However, HPLC analysis showed the presence of acetic acid, levoglucosan and furfural. In view of these identified compounds, those with carbon numbers ranging from C₄ to C_{12} can be transformed to hydrocarbon fuels if effective deoxygenation is performed [1].

ESI-MS (positive and negative ion) was used to characterize the oligomeric components in bio-oil (Figure 1) [7]. However, positive ion spectrum only shows part of the compounds in bio-oil while most oligomers were characterized by the negative ion MS. Nonetheless, the peak clusters in positive ion spectrum confirmed the existence of most of those compounds already identified by GC-MS, such as cresol ($[M+H]^+ = 109 \text{ m/z}$), guaiacol ($[M+H]^+ = 123 \text{ m/z}$), methyl-guaiacol ($[M+H]^+ = 137 \text{ m/z}$), ethyl-guaiacol ($[M+H]^+ = 151 \text{ m/z}$), propenyl-guaiacol ($[M+H]^+ = 165 \text{ m/z}$) (Figure 1a). In the negative ion ESI-MS (Figure 1b), oligomers with molecular weight ranging from 400 to 2000 g/mol were identified which cannot be detected by GC-MS. The M_n and M_w calculated from negative ion ESI-MS were 691 and 1197 g/mol, respectively.



Figure 1: Positive and negative ion ESI-MS of Douglas-fir fast pyrolysis bio-oil.

| Retention time | Identified compounds | Conc. | \mathbf{M}^+ |
|----------------|--|--------|----------------|
| (min) | | (mg/g) | (m/z) |
| 2.29 | acetic acid | 24.3 | 84 |
| 3.68 | ethylene glycol monoacetate | 10.6 | 104 |
| 3.87 | butanedial | 6.7 | 86 |
| 4.05 | 2-ethylbutyl acetate | 18.5 | 144 |
| 4.92 | furfural | 19.7 | 96 |
| 5.45 | furfural alcohol | 12.6 | 98 |
| 5.81 | 2-propanone,1-hydroxy-acetate | 4.9 | 116 |
| 6.25 | styrene | 3.8 | 104 |
| 6.71 | 2-methyl-2-cyclopentenone | 4.2 | 96 |
| 6.97 | 2(5H)-furanone | 8.5 | 84 |
| 7.19 | 1,2-cyclopentanedione | 9.6 | 98 |
| 8.29 | 5-methyl-2-furaldehyde | 6.6 | 110 |
| 8.86 | phenol | 12.7 | 94 |
| 10.10 | 2-hydroxy-3-methyl-2-cyclopenten-1-one | 13.7 | 112 |
| 10.94 | m-cresol | 11.4 | 108 |
| 11.56 | p-cresol | 17.4 | 108 |
| 11.89 | guaiacol | 31.9 | 124 |
| 13.61 | 2,3-dimethyl-phenol | 14.3 | 122 |
| 14.85 | 4-methyl-guaiacol | 39.4 | 138 |
| 15.16 | 1,2-benzenediol | 15.7 | 110 |
| 16.14 | 5-ethyl-m-cresol | 5.1 | 136 |
| 17.23 | 4-ethyl-guaiacol | 17.4 | 152 |
| 17.64 | 4-methyl-1,2-benzenediol | 15.7 | 124 |
| 18.18 | 4-vinyl-guaiacol | 27.6 | 150 |
| 19.31 | 4-(2-propenyl)-guaiacol | 14.9 | 164 |
| 19.56 | 4-propyl-guaiacol | 5.9 | 166 |
| 20.45 | vanillin | 6.4 | 152 |
| 20.62 | 4-(1-propenyl)-(E)-guaiacol | 10.8 | 164 |
| 21.66 | 4-(1-propenyl)-(Z)-guaiacol | 41.2 | 164 |
| 22.61 | 4-hydroxy-3-methoxy-acetophenone | 8.3 | 166 |
| 23.66 | guaiacylacetone | 6.8 | 180 |
| 26.35 | 4-(ethoxymethyl)-2-methoxyphenol | 5.9 | 182 |
| 28.22 | 3-(4-hydroxy-3-methoxyphenyl)-propenal | 12.9 | 178 |
| 35.90 | cis-vaccenic acid | 27.8 | 282 |
| 36.54 | 13a-methyl-13-vinyl-podocarp-8-(14)-en-15-al | 9.1 | 286 |
| 37.50 | pimara-7,15-dien-3-one | 7.6 | 286 |
| 38.86 | 4-methoxy-2-hydroxystilbene | 25.9 | 226 |
| e | Ethyl pimarate | 13.9 | 330 |
| 41.07 | 13-isopropyl-podocarpa-8,11,13-trien-15-oic acid | 23.8 | 300 |
| 41.69 | abietic acid | 10.6 | 302 |

Table 1: Products in Douglas-fir Pyrolysis Bio-oil Identified by GC-MS

Upgrading Bio-oil

Direct hydrodeoxygenation (HDO) on raw bio-oil easily led to coke formation, which deactivated the catalyst. Therefore, the bio-oil was first separated into WS and WIS fractions (Figure 2). The reason for this process is that the WIS bio-oil was recognized as the main component for coke formation and has to be separated for further cracking before HDO. Consequently, two kinds of HDO on bio-oil was carried out: i) bio-oil WS fraction HDO, and ii) pyrolytic lignin WIS fraction hydrocracking and HDO.



Figure 2: Experimental approach to fractionate and HDO treat bio-oil.

The bio-oil WS fraction was HDO treated to give a top organic layer (17% yield) and an aqueous bottom layer (Figure 3). The composition of the organic layer was then characterized by GC-MS, which shows many volatile alkane products produced after HDO at 300° C and 2.8 MPa of H₂. Direct comparison of the identified compounds before and after HDO are given in Table 2. Results indicate the main products in the organic layer after HDO were phenol (7.4%), cyclohexane (4.8%), pentanol (4.0%), hexanol (4.0%), and methyl cyclohexane (2.1%). Alkanes including cyclohexane and methyl-cyclohexane were derived from phenol and methoxylated phenols after hydrogenation followed by dehydration. The products ranged from C₆ to C₉ and are partially in the range of gasoline and jet fuels.



Figure 3: GC-MS chromatograms of the Douglas-fir (a) WS of bio-oil and (b) HDO products in organic layer.

| Retention | Identified compounds | Area % of peaks in GC-MS | | \mathbf{M}^+ |
|------------|--|--------------------------|-----------|----------------|
| time (min) | lacitimed compounds | Before HDO | After HDO | (m/z) |
| 2.22 | cyclohexane | | 4.81 | 84 |
| 2.29 | tetrahydro-2-metylfuran | | 2.10 | 86 |
| 2.30 | acetic acid | 11.68 | | 60 |
| 2.46 | 2- pentanone | | 1.06 | 86 |
| 2.55 | 3-pentanone | | 1.46 | 86 |
| 2.65 | tetrahydropyran | | 1.28 | 86 |
| 2.84 | methyl-cyclohexane | | 2.11 | 98 |
| 2.98 | ethyl-cyclopentane | | 1.02 | 98 |
| 3.07 | 2-methyl-butanol | | 1.01 | 88 |
| 3.51 | 1-pentanol | | 4.02 | 88 |
| 3.66 | 1-hydroxy-2-butanone | 1.2 | | 88 |
| 3.72 | 1,2-ethanediol-momacetate | 2.74 | | 104 |
| 3.83 | 2-methyl-3-pentanone | | 1.9 | 100 |
| 3.90 | butanedial | 2.74 | | 86 |
| 3.91 | 2-hexanone | | 0.83 | 100 |
| 4.40 | n-butyl acetate | | 0.7 | 116 |
| 4.73 | ethylcyclohexane | | 2.59 | 112 |
| 4.95 | 2-methyl-cyclopentanone | | 1.51 | 98 |
| 4.98 | 2,5-dimethyl-furan | 3.14 | | 96 |
| 5.61 | 1-hexanol | | 3.97 | 102 |
| 5.93 | 1-methyl-2 propylcyclopetane | | 1.12 | 126 |
| 6.04 | 5-methyl-3-hexanone | | 1.11 | 114 |
| 7.01 | 2-(5H)-furanone | 3.7 | | 84 |
| 7.09 | propylcyclohexane | | 1.61 | 126 |
| 7.20 | butylcyclopentane | | 1.26 | 126 |
| 8.37 | 5-methyl-2-furaldehyde | 1.55 | | 110 |
| 8.72 | phenol | 1.35 | 7.42 | 94 |
| 9.95 | n-butylcyclohexane | | 0.48 | 140 |
| 10.19 | 2-hydroxy-3-methyl-2-cyclopenten-1-one | 4.24 | | 112 |
| 10.83 | o-cresol | 1.23 | 1.47 | 108 |
| 11.48 | p-cresol | 1.39 | 1.11 | 108 |
| 11.97 | guaiacol | 5.09 | | 124 |
| 13.51 | 3,4-xylenol | | 1.45 | 122 |
| 14.74 | 2-methoxy-p-cresol | | 0.86 | 138 |
| 14.94 | 4-methyl-guaiacol | 4.22 | | 138 |
| 15.24 | 1,2-benzenediol | 4.94 | | 110 |
| 17.11 | p-ethyl-guaiacol | 1.95 | 0.64 | 152 |
| 18.86 | p-ethenyl-guaiacol | 0.98 | | 150 |
| 19.44 | p-propylguaiacol | | 0.6 | 166 |
| 20.54 | vanillin | 1.26 | | 152 |
| 22.40 | propenyl-guaiacol | 3.21 | | 164 |
| 24.84 | o-cyclohexyl-phenol | | 0.88 | 176 |
| 25.79 | p-cyclohexyl-phenol | | 0.42 | 176 |

 Table 2: Identified Compounds from Douglas-fir Bio-oil WS Fraction Before and After HDO

It is known that pyrolysis bio-oil contains about 20% pyrolytic lignin (WIS fraction) [9,10]. These oligomers can easily block catalyst active sites during high temperature HDO (~300°C) to form coke. The bio-oil WIS fraction is predominately oligomeric pyrolytic lignin with minor amounts of monomeric phenolics and furans. The purpose of hydrocracking (HC) the bio-oil WIS fraction was to decrease the pyrolytic lignin molecular weight. Preliminary tests using Ni(65%)/SiO₂-Al₂O₃ catalyst for HC pyrolytic lignin into small phenolics was shown to work successfully. ESI-MS was employed to characterize the oligomeric material in the bio-oil WIS fraction before and after HC. Figure 4 (top) is an ESI-MS of the WIS fraction revealing the presence of oligomers between 400 and 2000 g/mol. More specifically, the ESI-MS showed peak clusters between 90 and 400 g/mol (monomers and dimers) and >400 g/mol (>trimers). After hydrocracking, the bio-oil HC-WIS fraction (Figure 4 bottom) showed the peaks >400 g/mol disappeared showing the presence of monomers and dimers. These results clearly show that hydrocracking of the bio-oil WIS fraction was successfully achieved. A proposed mechanism of lignin hydrocracking is shown in Figure 5.



Figure 4: Negative ion ESI-MS characterization on Douglas-fir bio-oil (top) WIS fraction before and (bottom) after hydrocracking (HC-WIS).



Figure 5: Proposed catalytic hydrocracking mechanisms in pyrolytic lignin.

The hydrocracked Douglas-fir bio-oil WIS fraction (HC-WIS) was then subjected to HDO treatment over Ni(65%)/SiO₂-Al₂O₃ or Ni(20%)-NS catalysts. Figure 6 shows the GC-MS chromatograms of Douglas-fir bio-oil HC-WIS fraction before and after HDO. More phenolics and furans were detected in the HC-WIS but these almost completely disappeared after the HDO reaction. As shown in Figure 6b, the main HC-WIS-HDO products were cycloalkanes and cyclohexanols. These alkanes can be directly employed as green gasoline. Most interestingly, there were di-cycloalkanes produced as well. These compounds were likely derived from aromatic ring condensation as observed in the products from HDO of phenol. These compounds have higher boiling points. In summary, it can be concluded that the water insoluble bio-oil can also be a promising feedstock for diesel or jet fuel production.



Figure 6: GC-MS chromatograms of Douglas-fir bio-oil HC-WIS (a) before and (b) after HDO treatment.

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APPENDIX

Publications, Presentations, Posters:

Oral presentations:

- 1. Armando McDonald, Mark Coleman (2014) "Utilization of Forest Biomass through Mobile Fast Pyrolysis" presented at the Northwest Wood Energy Team Forum held in Stevenson, WA, May 7th.
- Yinglei Han, Alexis Fouetio Kengne (2014) "Pyrolysis Bio-oil Upgrading to Renewable Fuels" NIATT Advisory Board Meeting, Best Western Inn, Moscow ID, April 30th.
- Alexis Fouetio Kengne, David McIlroy, Armando McDonald (2014) "XPS Study of a Cobalt Fisher-Tropsch Catalyst Supported on Silica Nanosprings During Reduction" Technical Research Exhibition (TRE), National Society Black Engineers (NSBE) National Convention, Convention Center, Nashville, TN March 27th.
- Alexis Fouetio Kengne, David McIlroy, Armando McDonald (2014) "XPS Study of a Cobalt Fisher-Tropsch Catalyst Supported on Silica Nanosprings During Reduction" 56th Annual Meeting of the Idaho Academy of Science (IAS), Best Western Inn, Moscow ID, March 20th.
- Yinglei Han, Armando McDonald, David McIlroy (2014) "Upgrading wood pyrolysis oil by hydrogenation using nanocatalysts to green transportation fuels" 2014 International Union of Forest Research Organizations World Congress, Salt lake City, October 6-10th.
- Alexis Fouetio Kengne (2014) "Surface Chemistry of Hierarchical Nanosprings for Sensing and Catalysis" Ph.D defense, University of Idaho, Moscow ID, September 11th.
- Yinglei Han (2014) "Upgrading of Pyrolysis Bio-oil to Renewable Fuels by Hydrodeoxygenation", M.S. defense, University of Idaho, Moscow ID, November 24th.

Poster presentations:

1. Armando McDonald, Randy Brooks, Mark Coleman (2014) "Utilization of Forest Biomass through Mobile Fast Pyrolysis" presented at the Washington State Department of Natural Resources-Mobile Pyrolysis Demonstration, at Bingen, WA, May 8-9th.

Written documents:

- 1. Alexis Fouetio Kengne (2014) "Surface Chemistry of Hierarchical Nanosprings for Sensing and Catalysis" Ph.D dissertation, University of Idaho, Moscow ID, December.
- 2. Yinglei Han (2014) "Upgrading of Pyrolysis Bio-oil to Renewable Fuels by Hydrodeoxygenation", M.S. thesis, University of Idaho, Moscow ID, December.