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1977 - 2017

Effect of Blended Feedstock on Pyrolysis Oil Composition

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ABSTRACT

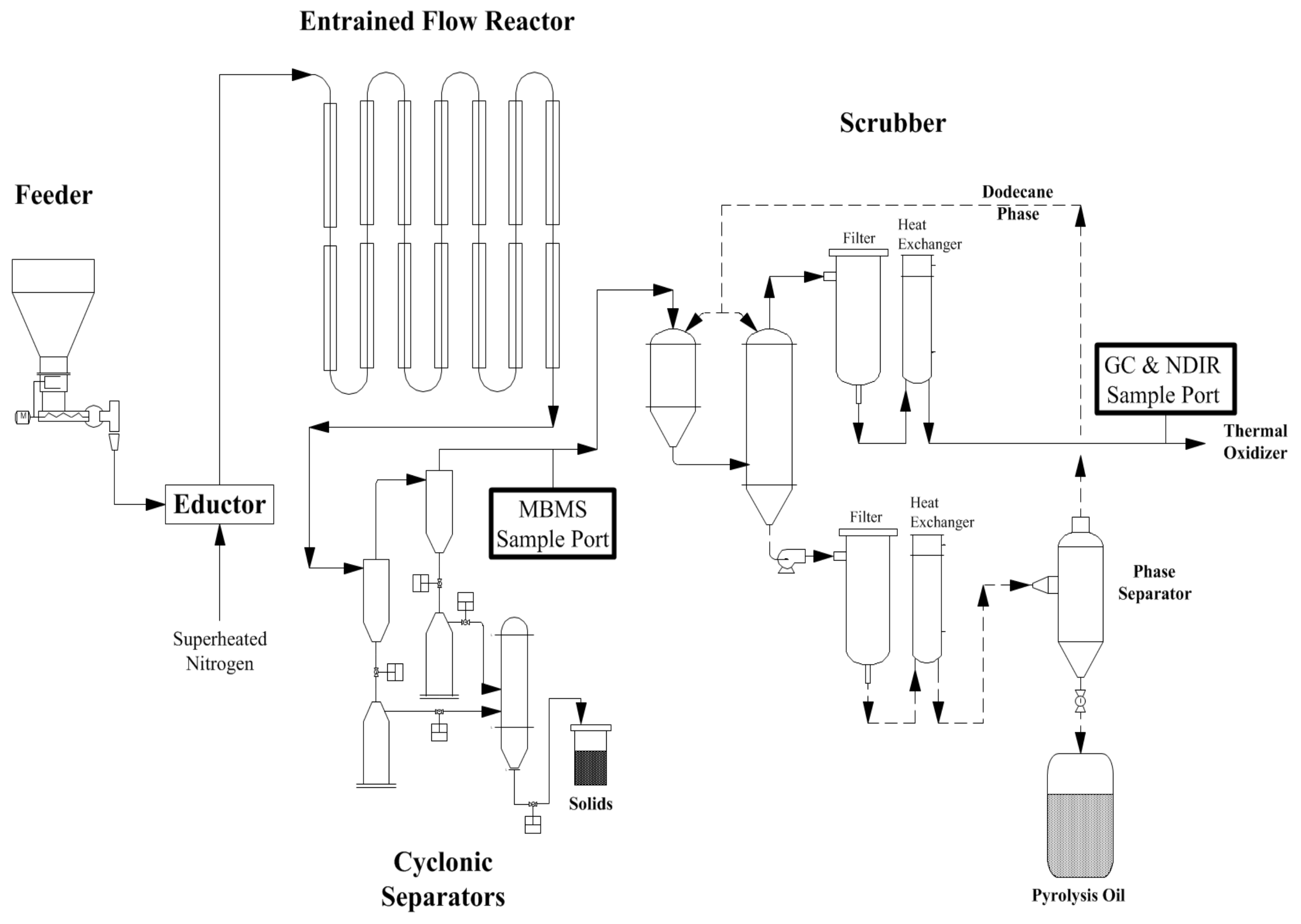
Current techno-economic analysis results indicate biomass feedstock cost represents 27% of the overall minimum fuel selling price for biofuels produced from fast pyrolysis followed by hydrotreating (hydrodeoxygenation, HDO) [1]. As a result, blended feedstocks have been proposed as a way to both reduce cost as well as tailor key chemistry for improved fuel quality. For this study, two feedstocks were provided by Idaho National Laboratory (INL). Both were pyrolyzed and collected under the same conditions in the National Renewable Energy Laboratory's (NREL) Thermochemical Process Development Unit (TCPDU). The resulting oil properties were then analyzed and characterized for statistical differences.

[1] Jones, Susanne, et al. NREL/TP-5100-61178. 2013.

APPROACH

FAST PYROLYSIS OPERATIONS IN THE TCPDU

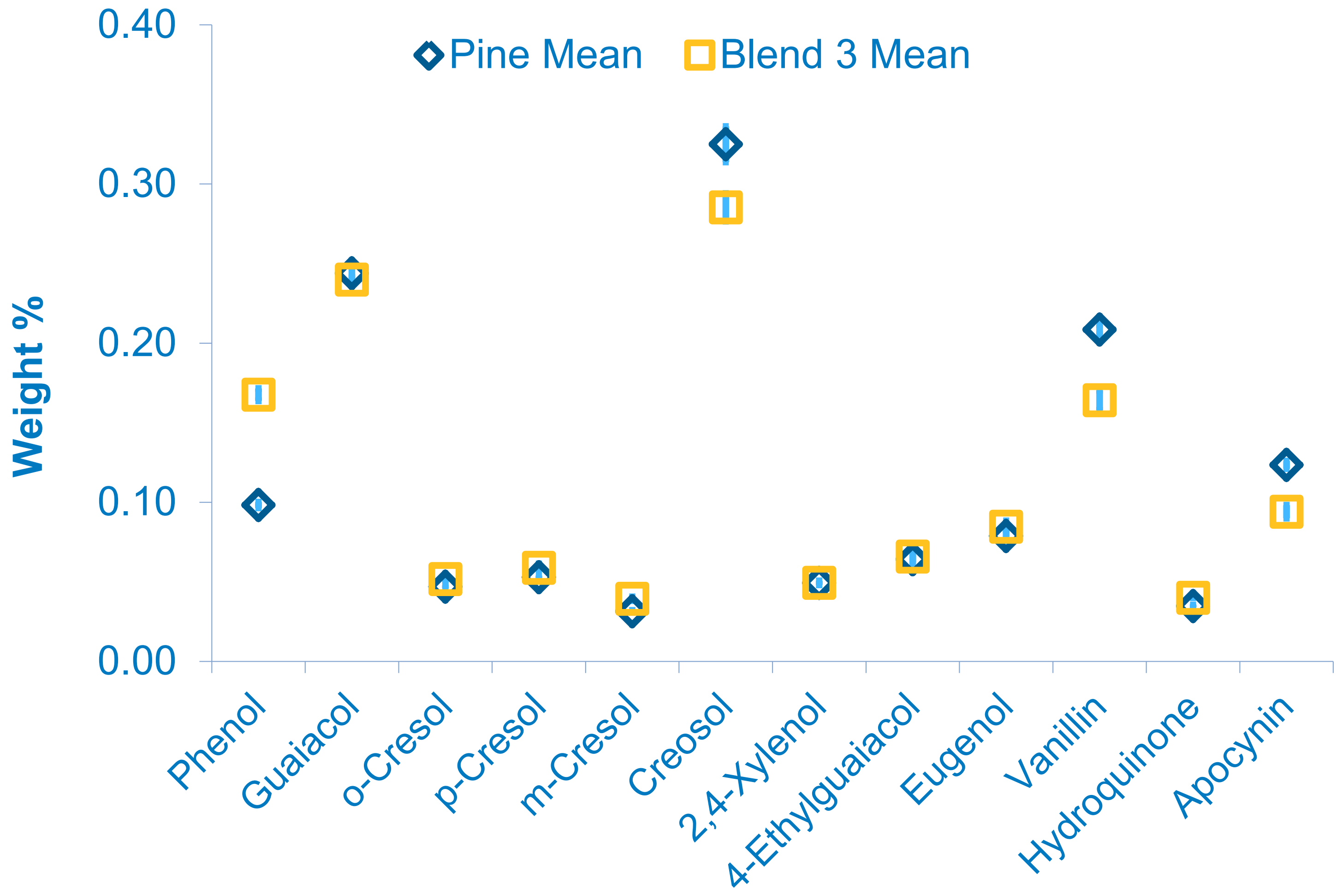
When configured for pyrolysis, the TCPDU consists of the following unit operations: feed transport system; entrained flow reactor; solids removal and collection; and liquid condensation, filtration, and collection. These operations are shown in the process flow diagram below for reference. Clean Pine and a low-cost "Blend 3" (comprised of 60% air-classified Forest Residues, 30% Clean Pine, and 10% Hybrid Poplar), were pyrolyzed at a feed rate and entrainment nitrogen flow rate of 15 kg/h each. The entrained flow pyrolysis reactor was controlled to an internal temperature of 500°C with a residence time of ~ 3 sec, while the solids removal and transfer piping were held at 400°C before quench. A molecular beam mass spectrometer (MBMS) provided real-time feedback on the hot pyrolysis vapors produced from each feedstock, while gas chromatographs provided characterization of the non-condensable tail gas stream.



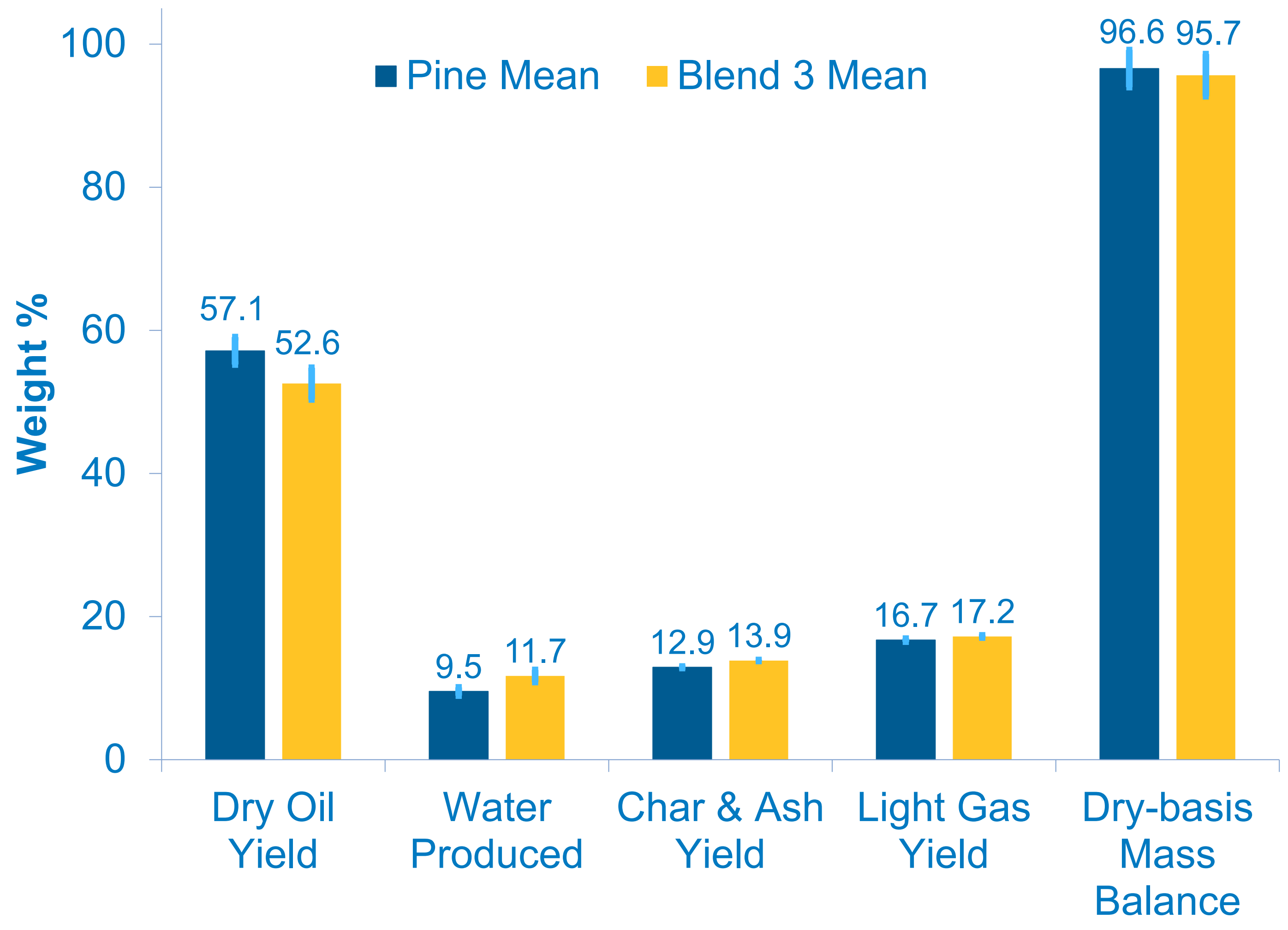
PYROLYSIS OIL ANALYSIS METHODS

The pyrolysis oils were fully characterized using a variety of analysis techniques. The oil was analyzed using an ASTM or published Laboratory Analytical Procedure (LAP). For characterizations without a published method, the current best NREL technique was used. To summarize, the oils were analyzed for the following properties:

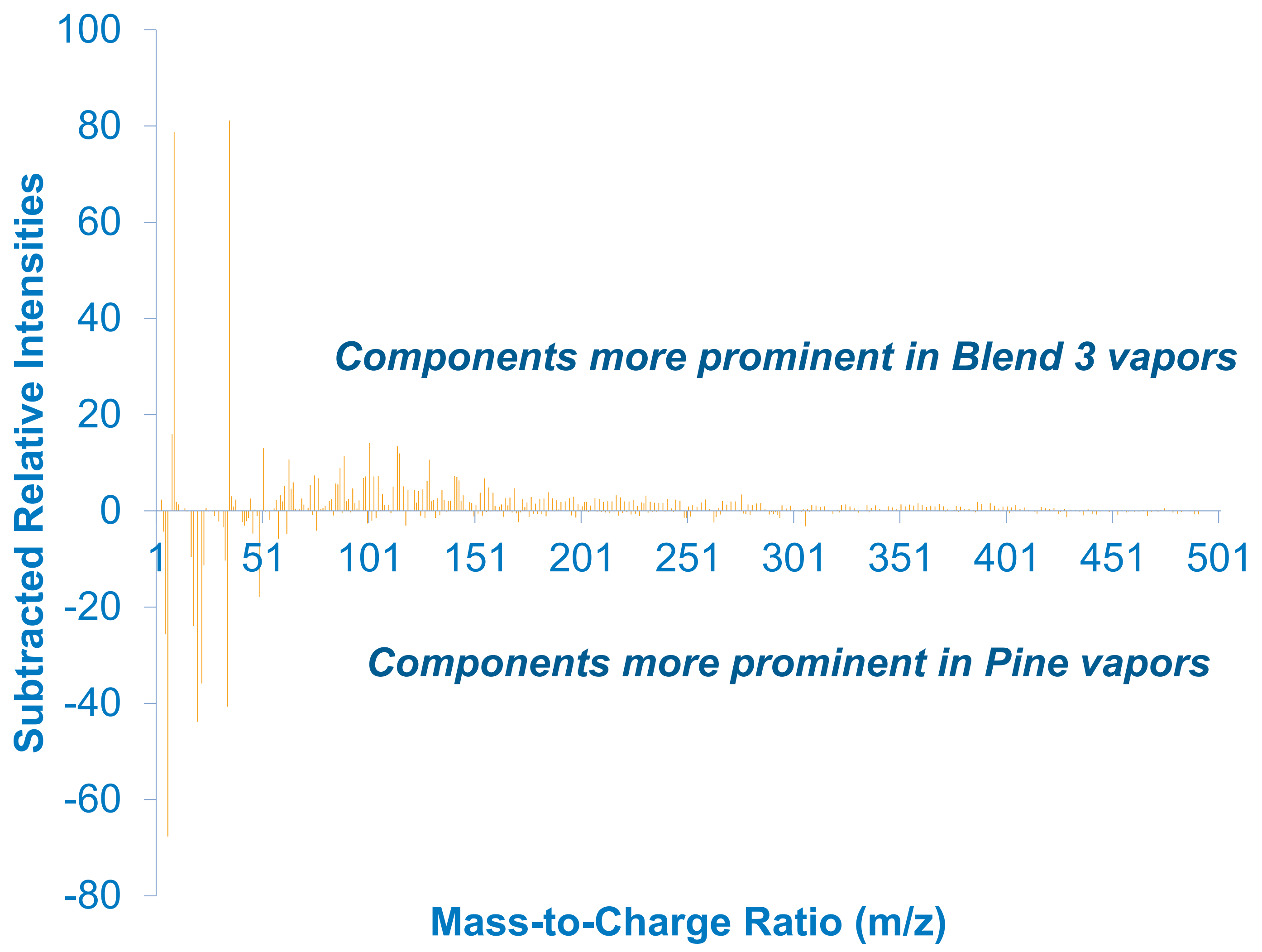
- Density
- Ash Content
- Proximate
- Water content by Karl Fischer
- Total Acid Number (TAN)
- Volatile oxygenate components and concentrations, including dodecane, by GC-MS
- Functional groups by ^{13}C-NMR
- Hydroxyl groups by ^{31}P-NMR
- Heating Value
- Ultimate
- Sulfur
- Insoluble Solids
- Carbonyl content by titration
- Molecular weight by Gel Permeation Chromatography (GPC)
- Viscosity/Aging



Lignin-derived compounds in pyrolysis oil by GC-MS. Phenol, creosol, vanillin, and apocynin are statistically different between the two feedstocks..



Yields of pyrolysis products and mass balance on dry basis. Blend 3 produces more water, while char and gas yields show little difference between the two feedstocks.



Subtracted MBMS spectrum (Blend 3 minus Pine) of the hot pyrolysis vapors. Middle-weight compounds are likely from the hybrid poplar component of Blend 3.

FINDINGS

MASS BALANCE AND YIELD CALCULATIONS

Mass balances were calculated on a dry-biomass basis from operational data collected from the Pine and Blend 3 runs. These yield calculations subtract the moisture that enters the process with the biomass (measured by Karl-Fischer analysis) and separate the oil yield into "dry" oil and produced water, using the Karl-Fischer water analysis of the final pyrolysis oil product.

STATISTICAL ANALYSIS

Statistical analysis was performed on all data according to the Student's t-Test, using the two-sample approach and assuming equal variances. Confidence intervals of 95% were calculated for each sample. Statistically-significant differences for each property were determined using three criteria: the result of the t-test, a substantial quantity of the property itself (i.e. larger than trace amounts were present), and the difference between the two means had to be significant compared to the baseline value (Pine).

RESULTS

In general, Pine and Blend 3 behaved very similarly, as expected since a large percentage of the blend is derived from two sources of pine. The oil, light gas, and char properties in many cases were indistinguishable between the two feedstocks according to the three selection criteria outlined above. The following were determined to be statistically different from each other for Pine and Blend 3:

Yield Calculations
- Water Produced
- Dry Oil Yield

Oil Properties
- Karl-Fischer Moisture
- Hydrogen (moisture-free)

Oil Properties by ^{13}CNMR
- Aliphatic C-O
- Levoglucosan (total)

N2-free Light Gas Analysis:
- Hydrogen
- Carbon dioxide
- Ethyne

Oil Properties by GC-MS:
- Phenol
- Creosol
- Vanillin
- Apocynin
- Glycolaldehyde
- Acetic Acid
- Propanoic acid
- 2-Cyclopenten-1-one
- Furfural
- 5-Hydroxymethylfurfural
- Levoglucosan

The dry oil yield for Blend 3 was slightly lower than that for Pine, and the water produced from pyrolysis reactions was slightly higher. The techno-economic analysis into which these numbers feed is especially sensitive to the dry oil yield; therefore, the lower Blend 3 yields will negatively impact the final minimum fuel selling price (MFSP).

Of note, carbon dioxide in the tail gas for Blend 3 was higher than that for Pine, which is consistent with the higher water production and lower dry oil yield. Combined with the higher concentrations in the Blend 3 GC-MS data for the smaller molecules associated with secondary pyrolysis reactions, namely phenol, acetic acid, and glycolaldehyde, it could indicate that Blend 3 is slightly more reactive than Pine during the pyrolysis process.

MBMS spectra of the hot pyrolysis vapors are very similar, with the middle-weight compounds being more prominent in the Blend 3 vapors. Comparison of these spectra with pyrolysis of hybrid poplar at the same conditions indicate these middle-weight components likely originate from the hybrid poplar fraction of the blended feedstock.

FUTURE WORK

While initial HDO screening experiments suggested that pine-derived and blend-derived pyrolysis oil could be upgraded economically, later tests revealed that HDO catalyst lifetimes were too short to be practical. As the catalyst was originally developed using an oak-derived pyrolysis oil, additional analyses into the minor differences between these pyrolysis oils and their potential role in the catalyst deactivation will be investigated in conjunction with Pacific Northwest National Laboratory (PNNL).

This work was funded through the Department of Energy's Bioenergy Technology Office

NREL is a national laboratory of the U. S. Department of Energy, Office of Energy Efficiency and Renewable Energy, operated by the Alliance for Sustainable Energy, LLC.

tcBiomass2017
Chicago, Illinois
September 19 - 21
NREL/PO-5100-70131