

FINAL REPORT

University of Maine and Marine Engine Testing and Emissions Laboratory (METEL) Led by Maine Maritime Academy

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1. Overview

The replacement of marine fuels with renewable biofuel has two immediate benefits: the reduction of fossil fuel dependency and the significant reduction, or even elimination, of sulfur-related pollution in ports emanating from vessels combusting high-sulfur fuels. At the University of Maine (UMaine), two processes have been developed for converting biomass into low-oxygen content fuels. These processes directly address the challenge of removing oxygen from the biomass while maintaining relatively high oil yields during chemical conversion. The overarching goal of this research was to develop, produce and evaluate marine diesel fuels that can replace bunker fuel based on UMaine's unique biomass-to-transportation fuel technologies.

2. Introduction

The significant challenge in converting biomass into a transportation fuel is the removal of oxygen which can affect both the stability of the fuel in addition to its compatibility with petroleum derived fuels and infrastructure. The University of Maine is developing two transformative chemical pathways to convert biomass into crude oils that are compatible with petroleum transportation fuels. These oils are highly stable and have oxygen contents ranging from 1-10 wt%. In the first pathway, called Thermal DeOxygenation (TDO), calcium salts of biomass-derived mixed organic acids can produce a hydrocarbon oil at high yields without catalysts, hydrogen or high pressures. Pyrolytic decomposition of the mixed organic acid salts produces a hydrocarbon oil which is almost devoid of oxygen and at bench scale, the yield has been demonstrated at 80% of theoretical based on organic acids or a calculated 56% of theoretical yield based on both acid hydrolysis of cellulose and TDO. It is possible to upgrade TDO oil, and fractionate it similarly to petroleum fuels, and UMaine has demonstrated that we can meet most of the specifications for jet fuels and diesel fuels with the appropriate fractions. UMaine and Maine Maritime Academy have been determining what blending levels are possible for use in diesel applications.

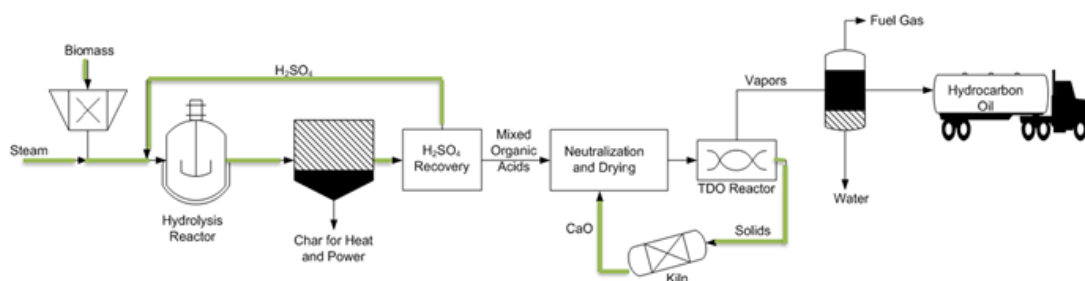


Figure 1. Conceptual process diagram for UMaine's Thermal DeOxygenation (TDO) process which includes acid hydrolysis/dehydration, TDO, and recycle of inorganics.

A second biomass-to-transportation fuels technology is called Formate-Assisted Pyrolysis (FAsP) and is based on the co-pyrolysis of biomass with calcium formate salt resulting in low-oxygen oil. The presence of reductive gases like CO and H₂ during pyrolysis may play an important role in simultaneously removing oxygen and eliminating unstable pyrolysis intermediates. This unique pyrolysis chemistry

ultimately improves both oil quality and yield. A goal of this project was to examine the effects of changing the FAsP chemistry to vary the oxygen content of the oil to determine the effects on yield and ability to upgrade the various oils by hydrotreating.

3. Experimental Description

3.1 Thermal Deoxygenation (TDO) oil production

Calcium levulinate/formate salts were prepared by mixing levulinic acid and formic acid at a molar ratio of 1:1 with 20 % excess calcium hydroxide in a neutralization kettle. The salt slurry was placed in metal trays and dried in an industrial oven at 120 °C for 24 hours and at 250 °C for 4 hours. Dried calcium levulinate/formate salt chunks were ground into small particles using a hammer mill. Approximately 20 kg of powdered salts were loaded in to a 50 L semi-batch reactor (Figure 2). The reactor was purged continuously with nitrogen and heated to 450-550 °C and soaked for 8-10 hours. The 50 L semi-batch reactor and the thermal deoxygenation process were described in detail by Eaton et al. [1, 2]. Collected TDO oils were cleaned by removing sediments and water. Suspended solids in the crude oil was removed by filtering the oil to 25 microns. Water in the crude oil was removed in liquid form by gravity separation and in the form of ice by cooling the filtered oil to 0 °C. Cleaned TDO oils were then used for hydrogenation, distillation, and preparing diesel blends.

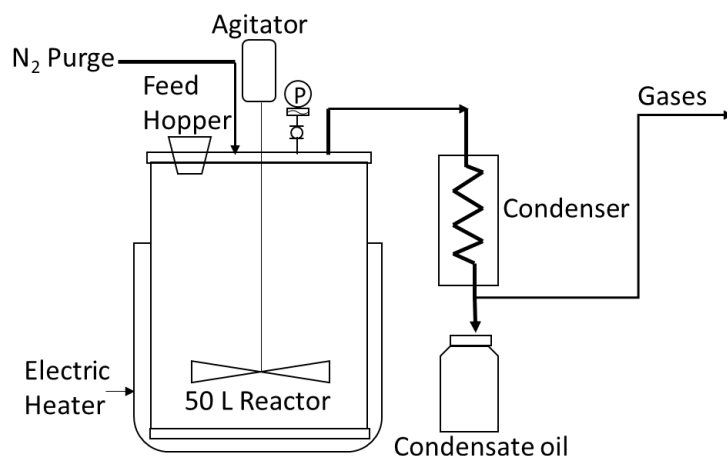


Figure 2. Schematic of the 50 L semibatch thermal deoxygenation (TDO) reactor, as adapted from Eaton *et al.* 2015.

3.2 TDO oil hydrogenation and distillation

Crude oils were hydrotreated using Ni on Si-Al (65 wt % Ni) catalyst in a bench scale continuous flow tubular reactor (Parr, Model 5402). The hydrogenation reaction was carried out at 300 °C and 750 psig of hydrogen with a weight hourly space velocity of 0.3 hr⁻¹. In addition to hydrogenation of TDO oil using Ni/Si-Al, selective ring opening reactions were investigated on Ni-Ir/Si-Al (65 wt% Ni, 1 wt% Ir) using 1-methylnaphthalene as a probe molecule in a scaled-

down trickle bed reactor to determine cracking activity. The reactions were completed at 0.1 hr⁻¹ weight hourly space velocity over a temperature range of 280-310 °C at 750 psig.

Distillations were performed on a BR instrument 9400 fractional distillation apparatus that meets ASTM D2892 specifications. The distillations of crude and hydrotreated thermal deoxygenation oils were performed over the atmospheric equivalent temperature range of 40-350 °C in four different increments, consecutively 135 °C, 25 °C, 125 °C, and 25 °C. All the distillations were performed under vacuum (50 mmHg pressure) and the maximum flask (pot) temperature was limited to 290 °C to prevent thermal cracking of hydrocarbons in the oil. During each run 2 L distillation flask was loaded with 1.5 L of crude or hydrotreated oil. Distillate fractions collected from 200 °C to 325 °C were blended before using for analysis and combustion performance research at Maine Maritime Academy.

3.3 Preparation and physicochemical characterization of TDO oil blends

Fuel blends were prepared in the Marine Engine Testing and Emissions Laboratory (METEL) at the Maine Maritime Academy. Sixteen different fuel blends were made by blending four different blend stocks, viz., thermal deoxygenation (TDO) oil, hydrotreated TDO (HDO) oil, distilled TDO oil (200 °C -325 °C), and distilled HDO oil (200 °C -325 °C) with Ultra-Low Sulfur Diesel (ULSD) in four different volume percent (5 %, 10 %, 15%, and 20%). Approximately 4 L of fuel was prepared for each fuel blend by mixing measured volume (0.2 L, 0.4 L, 0.6 L, or 0.8 L) of blend stock with measured volume (3.8 L, 3.6 L, 3.4 L, or 3.2 L) of ULSD (Diesel No. 2 Test Fuel from Chevron Phillips Chemical, Lot Number: 17LPUL701).

ULSD, four blend stocks, and 16 different fuel blends were characterized based on physical and chemical properties of the fuel. Specific gravity/ API gravity (at 60 °F), viscosity (at 40 °C), heat of combustion, and Carbon, Hydrogen, and Nitrogen content of fuels were measured according to ASTM D1298, ASTM D445, ASTM D5291, and ASTM D4809 respectively in laboratory facilities at University of Maine and Maine Maritime Academy.

Samples from each blend stocks, 10 vol % blends, and 20 vol % blends (12 samples) were sent to a fuel testing laboratory in Chelsea, MA for testing ignition delay and derived cetane number (ASTM D6890), boiling range distribution (ASTM D2887), lubricity (ASTM D6079), Carbon residue (ASTM D524), acid and base number (ASTM D974), and hydrocarbon types in middle distillates (ASTM D2425) of fuels.

3.4 Formate-assisted fast pyrolysis (FAsP) oil hydrotreating

Pyrolysis oils of three different oxygen contents (18, 21, and 26 wt%) prepared using formate-assisted pyrolysis were hydrotreated under similar conditions (300°C and 52-97 bar) using a commercial nickel alumina-silica catalyst in a single-stage process. The results indicate a clear relationship between catalyst performance and robustness and the oxygen content of the feedstock oil.

The feedstock used for these experiments was pine sawdust (*pinus strobus*) with moisture content between 5 and 10%. The element analysis of pine sawdust is given in Table 1. The sawdust was ground and sieved to achieve a particle size less than 1.5 mm for feed consistency. Three feedstocks were prepared for pyrolysis with different calcium formate (GEO Specialty Chemicals) loading per 100 g of pine sawdust: 140 g (CaFo-1A and CaFo-1B), 122.5 g (CaFo-2) and 70 g (CaFo-3). The calcium formate was loaded onto the pine sawdust in a slurry and then dried to approximately 10% moisture.

The untreated and pretreated sawdust was pyrolyzed with 40-60 mesh sand as a heat transfer medium in a 4.445 cm x 30 cm fluidized bed reactor described in detail elsewhere.[17] The reactor temperature was measured using two K-type thermocouples located on the vertical axis measured 3.0 and 9.5 in. from the top of the reactor. The pine/calcium formate mixture was metered through a screw feeder and pneumatically fed into the reactor, using a nitrogen flow rate of 6 L/min. The feed rate of the pretreated pine was between approximately 1 to 2.5 g/min, and up to 1.25 kg of material could be processed in a run. The pyrolysis temperature was 500 °C. Immediately downstream of the reactor, char was separated using a hot gas filter (HGF) also maintained at 500 °C. The total vapor residence time in the fluidized bed reactor and the HGF was 10.5 sec, with about 84% of that time in the HGF. After the vapor passed through the HGF, the liquid was collected in a condenser operated at 3 °C, followed by an electrostatic precipitator (ESP) to collect aerosols. Oils used as the feedstock for hydrotreating were taken from the ESP of the pyrolysis system.

Hydrotreatment of bio-oils was conducted using a 66±5% nickel on silica alumina (Ni/SiO₂-Al₂O₃) catalyst (Alfa Aesar) powder loaded into a vertical downflow tubular reactor. The reactor consisted of an electrically heated 12.7 mm ID X 457 mm long stainless steel tube and was loaded in the following configuration top to bottom: 4 g glass beads, 2 g sand, 0.2 g quartz wool, 10 g catalyst, 0.2 g quartz wool, 1 g sand, 2 g glass beads, 0.3 g quartz wool. Bio-oil and hydrogen were co-fed to the top of the reactor at 0.01 mL/min and 100 sccm, respectively. The bio-oil feed rate corresponded to a weight hourly space velocity (WHSV) of 0.06 hr⁻¹. The reactor was operated at 300°C and 52-97 bar. Liquid phase products were collected in a sample collection vessel and gas products were vented through a pressure regulator followed by a rotameter. The catalyst was activated with 100 sccm of H₂ at 350 °C and atmospheric pressure for 12 h. Samples were collected every 12 h for TOS up to 350 h. The hydrotreating exhaust gas was periodically measured using an SRI 8610C portable GC calibrated with a certified mixture of 1% methane, ethane, ethylene, acetylene, carbon monoxide and carbon dioxide in nitrogen. The exhaust gas flow rate was measured using a calibrated rotameter.

4. Results

4.1 TDO Oil Results

The yield of TDO oil at large scale was improved (approaching 80% of theoretical yield) by pretreating TDO feedstocks at 250 °C and size-reducing the resulting intermediates prior to pyrolysis. New understanding of the reactions involved in Thermal DeOxygenation shows that there are two distinct reaction regimes. The low temperature regime evolves water and forms a pumice-like material with reduced oxygen content. The decomposition reactions between 250°C and 500°C produce organic liquids. Because the pretreatment temperature is relatively mild, existing industrial equipment, such as porcupine processors, would be reasonable for the first-stage processing. Then, it will be worthwhile to identify the most effective pyrolysis method for second-stage processing, for instance fast versus slow pyrolysis.

The reaction achieved high oil saturation (H = 12.6 wt%) and exhibited evidence of deoxygenation activity with 89 g water/kg-oil obtained. The resulting oil products were compared using GC-MS as shown in Figure 3. The raw thermal deoxygenation oils (blue) show high percentages of polyaromatics and naphthols which were reacted to form a mixture of methyldecalin and decalin. The product oils are of higher fuel quality, but are not consistent with finished petroleum distillate fuels, indicating that ring opening reactions may be a beneficial reaction step to producing biofuels from thermal deoxygenation oils. Iridium improve cracking activity above 300°C resulting in approximately 40 mol% of the product as cycloalkanes as shown in Figure 4 Carbon losses were between 15-22 mol%.

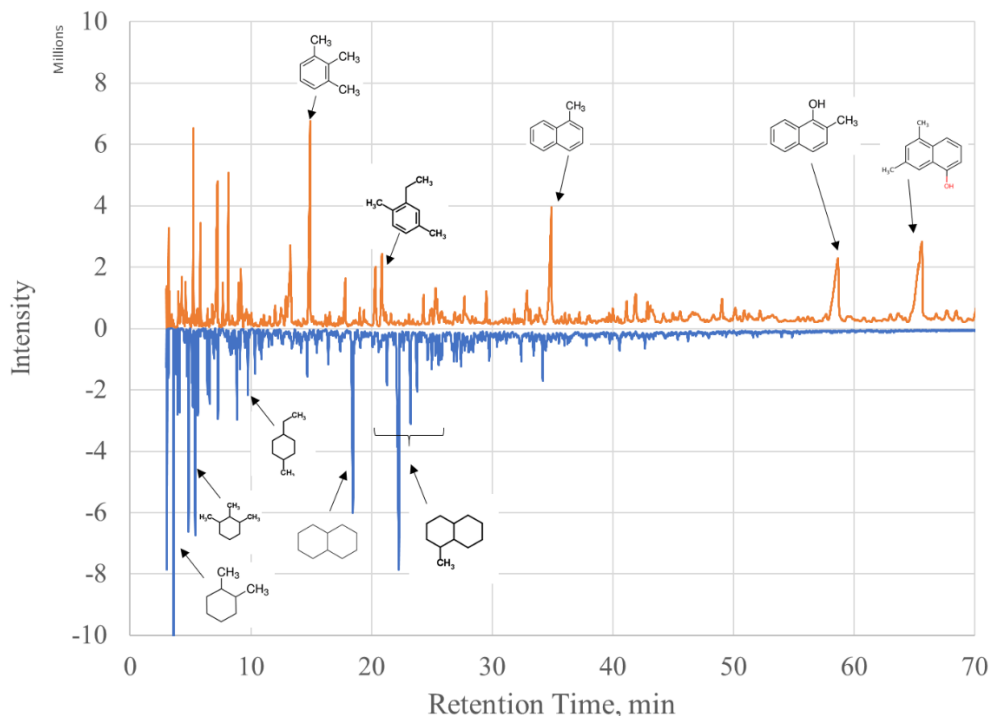


Figure 3. Comparison of raw thermal deoxygenation oils and hydrotreated products by GC-MS. The catalyst system was effective for raw oil saturation and deoxygenation to fuel products.

1-MN on Ni-Ir Resulting Molecules

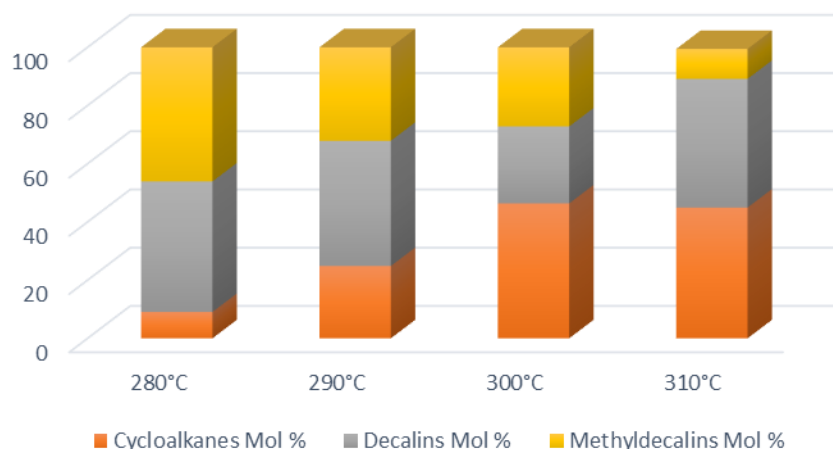


Figure 4. Product distribution of 1-methylnaphthalene hydroprocessing using Ni-Ir/Si-Al catalyst. Selective ring opening reactions result in nearly 40 mol% cracked cycloalkanes.

Figure 5 shows the color variation of ULSD, TDO oil, HDO oil, TDO oil distillate, HDO oil distillate, and different fuel blends. Opacity of the TDO oil, HDO oil, and TDO oil distillate blends reduces with decreasing blend percent. However, a noticeable difference in opacity is not shown in HDO oil distillate blends.

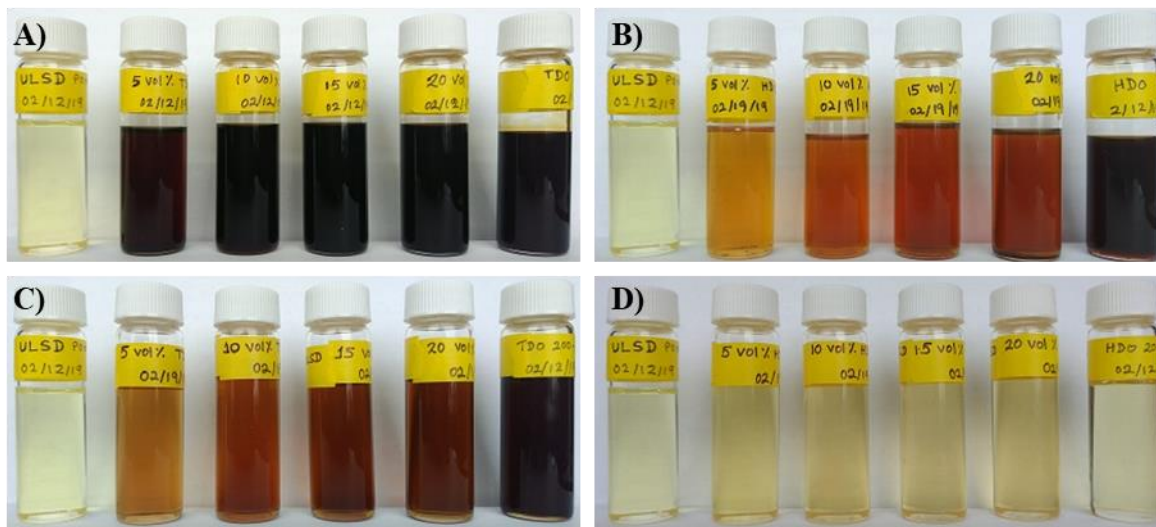


Figure 5. Color comparison of different fuel blends (in vol %) of Thermal deoxygenation (TDO) oil, Hydrotreated TDO (HDO) oil, TDO oil distillate (200 °C -325 °C), HDO oil distillate (200 °C -325 °C) with Ultra-Low Sulfur Diesel (ULSD), from left to right, (A) ULSD, 5 % TDO, 10 % TDO, 15 % TDO, 20 % TDO, and TDO oil from 50 L batch reactor (B) ULSD, 5 % HDO, 10 % HDO, 15 % HDO, 20 % HDO, and HDO oil (C) ULSD, 5 % TDO distillate, 10 % TDO distillate, 15 % TDO distillate, 20 % TDO distillate, and TDO oil distillate (D) ULSD, 5 % HDO

distillate, 10 % HDO distillate, 15 % HDO distillate, 20 % HDO distillate, and HDO oil distillate.

Figure 6 shows the change of fuel properties: specific gravity, viscosity, hydrogen content, and net heat of combustion with changing vol % of the fuel blends. All of the above properties change linearly with the blend %. Specific gravity of all the blends and viscosity of all the blends except the HDO oil increased with increasing vol % of the blend. Hydrogen content and net heat of combustion of all the blends decreased with increasing vol % of the blend. Boiling point distributions of TDO distillates, HDO distillates, and their blends are closer to the boiling point distribution of ULSD, as shown in Figure 7.

Specific gravity and viscosity of all the fuel blends exceed or within the specified range of ASTM D975 No.2 distillates and MIL-DTL-16884M fuel specifications (Table 1 and Table 2). Hydrogen (H) content (wt %) of TDO oil and TDO oil distillate fuel blends are comparatively lower than the H content of HDO oil and HDO oil distillate fuel blends. However, H content of all the fuel blends except the 15 % and 20 % blends of TDO and TDO distillate oil meet the MIL-DTL-16884M specifications. Net heat of combustion of all the fuel blends are approximately 42 MJ/kg or above. Heating value of HDO and HDO distillate fuel blends are higher than that of TDO and TDO distillate fuel blends. This could be due to high H content in hydrotreated oils. Only 5% and 10% blends HDO oil and HDO oil distillates blends meet the MIL-DTL-16884M specified cetane rating. Overall physicochemical properties of HDO oil fuel blends and HDO oil distillate fuel blends are closer to the properties of ULSD.

Table 1. Comparison of physicochemical properties of TDO oil, TDO oil distillates, and TDO oil derived fuel blends to ULSD, ASTM D975, and MIL-DTL-16884M fuel specifications

Property	ASTM Method	Fuel specification		Unit	Measured value											
		ASTM D975 No. 2 Distillates	MIL-DTL-16884M		ULSD	TDO oil					TDO oil distillates					
						5%	10%	15%	20%	100%	5%	10%	15%	20%	100%	
Specific Gravity (at 60 °F)	D1298		0.876 (max)		0.841	0.846	0.855	0.863	0.872	0.967	0.850	0.856	0.863	0.870	0.978	
API Gravity (at 60 °F)	D1298				36.7	35.7	33.9	32.4	30.8	14.9	35.0	33.8	32.5	31.2	13.2	
Viscosity (at 40)	D445	1.9-4.1	1.7-4.3	cSt	2.5	2.4	2.5	2.6	2.8	4.4	2.5	2.6	2.6	2.7	4.7	
Hydrogen content	D5291		12.5 (min)	Wt %	13.3	12.9	12.6	12.4	12.2	8.8	13.1	13.0	12.7	12.4	9.2	
Net Heat of Combustion	D4809			MJ/kg	42.8	42.5	42.2	42.0	41.6	37.9	42.6	42.4	42.1	42.0	38.6	
Ignition Delay (ID)	D6890			ms			5.05		6.12	> 6.50		5.3		5.97	> 6.5	
Derived Cetane Number (DCN)			42 (min)		46		41.4		35	< 33.0		39.7		35.7	< 33	
Average Charge Air Temperature							538.3		538.2	539.3		538.5		538.5	539.6	
Lubricity, at 60 °C,	D6079															
Major Axis				µm			310		260	250		290		260	290	
Minor Axis				µm				210		170	180		220		180	210
Wear Scar Diameter		520 (max)	460 (max)	µm	390			260		220	220		260		220	250
Ramsbottom Carbon Residue	D524	0.35 (max)	0.2 (max)	Wt %						0.76					0.14	
Acid Number	D664		0.3 (max)	mg KOH/g						1.55					2.9	
Initial Boiling Point	D2887			°C	172		116		110	57		118		119	112	
10% Boiling Point			Record	°C	208		187		186	159		194		196	215	
50% Boiling Point			Record	°C	257		256		260	285		261		262	264	
90% Boiling Point		282-338	357 (max)	°C	312		331		342	412		331		329	314	
Final Boiling Point			385 (max)	°C	347		449		464	504		423		427	424	

Table 2. Comparison of physicochemical properties of HDO oil, HDO oil distillates, and HDO oil derived fuel blends to ULSD, ASTM D975, and MIL-DTL-16884M fuel specifications

Property	ASTM Method	Fuel specification		Unit	Measured value											
		ASTM D975 No. 2 Distillates	MIL-DTL-16884M		ULSD	HDO oil					HDO oil distillates					
						5%	10%	15%	20%	100%	5%	10%	15%	20%	100%	
Specific Gravity (at 60 °F)	D1298		0.876 (max)		0.841	0.845	0.845	0.846	0.848	0.863	0.846	0.849	0.852	0.855	0.903	
API Gravity (at 60 °F)	D1298				36.7	36.0	35.9	35.7	35.4	32.4	35.7	35.1	34.6	34.0	25.2	
Viscosity (at °40)	D445	1.9-4.1	1.7-4.3	cSt	2.5	2.4	2.4	2.3	2.3	1.7	2.5	2.5	2.5	2.5	2.7	
Hydrogen content	D5291		12.5 (min)	Wt %	13.3	13.2	13.3	13.1	13.1	11.8	13.3	13.3	13.2	13.2	11.5	
Net Heat of Combustion	D4809			MJ/kg	42.8	42.8	42.8	42.7	42.7	42.1	42.8	42.7	42.7	42.6	42.2	
Ignition Delay (ID)	D6890			ms			4.68		5.08	> 6.5		4.93		5.14	> 6.5	
Derived Cetane Number (DCN)			42 (min)		46		44.3		41.2	< 33		42.3		40.8	< 33	
Average Charge Air Temperature							538.3		538.7	538.5		538.6		538.6	538.5	
Lubricity at 60 °C																
Major Axis	D6079			µm			310		300	300		300		330	280	
Minor Axis				µm			240		230	270		280		290	170	
Wear Scar Diameter		520 (max)	460 (max)	µm	390		280		260	280		290		310	220	
Ramsbottom Carbon Residue	D524	0.35 (max)	0.2 (max)	Wt %						0.31					0.09	
Acid Number	D664		0.3 (max)	mg KOH/g						<0.10					< 0.10	
Initial Boiling Point	D2887			°C	172		91		75	38		118		115	95	
10% Boiling Point			Record	°C	208		181		173	120		194		196	208	
50% Boiling Point			Record	°C	257		257		254	216		260		258	251	
90% Boiling Point			282-338	357 (max)	°C	312		332		333	332		331		328	307
Final Boiling Point				385 (max)	°C	347		410		431	472		412		412	342

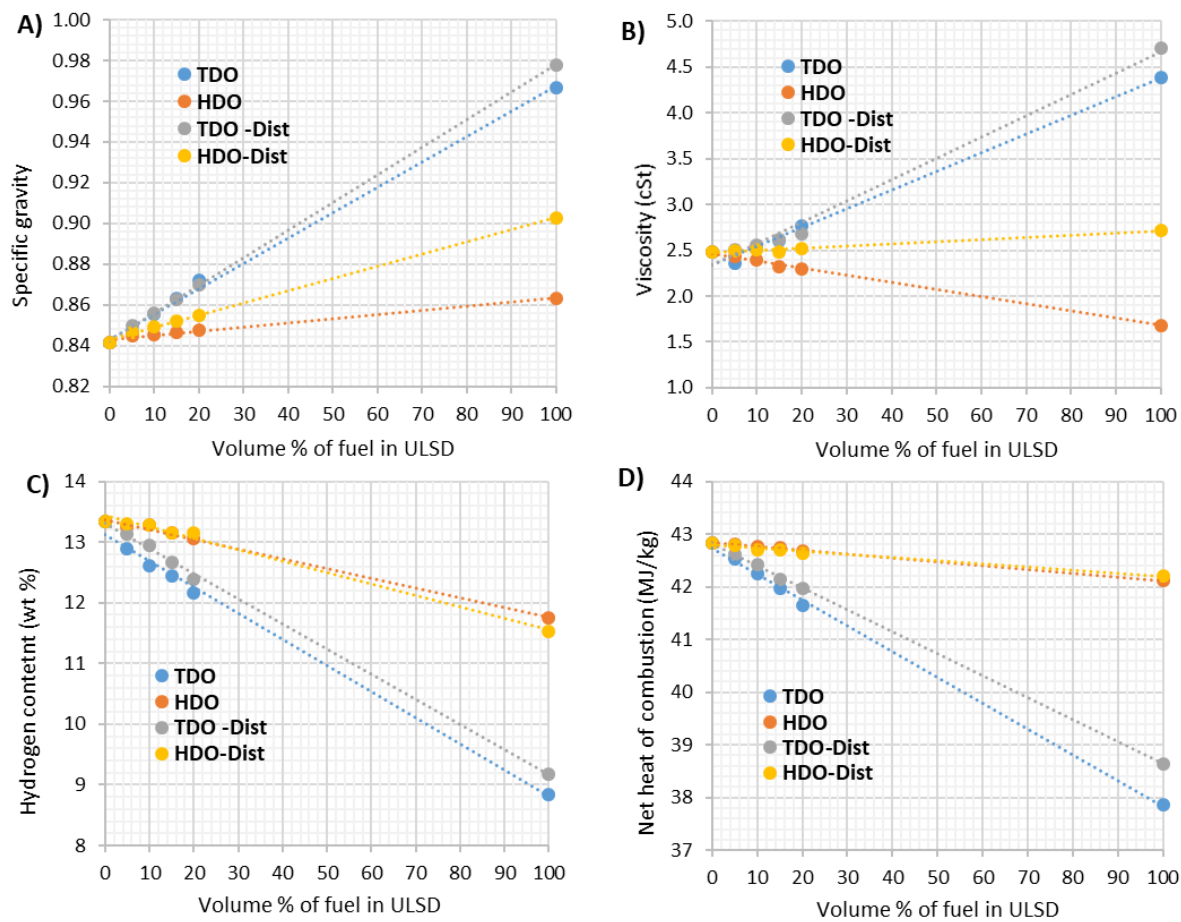


Figure 6. Change of fuel properties A) specific gravity, B) viscosity, C) hydrogen content, and D) net heat of combustion with vol % of the fuel blends. ULSD is represented by the 0 vol % while any blend stock is represented by 100 vol %. TDO: Thermal deoxygenation oil, HDO: Hydrotreated TDO, TDO-Dist: TDO distillate (200 °C -325 °C), and HDO-Dist: HDO distillate (200 °C -325 °C). R^2 values of all the fitted regression lines are over 0.98.

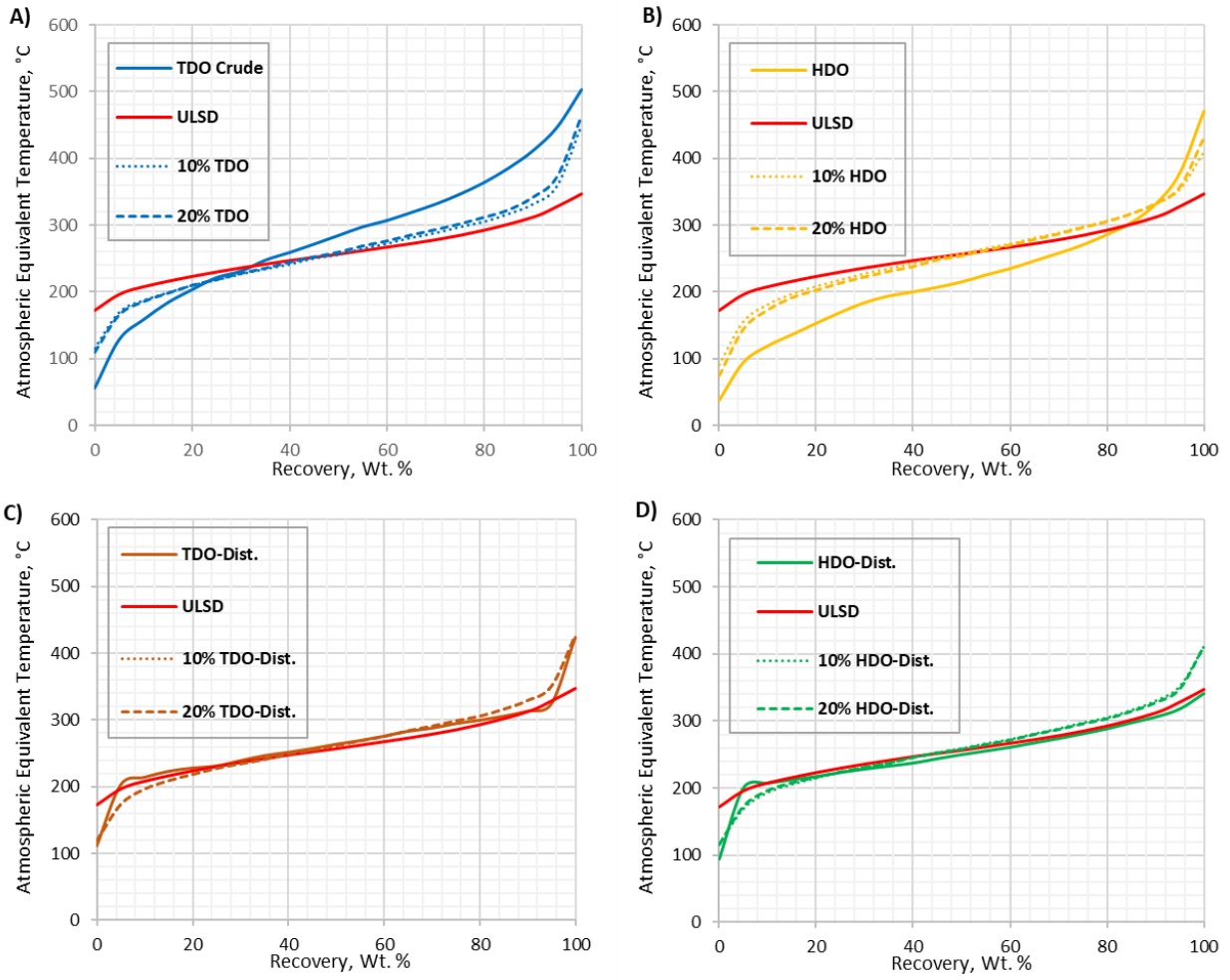


Figure 7. Boiling point distributions of A) Crude TDO, B) HDO, C) TDO Distillate, and D) HDO Distillate and their fuel blends compared to ULSD.

4.2 FAsP Oil Hydrotreating Results

CHNO data for bio-oils generated from the three different calcium formate pretreated pine and untreated pine feedstocks are shown in Table 3. The data indicate that pyrolysis oil oxygen content decreased from 26 to 18 percent as calcium formate loading was increased in the pine feed.

Table 3. FAsP oil feedstocks for hydrotreating.

	Pine Feed	Pine oil	CaFo-1A oil	CaFo-1B oil	CaFo-2 oil	CaFo-3 oil
C (wt.%)	45.1	64.3	75.0	74.6	71.5	65.9
H (wt.%)	6.8	7.2	7.4	7.3	7.4	7.1
N (wt.%)	0.0	1.2	0.8	0.1	0.1	0.5
O (wt%)*	48.1	27.3	16.8	18.0	21.0	26.5
O:C	0.80	0.31	0.16	0.18	0.22	0.30
H:C	1.80	1.34	1.19	1.18	1.24	1.29

*by difference

Chemical composition of the oil from ^{13}C NMR is shown in Table 4. As more oxygen is removed from the oil via increasing calcium formate in the feed, a decrease in methoxy/hydroxyl, carbohydrate, and carbonyl carbon are observed, while an increase in aromatic carbon is observed. Compared to conventional pyrolysis, the oils obtained from calcium-formate pretreated feedstock contain increased alkyl, decreased methoxy/hydroxy, and increased carbonyl hydrocarbons.

Table 4. Carbon NMR of FAsP oil feedstocks.

		CaFo-1A	CaFo-1B	CaFo-2	CaFo-3
Carbon type	Chemical Shift, δ(ppm)	Carbon %	Carbon %	Carbon %	Carbon %
alkyl	0-54	30.0%	30.1%	30.8%	28.5%
methoxy/hydroxy	54-70	5.0%	4.6%	7.0%	7.8%
carbohydrate	70-103	9.0%	7.9%	10.5%	11.3%
aromatic	103-163	39.2%	41.4%	33.6%	34.6%
carbonyl	163-215	16.8%	16.0%	18.0%	17.8%

The results of hydrotreating the FAsP oils are summarized in Table 5. Mass balance data are shown for select samples of the hydrotreated FAsP oils. Samples were collected approximately every 12 h during hydrotreating experiments. Samples which were chosen for analysis were closer to the end of the experiment (as indicated by the time-on-stream in Table 5), representing

a quasi-steady-state. In each sample the aqueous and oil phases were separated, weighed and analyzed for CHNO. The gas was analyzed with a GC periodically during each experiment. Unaccounted carbon could be partially explained by coking in the catalyst bed.

Comparing the experiments run at 97 bar the lower oxygen content feedstock (CaFa-1B) resulted in the highest carbon yield in the product oil, ~92%. Consistent with the high carbon yield is the lowest amount of carbon in the gas product (2.5%) and the lowest amount of unaccounted carbon (~5%). The carbon yield in the product oil decreased to ~82% and ~61%, the carbon yield in the gas products increased to 6 and 14%, and the unaccounted carbon increased to 11 and 24%, using the feedstocks with 21 and 26% oxygen, respectively.

Hydrotreating results were obtained for the lower oxygen feedstock run at 52 and 97 bar reactor pressures. An increase in carbon yield in the product oil was measured, from 79 to 92% when increasing the reactor pressure. The gas products were not collected or analyzed for HT-CaFo-1A which was run at 52 bar reactor pressure.

Hydrogen consumption was calculated by summing increased hydrogen in the product oil (relative to the feed), hydrogen in the aqueous product fraction (corrected for water in the feed), and hydrogen in the gas stream as the amount measured in permanent hydrocarbon gases. The mass of permanent hydrocarbon gases were quantified using a micro-GC to measure selectivity and a flow meter to measure mass flow.

Table 5. FAsP oil hydrotreating results.

Time on stream (hr)	Mass yield of product oil, wt%	Mass yield of aqueous fraction, wt%	Mass yield of product gas, wt%	Mass balance, %	Carbon yield of product oil, %	Carbon yield of aqueous fraction, %	Carbon yield of product gas, %	Carbon balance, %	H ₂ consumed, g of H ₂ in oil per g of dry bio-oil
HT-CaFo-1A									
240-264	66.8	21.2	-----	88.1	79.4	0.1	-----	79.5	-----
HT-CaFo-1B									
321-334	79.4	15.9	2.3	97.5	91.8	0.2	2.5	94.5	0.035
HT-CaFo-2									
255-266	66.5	16.4	5.3	88.2	82.4	0.1	6.0	88.5	0.029
HT-CaFo-3									
151-162	52.4	21.6	11.3	85.3	61.3	0.1	14.1	75.5	0.032

The results indicate a clear relationship between catalyst performance and robustness and the oxygen content of the feedstock oil. The 26% oxygen feedstock resulted in reactor plugging at 200 h TOS, whereas reactions were run to 350 h TOS with lower oxygen content feedstock. In the case of the 18% oxygen feedstock, the reactor was stopped due to running out of liquid feed. Hydrocarbon oil yield and carbon yield in the oil improved with reduced oxygen in the feed, reaching 79 and 91.8%, respectively, for the 18% oxygen feed. The lower oil yields and carbon oil yields were a result of increased production of gases and unaccounted mass and carbon. It is assumed that some of the unaccounted mass and carbon was due to tar formation in the catalyst bed that led to reactor plugging and decreased catalyst activity. Increasing reactor pressure from

52 to 97 bar using the 18% oxygen content oil also improved mass and carbon yields of the oil product.

Publications, conference papers, and presentations

Journal Publications:

- Scott J. Eaton, Sedat H. Beis , Sampath A. Karunarathne , Hemant P. Pendse, and M. Clayton Wheeler; "Hydroprocessing of Biorenewable Thermal Deoxygenation Oils," *Energy Fuels*, 2015, 29 (5), pp 3224–3232 <http://pubs.acs.org/doi/abs/10.1021/acs.energyfuels.5b00396>
- DeSisto, W.J. and M.C. Wheeler, A funnel plot to assess energy yield and oil quality for pyrolysis-based processes, *Biomass and Bioenergy*, 93 (2016) 254-258.
- Carrasco, J.L., S. Gunukula, A.A. Boateng, C.A. Mullen, W.J. DeSisto, and M.C. Wheeler, Pyrolysis of forest residues: An approach to techno-economics for bio-fuel production, *Fuel* 193 (2017) 477-484.
- Eaton, S.J. and M.C. Wheeler, Decomposition reactions and kinetics of alkaline-earth metal levulinate and formate salts, *ACS Sustainable Chem. Eng.* 2017, 5, 3039–3045.
- AlMohamadi, H, Gunukula, S., DeSisto, W. J. and Wheeler, M. C., "Formate-assisted pyrolysis of biomass: an economic and modeling analysis," *Biofuels, Bioprod. Bioref.* 12:45-55 (2018); DOI: 10.1002/bbb.1827 <http://onlinelibrary.wiley.com/doi/10.1002/bbb.1827/epdf>.
- Gunukula, S., Klein, S.J.W., Pendse, H.P., DeSisto, W.J., and Wheeler, M.C., "Techno-economic analysis of thermal deoxygenation based biorefineries for the coproduction of fuels and chemicals," *Applied Energy* (2018) <https://doi.org/10.1016/j.apenergy.2018.01.065>
- Khlewee, M. Gunukula, S., Wheeler, M.C., and DeSisto, W.J., "Hydrotreating of reduced oxygen content bio-oil produced by Formate-Assisted Pyrolysis," Submitted to *Fuel* February 22, 2019.

Books or other non-periodical, one-time publications:

- Scott Eaton, Ph.D. Thesis, Chemical Engineering, University of Maine, August 2015: "Thermal Deoxygenation of Levulinated and Formate Salts for the Production of Transportation Fuels."
- Paige Case, Ph.D. Thesis, Chemical Engineering, University of Maine, May 2015: "Fundamentals of Pyrolysis of Pretreated Biomass."
- Hamad AlMohamadi, M.S. Thesis, Chemical Engineering, University of Maine, December 2014: "Techno-Economic Analysis of Formate Assisted Pyrolysis."
- Chi Truong, Pressurized Fast Pyrolysis of Calcium Formate-Pretreated Biomass, University of Maine Master's Thesis, 2016.
- Khlewee, Abdulazeez, "Characterization of Catalysts for Hydrodeoxygenation of Bio-Oils using Phenol as a Model Compound," University of Maine M.S. Thesis, 2017.
- Khlewee, Mubarak, "Production of Bio-Oil with Different Oxygen Content and Characterization of Catalytic Upgrading to Transportation Fuel," University of Maine M.S. Thesis 2017.

Other publications, conference papers and presentations:

- S.J. Eaton, P.A. Case, W.J. DeSisto, and M.C. Wheeler, Poster: “Decomposition Pathways during Pyrolysis of Hydrolyzate Salts,” tcs2014: Symposium on Thermal and Catalytic Sciences for Biofuels and Biobased Products, Denver, CO, September 2-4, 2014.
- P.A. Case, M.C. Wheeler, and W.J. DeSisto, Second Place Student Poster Competition: “Proposed Mechanisms for Pyrolysis of Calcium Pretreated Pine,” tcs2014: Symposium on Thermal and Catalytic Sciences for Biofuels and Biobased Products, Denver, CO, September 2-4, 2014.
- Scott Eaton and M. Clayton Wheeler, Contributed Presentation: “Levulinate and Formate Salt Reactions during Thermal Deoxygenation (TDO),” 14AIChE Annual Meeting, Atlanta, GA, November 19, 2014.
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- Clayton Wheeler, Invited Presentation: “UMaine Forest Bioproducts Research Institute: Transportation Biofuels,” University of New Mexico Department of Chemical and Nuclear Engineering, May 1, 2015.
- Chi Truong, M. Clayton Wheeler, William J. DeSisto, Paige A. Case and Brian G. Frederick, Pressurized fast pyrolysis of calcium formate-pretreated pine, International Bioenergy & Bioproducts Conference in Atlanta, GA, 2015
- Wheeler, M.C., S.J. Eaton, and W.J. DeSisto, Transportation Fuels via a Two-Stage Thermal Deoxygenation Process, oral presentation at the 252nd American Chemical Society National Meeting and Exposition, Philadelphia, PA, August 21, 2016.
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- DeSisto, W.J. and Wheeler, M.C., “Formate-Assisted Pyrolysis of Biomass,” Presented at the New England Energy Research Forum, Worcester MA, June 28, 2017.
- Gunukula, S., DeSisto, W.J., Pendse, H.P., and Wheeler, M.C., “Economic and Modeling Analysis of Product and Energy Driven Biorefineries Based on Thermal Deoxygenation Pathway,” Presented at tcbiomass, Chicago IL, September 20, 2017.
- Gunukula, S., DeSisto, W.J., Pendse, H. and Wheeler, M.C., Economic and Modeling Analysis of Product and Energy Driven Biorefineries Based on Thermal Deoxygenation Pathway, AIChE Annual Meeting, Minneapolis MN, November 2017.
- Gunukula, S., DeSisto, W.J., Pendse, H. and Wheeler, M.C., Assessment of Economic Potential of Furfural Platform. AIChE Annual Meeting, Minneapolis MN, November 2017.

5. Conclusions and Future Work

Physicochemical of TDO and upgraded TDO oils suggest that they are suitable candidates for making fuel blends with petroleum products. Furthermore, the production and upgrading processes of the TDO oils are potentially compatible with existing petroleum refinery operations. However, more research is needed on TDO oil upgrading to meet the standard fuel specifications for example, higher H content and improved cetane rating. Furthermore, technoeconomic studies in the production of TDO oil indicate that co-products are an important factor in commercial viability.

Hydrocarbon yield and oxygen content in the hydrotreated FAsP oil were sensitive to the oxygen content in the FAsP oil. The lowest oxygen content feedstock resulted in 91.8% carbon yield in the product oil which contained oxygen between 0.5 and 6% throughout a 350 h time on stream continuous run. Data from this work was added to the literature of hydrotreating of reduced-oxygen content pyrolysis oils. Techno-economic analysis indicates that yield improvements in FAsP are still required to provide economic benefit relative to hydrotreating higher oxygen-content pyrolysis oils.

References

- [1] Scott J. Eaton , Sedat H. Beis , Sampath A. Karunaratne , Hemant P. Pendse , and M. Clayton Wheeler; "Hydroprocessing of Biorenewable Thermal Deoxygenation Oils," *Energy Fuels*, 2015, 29 (5), pp 3224–3232 <http://pubs.acs.org/doi/abs/10.1021/acs.energyfuels.5b00396>
- [2] Scott J. Eaton, Ph.D. Thesis, Chemical Engineering, University of Maine, August 2015: "Thermal Deoxygenation of Levulinated and Formate Salts for the Production of Transportation Fuels."