Catalytic Deoxygenation of Liquid Biomass for Hydrocarbon Fuels

Howard Mayfield, Ted Marolla, and Bob Nichols, AFRL, Tyndall Air Force
Mike Mashburn, Physics Department, Florida State University
Kyung C Kwon, Chemical Engineering Department, Tuskegee University,Tuskegee,
AL 36088, Tel. 334-727-8976/724-4528, kwonk@tuskegee.edu

Abstract

Neat methyl laurate was chosen as a model compound of liquid biomass for this research. Removal of oxygen from liquid biomass is a key step in the elevation of their energy intensities. Canola oil and its biodiesel, spent waste kitchen oil and its biodiesel, NSWC-02 biodiesel (6/13/08), Energy BLD 9738 (1/8/08), and Wallace biodiesel (7/14/2008), in addition to methyl laurate were deoxygenated with hydrogen and a catalyst.

Oxygen from methyl laurate and liquid biomass is removed at 250 – 1220 psig initial cold hydrogen pressure and 300 – 400^{o}C, using a 316 stainless steel batch reactor. Removal of oxygen from liquid methyl laurate and other biomass is evaluated with a GC/MS analyzer for liquid reaction products, while consumption of hydrogen and conversion of liquid biomass to gaseous reaction products are analyzed with another GC. The range of reaction duration of liquid biomass in the batch reactor is 30 – 60 minutes under the deoxygenation conditions. Consumption of hydrogen and conversion of liquid biomass into gaseous products are evaluated with analyzing gaseous reaction products and making a mass balance on hydrogen.

The objective of this research is to develop an efficient method of removing oxygen from liquid biomass to produce liquid petroleum-comparative hydrocarbons with the following specific aims:

1. Formulate catalysts for the removal of oxygen from liquid biomass.
2. Test capabilities of formulated catalysts for the deoxygenation and isomerization of liquid biomass.
3. Identify reaction conditions suitable for the conversion of liquid biomass into liquid hydrocarbon fuels
4. Determine reaction mechanisms on the removal of oxygen compounds from liquid biomass.
5. Develop an economic method of regenerating catalysts deactivated with carbonaceous deposits and sulfur loss.

Introduction

Liquid biomass such as methyl laurate, methyl stearate, canola oil and others are chosen to study deoxygenation and isomerization of liquid biomass. Removal of oxygen from liquid biomass for renewable energies and isomerization of liquid biomass are needed to increase its energy intensity, stability, and decrease its viscosity. Liquid biomass will be deoxygenated with hydrogen and active catalytic metal candidates such as Ni, Mo, Pd, Co, and Zn. Liquid biomass will be isomerized with hydrogen and Al_2O_3 or SiO_2. These metals will be impregnated into a γ-alumina support.

Conversion of liquid biomass to hydrocarbon fuels is the primary step in refining liquid biomass produced from vegetable oils, animal fats, biodiesels, and waste cooking oils. Removal of oxygen from biofuels is needed to enhance fuel enthalpies, decrease viscosity of biomass, and stabilize biofuels. Current method of deoxygenating liquid biomass with pellet catalysts is equipment intensive and expensive, requiring a packed beds reactor, a fluidized beds reactor, and a trickle bed reactor.

Many researchers are developing the Catalytic Conversion Process (CCP) of liquid biomass for hydrocarbons, using catalyst pellet particles and hydrogen in a packed-bed reactor, a fluidized bed reactor, and a trickle bed reactor to deoxygenate and isomerize liquid biomass. However, significant pressure drops and non-uniform flow of liquid biomass and gaseous hydrogen were experienced over a packed-bed reactor. Tuskegee University undertakes a feasibility study on replacing catalysts in fine pellet form with monolithic form for the CCP process.

Hydrogen and liquid biomass are fed downward into a vertical monolithic catalyst reactor at 250 to $450^{o}C$ in the CCP process for the conversion of liquid biomass into liquid hydrocarbons to enhance heating values of biofuels, stabilize biofuels, and decrease viscosity of biofuels. In the CCP process, liquid biomass and hydrogen can be mixed and converted uniformly with honeycomb monolithic catalysts in comparison with a pellet-packed reactor. Regeneration of monolithic catalyst is simple in comparison with pellet-type catalysts

Various catalysts in addition to $NiMo/\gamma\text{-}Al_2O_3$ and $CoMo/\gamma\text{-}Al_2O_3$ are well known for deoxygenating liquid biomass; however, these catalysts were formulated and tested mostly for refining and hydro-cracking petroleum products. Research is needed in the development of dual function catalysts suitable for both deoxygenizing and isomerizing functions to advance the CCP process, in which liquid hydrocarbons are formed. In this paper, preliminary results of experiments on removal of oxygen from liquid biomass, using a batch reactor, a GC/MS, and a GC, are described.

Objectives

The objective of this research is to develop an efficient removal method of oxygen from biofuels to minimize oxygen contents in biofuels with suitable catalysts with the following specific aims:

1. Formulate catalysts for the removal of oxygen from liquid biomass.

2. Test capabilities of formulated catalysts for the deoxygenation and isomerization of liquid biomass.

3. Identify reaction conditions suitable for the conversion of liquid biomass into liquid hydrocarbon fuels

4. Determine reaction mechanisms on the removal of oxygen compounds from liquid biomass.

5. Develop an economic method of regenerating catalysts deactivated with carbonous deposits and sulfur loss.

Biomass such as methyl laurate, methyl stearate, canola oil, and others are chosen as a liquid biomass for this preliminary research. Removal of oxygen from liquid biomass and isomerization of liquid biomass are needed to increase its energy intensity, stabilize it, and decrease its viscosity. Oxygen from liquid biomass is removed and liquid biomass is isomerized at 100 – 1250 psig initial cold hydrogen pressure and 250 – 450^{o}C, using a batch reactor. Removal of oxygen from liquid biomass and consumption of hydrogen is analyzed with a GC/MS for liquid reaction products. Gaseous reaction products were analyzed with a GC. The reaction duration range of liquid biomass in a monolithic catalyst flow reactor is 10 – 60 minutes under the deoxygenating conditions. Consumption of hydrogen and conversion of liquid biomass into gaseous products are evaluated by analyzing gaseous reaction products with the GC and making a mass balance on hydrogen.

Experimental Setup

Oxygen from methyl laurate and biomass is removed at 250 – 1220 psig and 300 – 400^{o}C, using a 35-cm^3 batch reactor made of 316 stainless steel. Removal of oxygen from liquid methyl laurate and other biomass is evaluated with a GC/MS analyzer for liquid reaction products and gaseous reaction products are analyzed with another GC. The range of reaction duration of liquid biomass in the batch reactor is 30 – 60 minutes under the deoxygenating conditions.

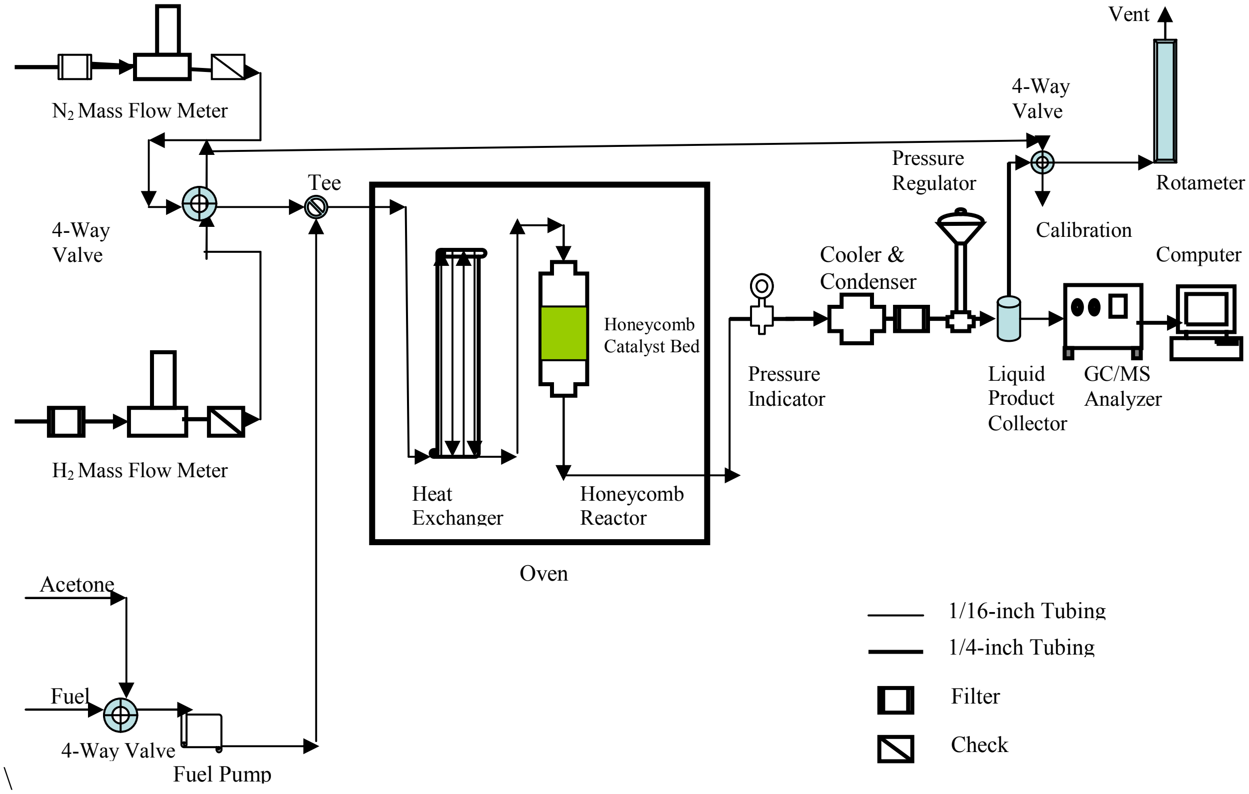


Figure 1. Schematic Diagram on a deoxygenation reactor assembly

Typical Reaction Conditions

- Batch Reactor Volume, cm3: 35
- Temperature, oC 300 – 400
- Initial Cold Hydrogen Pressure, psig: 250 – 1220
- Amount of Biomass, g: 2
- Amount of Catalyst, g: 0 – 0.2
- Biomass:
  - Methyl Laurate
  - Canola Oil and its Biodiesel
  - Spent Waste Kitchen Oil and its Biodiesel
  - NSWC-02 Biodiesel (6/13/08)
  - Energy BLD 9738 Biodiesel (1/8/08)
  - Wallace Biodiesel (7/14/08)

Equipment

- GC/MS for Liquid Reaction Products:
- GC for Gas Products:
- Batch Reactor
- Heater and its Temperature Controller
- Wrist-Arm Shaker and Horizontally-Moving Orbital Shaker

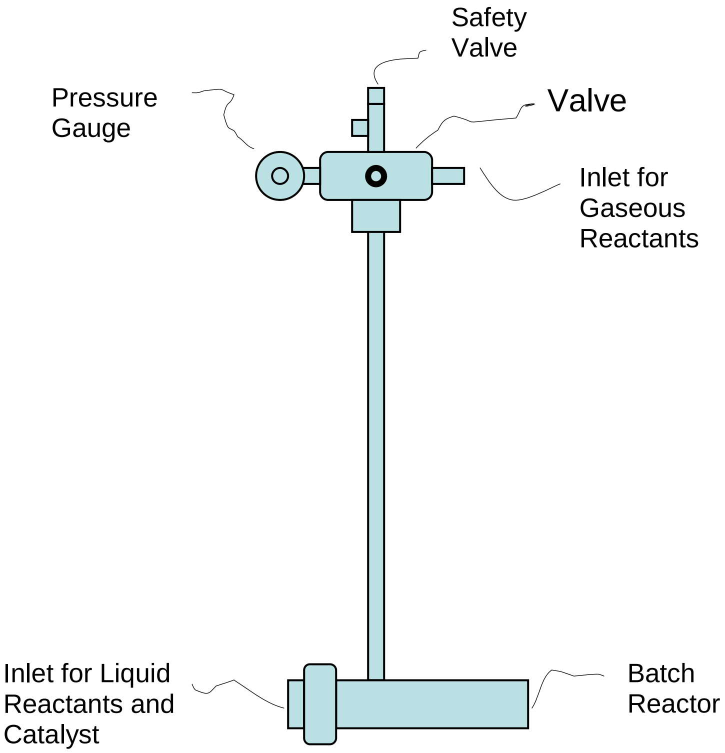


Figure 2. High-pressure and high-temperature batch reactor

Reaction Pathways

Biomass → Biodiesel
Biodiesel → $H_2O + CO_2 + CH_4$ + Hydrocarbons
Biomass → $H_2O + CO_2 + CH_4$ + Hydrocarbons

Conversion of Methyl Laurate into Dodecane

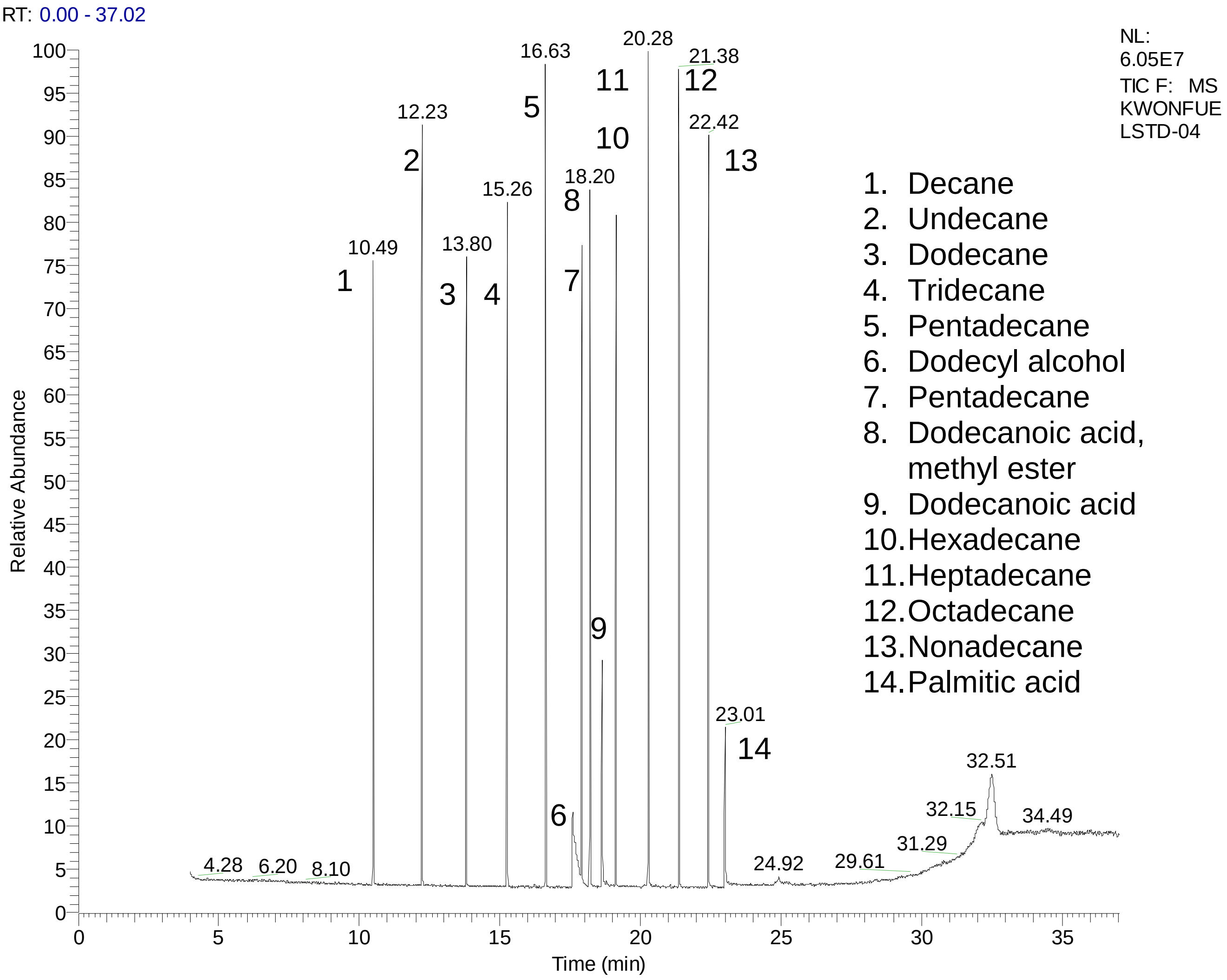
$CH_3(CH_2)_{10}COOCH_3 + 3H_2 \rightarrow CH_3(CH_2)_{10}CH_3 + H_2O + CH_4$

Conversion of Methyl Laurate into Undecane

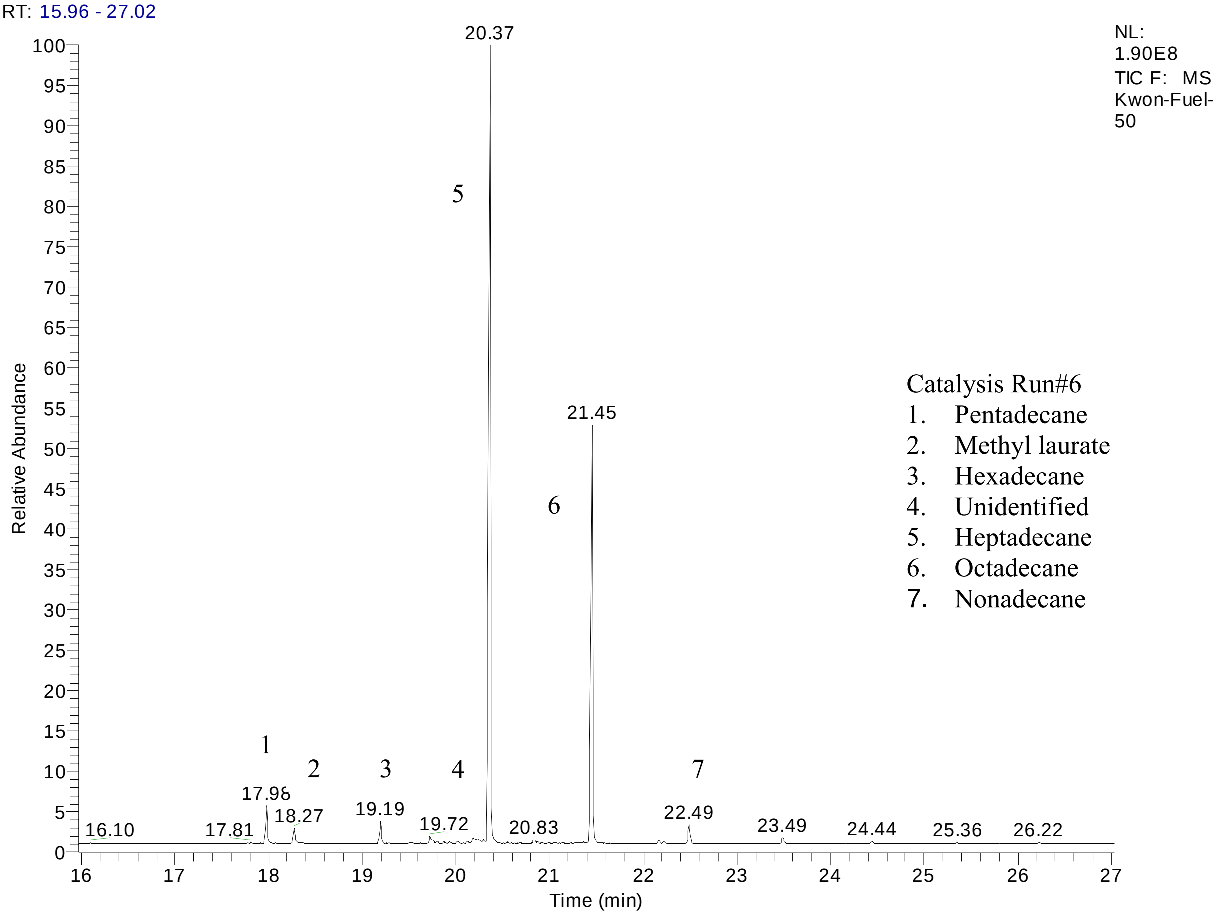
$CH_3(CH_2)_{10}COOCH_3 + H_2 \rightarrow CH_3(CH_2)_9CH_3 + CO_2 + CH_4$

Results

GC/MS Analysis: Identification/Quantitation Standard



Catalytic Hydrogenation of Canola Oil



Catalytic Hydrogenation of Methyl Laurate

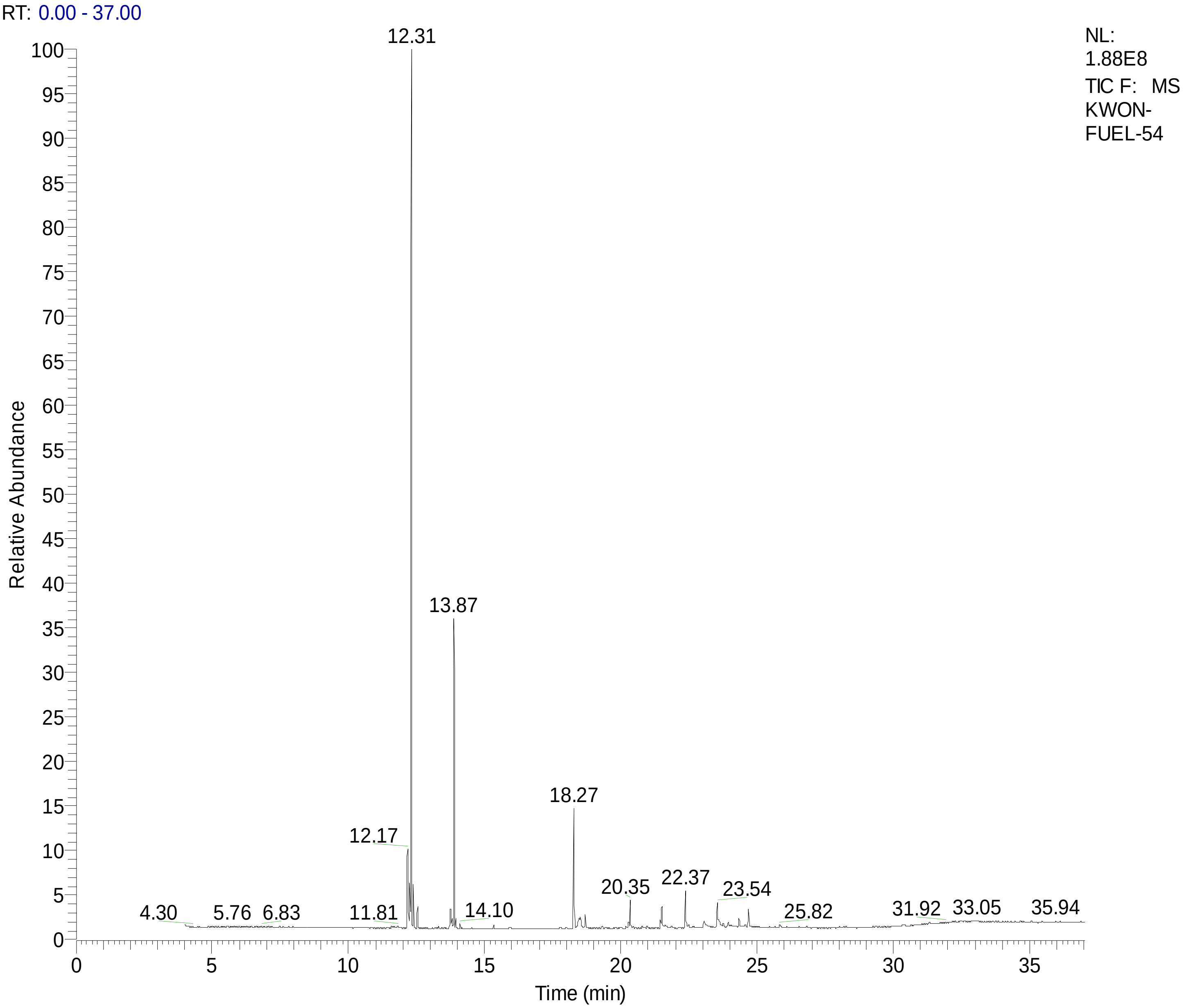


Table 1. Results on catalytic deoxidizing biomass at 300 – 400 °C and 250 - 1220 psig cold initial hydrogen pressure

	Run #	1	2	3	4	5	6	7	8	9	10	11	12	13
	Date	7/9/08	7/9/08	7/10/08	7/11/08	7/11/08	7/11/08	7/11/08	7/14/08	7/14/08	7/15/08	7/15/08	7/16/08	7/16/08
	Temp, oC	350	350	350	350	350	350	350	350	350	350	350	350	350
	Reaction Duration, min	30	30	30	30	30	30	30	30	30	30	30	30	30
Reactor Charge, g	NiMo catalyst	0.101	0.1038	0.1035	0.1010	0	0.1032	0.1003	0.1022	0.0512	0.0258	0.104	0.1259	0.1026
	Methyl Laurate	3.0200	1.8618	2.0011	1.9605	2.0128		1.9997	1.9325	2.0126	1.9935	1.971	1.9895	
	Canola Oil						2.0157							
	Spent Waste Kitchen Oil													1.9992
	Decane	6.863	3.0004											
H_2 Press, psig	t=0 min, T=25°C	na	na	680	330	670	650	520	670	670	660	660	680	670
	t=30 min, T=25°C	na	na	610	340	670	470	480	670	600	640	600	580	590
	t=30 min, T=T°C	na	na	1190	720	1100	840	930	1080	1130	1120	1120	1130	970
Liquid Products, Weight %														
	decane	73.07	53.80											
	undecane	3.22	2.29	39.03	33.38	1.81		40.17	0.91	41.58	11.20	55.17	60.65	8.10
	dodecane	1.54	1.66	28.84	10.49	0.51		18.20	0.21	24.06	4.15	31.73	34.67	
	dodecanol	0.00	11.99	8.37										
	methyl_laurate	20.89	24.28	9.08	8.16	95.22	1.58	6.27	75.44	12.48	25.64	6.45	0.79	5.40
	lauric_acid	1.69	2.34	1.32	2.67	2.35		2.60	21.44	4.49	6.81			
	hexadecane						1.82							
	heptadecane						57.23	1.13						44.57
	octadecane				3.62		34.50	1.64						20.26
	nonadecane				5.24		1.47	2.20		1.04				
	heptadecanoic_acid							3.53						
	unaccountable	-0.41	3.59	13.16	35.84	0	3.41	23.78	1.02	15.49	50.82	6.43	3.49	21.67
Gaseous Products	H_2 V % in gas product	na	na	na	48.95	98.28	43.59	49.41	96.46	78.82	90.4	79.3	77.88	95.65
	CH_4 V % in gas product	na	na	na	0	0	0	28.74	3.29	18.2	10.2	20.6	16.06	0
	H_2 Initial Amount , g	na	na	0.1363	0.0676	0.1343	0.1304	0.1049	0.1343	0.1343	0.1324	0.1324	0.1363	0.1343
	H_2 Consumption, g	na	na	na	0.0336	0.0023	0.0890	0.0569	0.0048	0.0393	0.0163	0.0367	0.0454	0.0209
	H_2 Consumption, w %, basis on initial H_2	na	na	na	49.63	1.72	68.214	54.286	3.54	29.24	12.28	27.75	33.3306	15.5257
	H_2 Consumption, %, basis on initial biomass	na	na	na	1.7120	0.1148	4.4133	2.8479	0.2461	1.9516	0.8154	1.8637	2.2834	1.0432
	CH_4 Production, g	na	na	na	0.0000	0.0000	0.0000	0.2219	0.0352	0.1746	0.1042	0.1977	0.1491	0.0000
	CH_4 Production, w %, basis on initial biomass	na	na	na	0.0000	0.0000	0.0000	11.099	1.8196	8.6772	5.2291	10.0032	7.4938	0.0000

Table 2. Results on catalytic deoxidizing biomass at 300 – 400 °C and 250 - 1220 psig cold initial hydrogen pressure

	Run #	14	15	16	17	18	19	20	21	22	23	24	25
	Date	7/21/08	7/21/08	7/21/08	7/21/08	7/22/08	7/22/08	7/22/08	7/23/08	7/23/08	7/23/08	7/23/08	7/23/08
	Temp, oC	350	350	300	325	375	375	400	350	350	350	350	350
	Reaction Duration, min	30	30	30	30	30	30	30	30	30	30	30	30
Reactor Charge, g	NiMo catalyst	0.102	0.0267	0.1053	0.1022	0.1008	0.1006	0.1008	0.1005	0.1006	0.2002	0.026	0.0505
	Methyl Laurate	1.9445	1.9986	2.0836	2.0003	1.9861			0.0000	0.0000	0	0	0
	Canola Oil						2.0303	1.9974	0.5012	1.006		2.044	2.0183
	Spent Waste Kitchen Oil								1.4912	1.036	1.9978	0	0
	Decane												
H_2 Press, psig	t=0 min, T=25ºC	360	670	670	660	660	660	660	660	670	670	670	670
	t=30 min, T=25ºC	370	670	590	530	610	570	520	570	590	470	410	525
	t=30 min, T=TºC	590	1110	940	930	1190	980	1020	980	1015	820	700	900
Liquid Products, Weight %		Run 14	Run 15	Run 16	Run 17	Run 18	Run 19	Run 20	Run 21	Run 22	Run 23	Run 24	Run 25
	decane												
	undecane	5.45	5.20	1.49	3.54	42.18							
	dodecane	1.99	2.07	1.44	2.33	17.19							
	dodecanol												
	methyl_laurate	51.67	68.45	82.78	67.93	7.92	5.65	8.83	3.80	3.01	3.50	1.01	1.46
	lauric_acid	24.87	14.63	12.05	19.47	4.74							
	hexadecane						1.61	2.33	1.39	1.28	1.42		
	heptadecane						27.78	33.19	20.30	19.37	14.82	8.80	14.20
	octadecane						10.63	11.78	10.21	11.30	8.13	2.39	4.61
	nonadecane												
	heptadecanoic_acid						9.69	6.39	8.10	10.43	16.16	8.29	6.93
	unaccountable	15.50	9.13	1.98	6.46	27.70	40.01	35.23	55.42	53.86	55.33	78.98	71.88
Gaseous Products	H_2 V % in gas product	89	98.84	99.86	96.6	86	96.67	92.83	98.3	99.5	95	98.61	96.34
	CH_4 V % in gas product	11.3	4.18	3.21	5.9	12.34	0	0	0	0	0	0	0
	H_2 Initial Amount , g	0.0735	0.1343	0.1343	0.1324	0.1324	0.1324	0.1324	0.1324	0.1343	0.1343	0.1343	0.1343
	H_2 Consumption, g	0.0063	0.0016	0.0159	0.0291	0.0270	0.0215	0.0350	0.0196	0.0163	0.0440	0.0522	0.0323
	H_2 Consumption, w %, basis on initial H_2	8.625	1.16	11.808	22.013	20.373	16.225	26.432	14.812	12.13	32.749	38.84	24.0621
	H_2 Consumption, %, basis on initial biomass	0.3261	0.0780	0.7613	1.4567	1.3579	1.0579	1.7517	0.9841	0.7978	2.2021	2.5525	1.6015
	CH_4 Production, g	0.0679	0.0447	0.0303	0.0502	0.1203	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
	CH_4 Production, w %, basis on initial biomass	3.4898	2.2354	1.4542	2.5079	6.0588	0.0000	0.000	0.0000	0.0000	0.0000	0.0000	0.0000
Gas Product mass, g	Total	0.404	0.3883	0.3442	0.2657	0.4913	0.4692	0.419	0.3785	0.344	0.3687	0.245	0.34234
	H_2	0.067	0.1328	0.1185	0.1032	0.1054	0.1109	0.0974	0.1128	0.118	0.0903	0.082	0.10201
	Others	0.337	0.2555	0.2257	0.1625	0.3859	0.3583	0.3216	0.2657	0.226	0.2784	0.163	0.24033
Gasified Biomass, w %, basis on initial biomass		17.34	12.78	10.83	8.12	19.43	17.65	16.10	13.34	11.07	13.93	7.96	11.91

Table 3. Results on catalytic deoxidizing biomass at 300 – 400 °C and 250 - 1220 psig cold initial hydrogen pressure

	Run #	26	27	28	29	30	31	32	33	34	35	36	37
	Date	7/24/08	7/24/08	7/24/08	7/24/08	7/24/08	7/25/08	7/25/08	7/29/08	7/29/08	7/29/08	7/29/08	7/29/08
	Temp, oC	350	350	350	350	350	350	350	350	350	350	350	350
	Reaction Duration, min	30	30	60	30	60	30	30	30	30	30	30	
Reactor Charge, g	NiMo catalyst	0.076	0.1016	0.1	0.1002	0.1015	0.1004	0.0999	0.1007	0.1017	0.1002	0.102	0.1002
	Methyl Laurate	0	0	0	0	0	1.9797	0					
	Canola Oil	2.042	1.9954	2.0042	2.0005	2.0379	0	2.0145					
	Spent Waste Kitchen Oil												
	canola biodiesel								2.0448				
	spent Oil biodiesel									2.006			
	NSWC-02 (6/13/08)										2.0468		
	Energy BLD 9738 (1/8/08)											2.008	
	wallace biodiesel 7/13/08												2.035
	Decane												
H_2 Press, psig	t=0 min, T=25°C	670	670	660	250	1220	660	670	660	660	660	650	660
	t=30 min, T=25°C	620	490	185	220	500	610	580	585	580	650	590	610
	t=30 min, T=T°C	1020	870	370	350	940	1120	1020	1020	980	1060	1000	1040
	decane												
	undecane						14.41				1.60		
	dodecane						12.32				1.49		
	dodecanol											3.19	1.38
	pentadecane				1.45	4.76		1.70	1.25	1.66	4.52		
	methyl_laurate	1.85	2.10	1.82			57.58	3.72			2.59		
	lauric_acid						8.51						
	hexadecane					1.75					2.20		
	heptadecane	19.64	20.58	16.18	17.07	46.97		17.15	12.98	8.08	21.66	6.40	4.77
	octadecane	6.22	6.54	3.78	4.85	23.35		10.20	4.64	2.21	14.16	1.88	1.33
	nonadecane					1.70			2.40		3.47	6.64	7.56
	heptadecanoic_acid	4.86	5.31	5.18	2.77			3.63		2.81		3.62	5.33
	unaccountable	66.24	64.03	71.80	72.73	21.20	5.46	60.76	77.52	84.72	46.43	77.56	78.99
Gaseous Products	H_2 V % in gas product	99.67	97.87	81.12	91.37	90.42	91.31	95.37	92.32	94.52	96.14	95.11	97
	CH_4 V % in gas product	0.00	0.00	0.00	0.00	0.00	7.86	0.00	7.39	6.09	2.93	4.99	3.93
	H_2 Initial Amount , g	0.1343	0.1343	0.1324	0.0519	0.2422	0.1324	0.1343	0.1324	0.1324	0.1324	0.1304	0.1324
	H_2 Consumption, g	0.0102	0.0374	0.1006	0.0099	0.1509	0.0205	0.0231	0.0238	0.0221	0.0070	0.0176	0.0135
	H_2 Consumption, w %, basis on initial H_2	7.608	27.856	75.989	18.982	62.306	15.456	17.167	17.942	16.69	5.2849	13.48	10.1884
	H_2 Consumption, %, basis on initial biomass	0.5005	1.8753	5.0189	0.4928	7.4062	1.0335	1.1447	1.1615	1.1011	0.3418	0.8754	0.6627
	CH_4 Production, g	0.0000	0.0000	0.0000	0.0000	0.0000	0.0767	0.0000	0.0692	0.0565	0.0304	0.0471	0.0383
	CH_4 Production, w %, basis on initial biomass	0.000	0.000	0.000	0.000	0.000	3.874	0.000	3.383	2.818	1.485	2.346	1.883
Gas Product mass, g	Total	0.338	0.334	0.291	0.2989	0.4533	0.4006	0.4067	0.330	0.407	0.423	0.435	0.401
	H_2	0.124	0.097	0.032	0.0421	0.0913	0.1119	0.1113	0.109	0.110	0.125	0.113	0.119
	Others	0.214	0.237	0.259	0.2568	0.362	0.2886	0.2954	0.221	0.296	0.297	0.322	0.282
Gasified Biomass, w %, basis on initial biomass		10.48	11.90	12.93	12.84	17.76	14.58	14.66	10.83	14.77	14.52	16.04	13.84
Remarks													