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2. Project title: Energy and Nutrient Recovery from Co-Solvent Hydrothermal Liquefaction of Wastewater-Grown Algae

3. Description of research problem and research objectives.

Among plenty of biomass, algae have been developed rapidly, which can grow in both fresh and saline water even non-arable lands among the fastest-growing plants in the world, and can convert sunlight in the form of energy-rich organic compounds[1]. *Galdieria sulphuraria*, an acidophilic and moderately thermophilic algae, has an outstanding ability for eliminating BOD (biochemical oxygen demand), nitrogen and phosphorous from primary-settled wastewater[2], which indicates the potential application of *G. sulphuraria* on wastewater treatment and preventing eutrophication. Therefore, *G. sulphuraria* is selected as algal feedstock to cultivate in the primary-settled wastewater by Dr. Nagamany Nirmalakhandan's group in NMSU, Las Cruces, NM. in a low-cost, closed photobioreactor (PBR)[2]. It shows that the growth rate of *G. sulphuraria* in the primary-settled wastewater is comparable to those in the control medium[3,4]. Furthermore, among several algal biorefinery processes, hydrothermal liquefaction (HTL) has been considered as one of promising thermochemical conversion for biofuel production. In our previous research on HTL, it has been proved that *G. sulphuraria*, presented low-lipid algae, retains the highest yield of bio-crude oil (~31%)[5]. Additionally, the quality of bio-crude oils from *G. sulphuraria* is not as good enough to become potential bio-fuel alternative. The bio-crude oils has high fractions of nitrogen (4-5%) and oxygen (3%)[6] compared with petroleum fuel. In this research, we aim to promote the production of bio-crude oils, and to enhance energy and nutrient recovery with addition of alcohols (ethanol, isopropanol and glycerol) as co-solvents into HTL of *G. Sulphuraria*. Also, we will explore the influences of alcohols with water on optimized condition of HTL, product distribution and characterization. which provides a basis for building up an algal wastewater treatment-HTL system.

Objectives
(1) evaluate the yield and quality of bio-crude oil from G. sulphuraria when alcohols were added;
(2) study the possible mechanisms of different alcohols promoting bio-crude oil production;
(3) investigate the feasibility of wastewater treatment (WWT) algal HTL with crude glycerol, in terms of productivity and quality of bio-crude oil, to explore the possibility of integrating the wastewater treatment process with the biodiesel production by co-solvent HTL.

4. Description of methodology employed.

The freshwater microalgae used, *Galdieria sulphuraria*, were provided by NMSU Algal Growth Facility. *WWT G. sulphuraria* was cultivated using a 700 L photobioreactor (PBR) fed with primary-settled wastewater at the Las Cruces Wastewater Treatment Plant (Las Cruces, NM). Crude

glycerol was provided from Rio Valley Biofuels (El Paso, TX). Rio Valley Biofuels (El Paso, TX) is a biofuel industry which use cottonseed and corn as feedstock to produce biofuels. HTL experiments have been performed in a 1.8 L Model 4572 stainless steel batch reactor with a Model 4848B controller unit (Parr Instrument Co., Moline, IL) in the presence of four different alcohols: ethanol (EtOH), isopropanol (IPA), glycerol (GLY) and crude glycerol (CGLY) as co-solvents. After the reactor cooling down, the product was separated to three phases: solid residue, aqueous phase and bio-crude oil. The experiment condition matrix is shown in Table 1.

Table 1: Experimental Conditions

Run Number	Temperature, °C	Time, min	Composition		
			Algae Solids Loading, wt.%	Co-solvent	Co-solvent Mass Ratio, wt.%
G. sulphuraria					
1	310	30	5	-	-
2	310	30	5	EtOH	40
3	310	30	5	IPA	40
4	310	30	5	GLY	40
5	330	30	5	GLY	40
6	350	30	5	GLY	40
WWT *G. sulphuraria*					
7	350	30	-	CGLY	100
8	350	30	5	CGLY	100
9	350	30	10	CGLY	100

To set up a mass balance and energy balance, the composition of bio-crude oils was analyzed by Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS). Bio-crude oils and solid residue were analyzed by CHNS elemental analysis. To study the nutrients from aqueous phase, total organic carbon (TOC) and total nitrogen (TN) of the aqueous phase products were measured.

For HTL with water and ethanol or isopropanol, the product yield was calculated as:

$$Y_i = \frac{W_i}{\text{Dry algal weight}} \times 100\% \quad (1)$$

For HTL with water and glycerol or crude glycerol, the product yield was calculated as:

$$Y_i = \frac{Weight_i}{\text{Dry algal weight} + W_g} \times 100\% \quad (2)$$

where, Y_i is the yield of product fraction, W_i is the weight of each product fraction, and W_g represents the weight of glycerol or the weight of organic compounds in crude glycerol, i represents LBO, HBO, char, and non-volatile residue in the aqueous phase.

5. Description of results; include findings, conclusions, and recommendations for further research.

Product yield and Elemental Analysis

Figure 1 shows the product yields calculated by Eq. 1 based on dried algae weight. For *G. sulphuraria*, LBO yields showed significant increments with different co-solvents compared to water alone: 23.7-24.9 wt.% with co-solvents were approximately twice that of water (12.9 wt.%). GLY and IPA gave the highest LBO yields (24.9 wt.% at 310 °C for 30 min.) while EtOH was lower (23.7 wt.%). (The yields of non-volatiles in the aqueous phase of GLY-HTL were >100% calculated by dry algae base, so they are not shown in Figure 1.) GLY-HTL produced HBO under the same conditions, whereas other co-solvent- or water-HTL did not, which indicates that GLY favors biomass conversion into the heavy oil phase. Char yields decreased from 18.0 wt.% to 8.0 wt.%, 11.2 wt.% and 6.2 wt.% with EtOH, IPA, and GLY respectively, which suggests co-solvents favor the conversion of bio-crude oil. This resulted from the ability of alcohols as hydrogen donors to stabilize the fragments and prevent the condensation, cyclization, and re-polymerization of free radicals to reduce char formation [7]. Similar results have been reported by Hu et.al for co-HTL of algae biomass and sawdust in ethanol-water solvent. Co-solvents provide more free radicals to promote biomass cleavage and oil formation [8]. With temperature increasing, LBO yield of GLY-HTL increased up to 73.2 wt. %. Also, GTL-HTL at 350°C for 5 min achieved higher LBO yield (59.2 wt.%) than that at 310 °C for 30 min (24.9 wt.%), which is consistent with previous conclusions: temperature is the most important factor on bio-crude oil yield [1], and higher temperature reactions favor conversion of low-lipid algae [5].
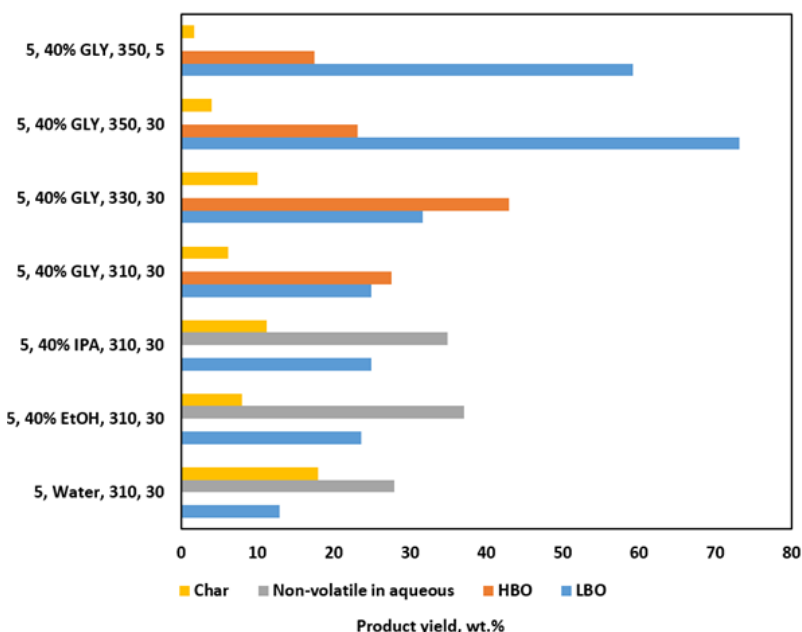

Figure 1: Product yield of HTL of *G. sulphuraria* with/without co-solvents calculated by Eq.1

Figure 2(a) shows the product yield of *G. sulphuraria* of GLY-HTL calculated by Eq.2, based on the total mass of dry algae and pure GLY. The most abundant product was non-volatile residue in the aqueous phase, which reached 59.4-86.1 wt. %, while the LBO yields were as low as 2.89-8.83 wt. %. This illustrated that most of the glycerol contributed to the aqueous phase while some helped increase the LBO yield. With temperature increasing, the yields of non-volatile residue in the aqueous phase decreased from 82.1% to 59.1%, which indicates that high temperature promoted organic compounds from the aqueous phase into the oil phase. The difference in yield results

between the two equations demonstrates that GLY provided hydrogen atoms and also reacted with biomass fragments. Smarrito et al. reported that glycerol provides precursors to participate in Maillard reaction with protein, and plays the same role as sugars [9].

The combination of WWT *G. sulphuraria* and CGLY achieved much higher increases in bio-crude oil production. The mixed slurry of 5 wt.% algae and CGLY produced 66.2 wt.% LBO at 350°C for 30 min. (Figure 2(b)). The absolute value of LBO mass was 216 g out of 324 g organic compounds from dry algae + CGLY. The same amount of CGLY (no algae) achieved 59.2 wt.% LBO under the same conditions. When the algae solids loading was increased from 5 wt.% to 10 wt.%, LBO yield decreased slightly from 66.2 wt.% to 59.3 wt.%, which means that CGLY might contributed more than algae for bio-crude oil production.
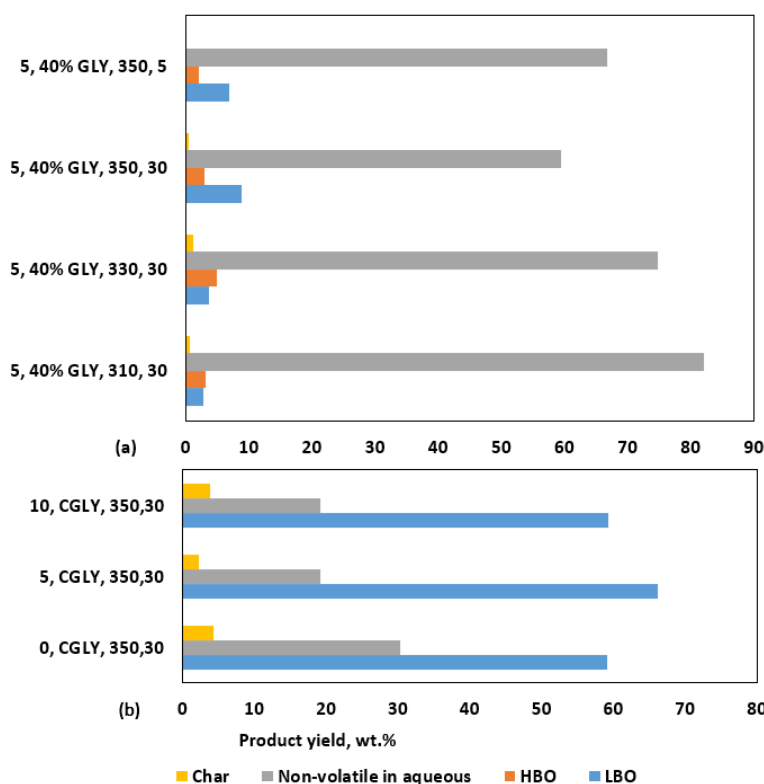

Figure 2: Product yield of (a) *G. sulphuraria* **of HTL with GLY (b) WWT** *G. sulphuraria* **with crude CGLY calculated by Eq. 2**

Table 2 showed the elemental distribution (carbon, hydrogen, nitrogen and oxygen) in light biocrude oils. At the same temperature of 310°C, the LBOs from HTL with co-solvents have a higher H/C ratio (1.50-1.75) higher O/C ratio (0.03-0.23) than LBO from water-HTL (1.48 and 0.03 respectively). EtOH-LBO has a lower N/C ratio (0.04) while others have a higher N/C ratio (0.05-0.05) than water-LBO (0.05). With temperature increasing, GLY-LBOs have a higher N/C (0.07) and O/C ratio (0.12), which is consistent with the result of LBO yield and TOC/TN results. High temperature is beneficial to the conversion of small fragments from aqueous to oil phase.

Total organic carbon (TOC) concentrations in the aqueous phase (135-202 g/L) from co-solvent HTL were much higher than that (8.7 g/L) from water-HTL under 310 °C and 30 min (Table 3). The recovered amount of carbon (62-87 g) in the aqueous phase were far more than the starting amount of carbon (11.6 g) from the algae. This result is in agreement with that reported in Han

et.al 's [7]. The "excess" carbon is a consequence of co-solvents incorporating into the aqueous phase and the inhibition of char formation. For GLY-HTL, TOC concentrations decreased as temperature increased from 310 to 350 °C, indicating that higher temperature promoted organic compounds fractionating into the oil phase. By total mass and density of the aqueous phase, the absolute mass value of TOC and TN can be calculated (Table 3). Absolute TN mass (0.31-0.41 g) in the aqueous phase from co-solvent HTL decreased compared to the value (1.64 g) of water-HTL. This is attributed to the ability of co-solvents to extract more protein fragments from the aqueous phase into the oil phase, which was also supported by the yield increases in LBO obtained from co-solvent HTL.

Table 2: Elemental distribution in light biocrude oils

Reaction Condition (Algae species, Solid content wt.%, Solvent, Temperature °C, Time min)	Elemental analysis, wt.%							
	C	H	N	S	O	H/C	N/C	O/C
GS, 5, Water, 310, 30	78.54±0.21	9.67±0.05	4.75±0.02	3.44±0.04	3.62±0.11	1.48	0.05	0.03
GS, 5, EtOH, 310, 30	64.81±0.89	9.45±0.04	3.07±0.11	3.04±0.08	19.64±0.45	1.75	0.04	0.23
GS, 5, IPA, 310, 30	77.30±0.16	9.70±0.21	5.35±0.06	3.20±0.11	4.39±0.14	1.50	0.06	0.04
GS, 5, GLY, 310, 30	78.69±0.52	10.40±0.34	4.43±0.16	2.95±0.09	3.54±0.32	1.59	0.05	0.03
GS, 5, GLY, 330, 30	73.69±0.45	8.14±0.00	5.91±0.12	2.61±0.35	9.66±0.29	1.32	0.07	0.10
GS, 5, GLY, 350, 30	72.46±0.45	8.57±0.02	4.76±0.11	2.27±0.09	11.95±0.24	1.42	0.06	0.12
GS, 5, GLY, 350, 5	73.57±0.12	7.94±0.06	5.54±0.04	2.48±0.05	10.48±0.07	1.30	0.06	0.11
WWTGS, 0, CGLY, 350, 30	74.40±0.02	10.34±0.29	0.14±0.00	1.90±0.02	13.23±0.15	1.67	0.00	0.13
WWTGS, 5, CGLY, 350, 30	72.74±0.10	9.90±0.12	0.93±0.03	1.87±0.14	14.58±0.10	1.63	0.01	0.15
WWTGS, 10, CGLY, 350, 30	68.79±0.79	9.88±0.03	2.66±0.08	3.41±0.13	15.27±0.40	1.72	0.03	0.17

Table 3: Total Organic Carbon (TOC) and Total Nitrogen (TN) analysis of Aqueous Phase

Reaction Condition (Solid content wt.%, Solvent, Temperature °C, Time min)	Aqueous Phase			
	TOC, g/L	TOC mass, g	TN, g/L	TN mass, g
G. sulphuraria				
5, Water, 310, 30	8.67	4.25	1.43	1.64
5, 40% EtOH, 310, 30	140.26	71.01	0.74	0.37
5, 40% IPA, 310, 30	135.15	62.09	0.68	0.31
5, 40% GLY, 310, 30	202.07	86.98	0.96	0.41
5, 40% GLY, 330, 30	158.80	70.12	1.38	0.61
5, 40% GLY, 350, 30	135.14	60.02	2.00	0.87
5, 40% GLY, 350, 5	154.36	66.76	2.14	0.93
WWT *G. sulphuraria*				
0, CGLY, 350,30	142.63	32.34	3.00	0.68
5, CGLY, 350,30	181.95	47.30	0.18	0.05
10, CGLY, 350,30	93.54	25.77	3.67	1.01

FTIR Analysis

Figure 3a shows the FTIR results of *G. sulphuraria* feedstock, LBO and HBO from HTL of 40%glycerol-HTL respectively. Consistent with our previous study[5], the typical peaks of *G. sulphuraria* feedstock including N-H stretching, C=O stretching (amide I band, 1643 cm−1), and N-H bending (amide II band, 1519 cm^{-1}), indicates the presence of proteins whereas the C-O-C stretching peak (1188–900 cm^{-1}) indicates the presence of carbohydrates. The P=O stretching peak1341–1188 cm^{-1}) is due to the phosphodiesters in the algal nucleic acids and phospholipids[4]. During the HTL with co-solvent/water, N-H stretching (amide II band), P=O stretching, and C-O-C stretching peaks disappeared as heteroatom-containing group were produced. The peaks of C-H stretching (2957, 2924 and 2854 cm^{-1}), C-H bending (1456 and 1377 cm^{-1}) and trans =C-H out of plane bending (954 cm^{-1}) are more obvious in the LBO of 40%glycerol-HTL, which suggests the presence of hydroxyl groups, such as unsaturated aliphatic groups[11]. By contrast, the intensities of C=O (1707 cm^{-1}), C-O (1216cm^{-1}), C-N stretching (1220-1041 cm^{-1}) and C(aromatic)=H out-of-plane (803-700 cm^{-1}) and C-X stretching (529cm^{-1}) are stronger in the HBO than LBO, which indicates that the heteroaromatic compounds increased such as ketones and phenolic derivatives. Also, the strong intensity at 3314cm^{-1} presents the O-H stretching in the HBO. The results may indicate that glycerol promotes the formation of heavy heteroaromatic molecules into HBO phase, while light unsaturated aliphatic compounds remains in LBO.

FTIR spectra for LBOs from HTL with different co-solvents are shown in Figure 3b. The peaks of N-H stretching (3400-3200 cm^{-1}), C-H stretching (2957, 2924 and 2854 cm^{-1}), C=O (1739-1671 cm^{-1}), C-H bending (1456 and 1379 cm^{-1}), and C(aromatic)-H out-of-plane bending peaks (803-700 cm^{-1}) were present in spectra with/without co-solvents, which implies the generation of fatty acid amides and heteroatom-containing, unsaturated aliphatic and cyclic compounds. The typical carbonyl group (C=O) stretching vibrations between 1710 and 1665 cm^{-1} indicate the presence of aldehydes, ketones, or carboxylic acids [12]. In the spectrum of LBO from EtOH-HTL, the peak appeared around 1739 cm^{-1} is attributed to the esterification of fatty acids, whereas the peak at 1710cm^{-1} might be due to ketones or aldehydes shown in all four spectra [13]. In the spectrum for LBO from IPA-HTL, there was a significant peak (1667 cm^{-1}) which indicated the presence of amides, most likely from cyclic amides and/or carbonyl compounds produced by amidation, rearrangement, and Maillard reactions of proteins and carbohydrates in *G. sulphuraria* microalgae [14]. At 1261cm^{-1}, the intensity of the peak in EtOH-HTL was much higher from other three, which presents C-O stretching. Also, the LBO of EtOH-HTL had stronger intensities at the peaks of 1108, 1028 and 807cm^{-1}. EtOH-HTL produced LBO with strong peaks of C-O stretching of ether (1260-1000 cm^{-1}) and para-aromatic structure (807 cm^{-1}) [15]. The strong peak of trans-C-H out-of-plane bending (955 cm^{-1}) appeared in the LBO of IPA-HTL and GLY-HTL spectra, while could hardly be seen in the LBO from water-HTL and EtOH-HTL. This finding may indicate that the addition of glycerol and isopropanol, favored to produce unsaturated aliphatic compounds rather than aromatic compounds. The peak of 1554 cm^{-1} disappeared in the spectrum from GLY-HTL, which suggests a decrease of C=N from imines or C=C from aromatic structures in LBO. This result is consistent with [16]. Overall, LBO composition with/without co-solvents was similar with slight differences. Ethanol co-solvent favored production of more ether, ester, and para-aromatic structures [13], while glycerol and isopropanol produced more trans-alkene structures.
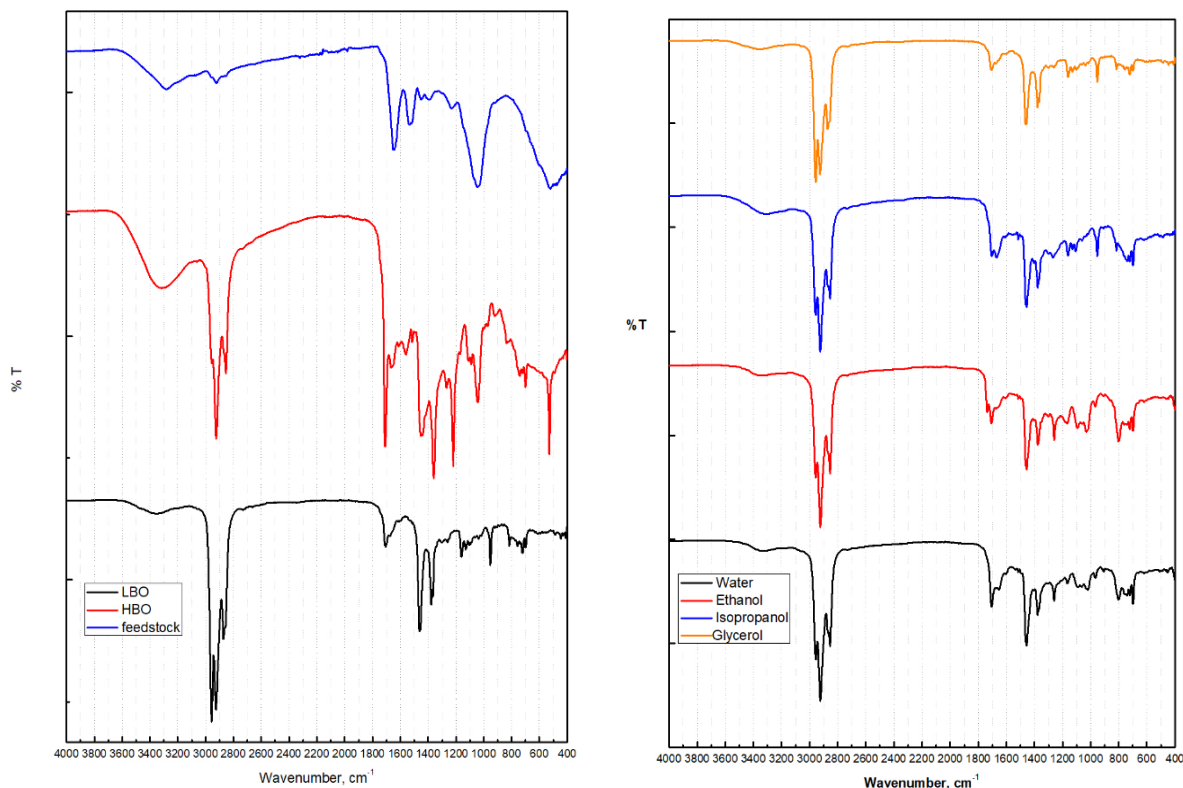
Figure 3: FITR Spectra of (a) algae feedstock, LBO and HBO from HTL of *G. sulphuraria* 40 wt.% GLY at 310°C for 30 min; (b)LBOs obtained from HTL of *G. sulphuraria* with pure water and 40 wt.% co-solvents at 310°C for 30 min.

FT-ICR MS analysis

Results of heteroatom class in LBOs from HTL with/without co-solvents at 310°C for 30 min were shown in Figure 4. Generally, the main heteroatom classes with/without co-solvents were similar: N_1O_{0-2}, N_2O_{0-2} and N_3O_{0-2}. The total relative abundance (%RA) of these classes was more than 70% of the summed abundance. With different co-solvents, the abundance of each class had different changes compared to water-HTL, suggesting the different mechanisms of co-solvents. Combined with the isoabundance-color contour plots of double bond equivalent (DBE) versus carbon number, an insight of the mechanisms of co-solvents in HTL was explored.
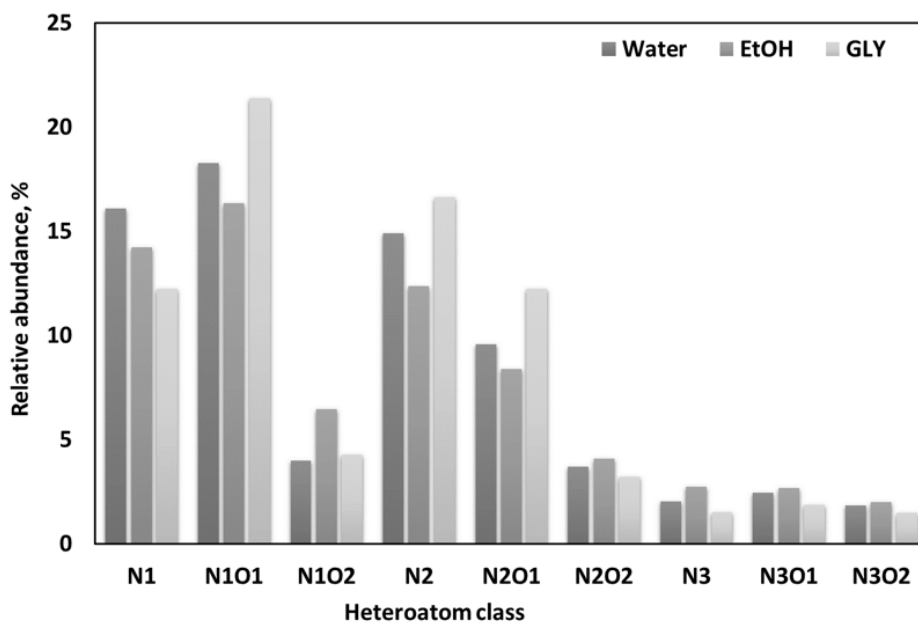
Figure 4: Heteroatom class distribution of LBOs produced from HTL of *G. sulphuraria* with pure water and 40 wt.% co-solvents at 310 °C for 30 min. EtOH: ethanol, and GLY: glycerol.

Effect of Ethanol

Figure 5 shows the compositional space distribution for the N_1O_{0-2} and N_2O_{0-2} species derived from the LBO from water-HTL and EtOH-HTL. LBO from EtOH has more unique N_1O_{0-2} species with low DBE of 1-4, whereas water-HTL contained more unique species with high DBE of 4-10. For the N_1O_1 class, Figure 5(a) shows the compositional space coverage of the EtOH LBO (C_6-C_{31} and DBE of 1-3) is broader and contains species with higher relative abundance than those in water LBO, indicating more fatty amide diversity within the EtOH LBO [17]. Similarly, for N_1O_2 class, the EtOH-LBO has a higher relative abundance of species at C_{22}-C_{28} and DBE of 1-3 than the water-LBO, which correlate with the esters with piperidine, amino acid esters and alkyl-substituted amides.

For the N_2 class, the EtOH-LBO has a higher relative abundance of more alkylated species (C > 15) than the water-LBO. There is an accelerating capability on the formation of mutagenic products for Maillard reaction in ethanolic system [18]. LBO with DBE >5 species are suspected to be amino-pyridine, quinoxaline and benzo-imidazole [17]. This accelerating ability is also observed in N_3 class (Figure 4). The proposed molecules of N_3 class are alkylated amino-imidazoles and amino-pyrazines [18]. For the N_2O_1 class, both water-LBO and EtOH have the same series of abundant species (C_6-C_{15} with DBE =4), which are likely oxygenated alkyl-imidazoles [17]. EtOH-LBO has a higher relative abundance of compounds of C_{15}-C_{25} with DBE of 7-12 than water-LBO, indicating the generation of more aromatic species with water as the co-solvent. For the N_2O_2 class, the relative abundance of the more alkylated species (e.g., outside of the red oval) in the water-LBO is higher than that in the EtOH-LBO, especially the species between C_{40}-C_{50} with DBE of 2-5. These species might include cyclic dipeptides such as diketopiperazines (DKP) formed by peptide coupling and cyclization of two amino acids [19]. Under reductive environment, cyclic dipeptides form to pyrazines [20]. It is likely that ethanol provides a reductive condition to promote this reaction.
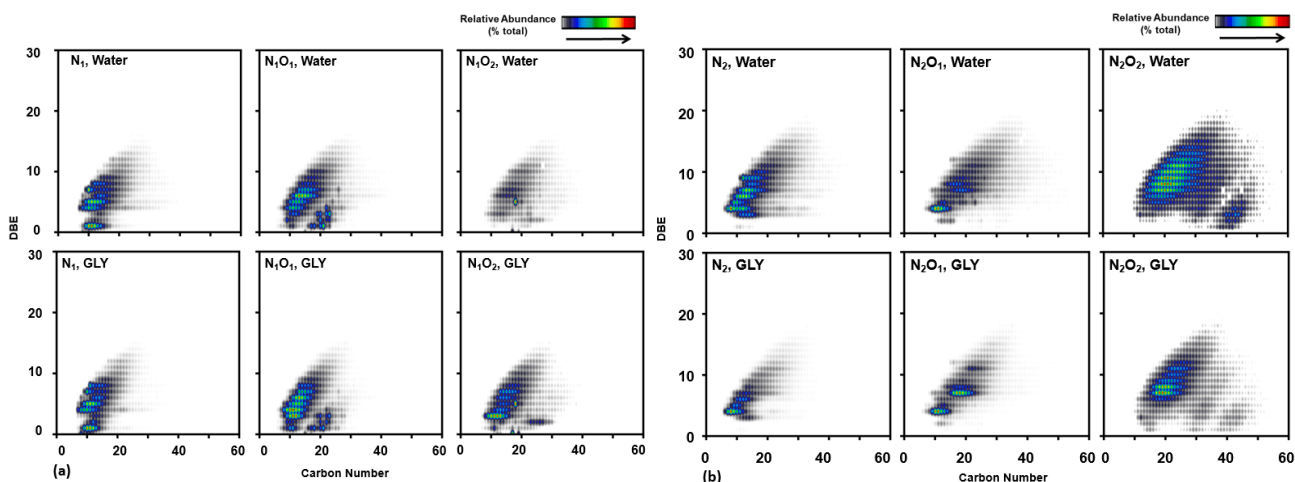
Figure 5: Color-coded abundance–contoured plots of DBE versus carbon number for heteroatom classes in LBOs from water and 40% EtOH under 310 °C and 30 min derived from FT-ICR MS. EtOH: ethanol.

Effect of Glycerol

The heteroatom class distribution of the GLY-LBO shows a higher relative abundance of N_1O_1, N_1O_2, N_2 and N_2O_1 species that the water or EtOH LBO. As shown in Figure 6, the most abundant species within the N_1O_1 and N_1O_2 classes (C_8-C_{18} with DBE of 3-8) of GLY-LBO cover broader compositional space and have more abundance of species at lower DBE values than that water-LBO, whereas water-LBO has a higher relative abundance of species at higher carbon numbers and DBE values (C >16 and DBE >7) than GLY-LBO. For the N_2 class, the compositional space coverage in GLY-LBO is less broad (particularly in carbon number) than that in water-LBO, whereas the N_2 species in GLY-LBO have a broader distribution of highly abundant species ranging from C_8-C_{20} and DBE 3-11. Those N_2 compounds of C_8-C_{14} with DBE of 4-7 are likely indole-amines, pyrazines and pyridines. Glycerol is not only a hydrogen donor, but can also participate in Maillard reactions [9]. Cerny and Dubini used ^{13}C-labled glycerol to propose that glycerol provides carbon atoms to pyrazine, which is the main product of the Maillard reaction between amino acids and reduced sugar [21]. The glycerol dehydration products, 2-oxopropanal and glyceraldehyde, are the intermediates. For the N_2O_1 class, the diversity of compounds in GLY-LBO is lower than water-LBO. The most abundant species within the N_2O_1 class of GLY-LBO range from C_{10}-C_{16} with DBE of 4 and C_{15}-C_{23} with DBE of 7, whereas the most alkylated species (e.g. higher carbon number per DBE) within the in water-LBO are either not present or are of lower relative abundance within the GLY-LBO.
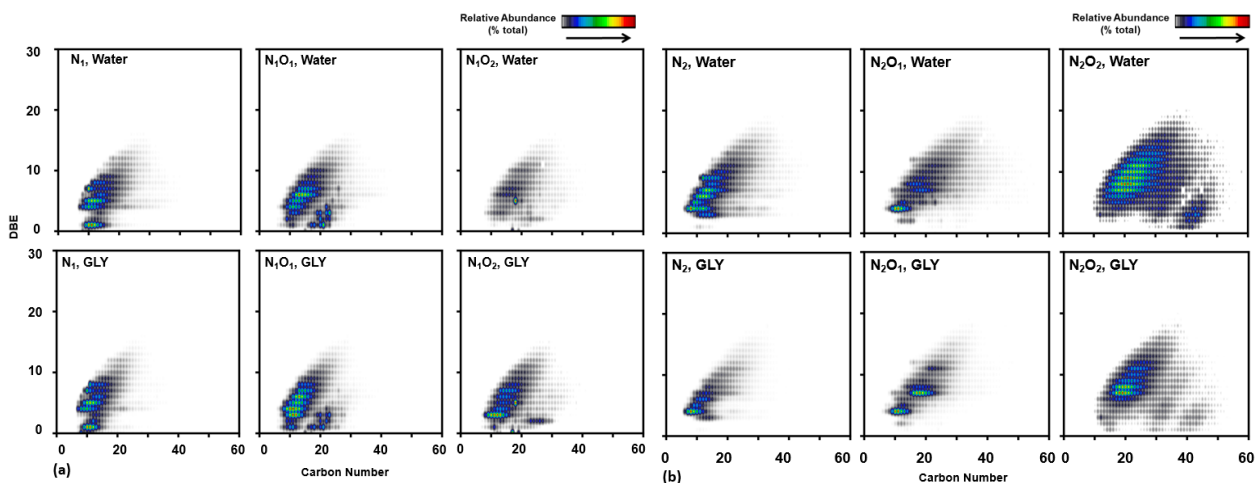
Figure 6: Color-coded abundance–contoured plots of DBE versus carbon number for heteroatom classes in LBOs from water and 40% GLY under 310 °C and 30 min derived from FT-ICR MS. GLY: glycerol.

Thermogravimetric analysis of feedstock and light bio-crude oils

Figure 7 shows the thermogravimetry (TG) and the differential thermogravimetric (DTG) curves for algae biomass and CGLY. There was almost no difference between the curves of *G. sulphuraria* and *WWT G. sulphuraria*, which is consistent with [5]. Algae biomass has a fast weight loss between 220-320°C due to the decomposition of its high protein content. Unlike algae biomass, CGLY showed three main stages of weight loss. The first stage was at 150-220°C (weight loss approximately 40 wt.%), which was ascribed to the decomposition of pure GLY [22]. The second stage happened at 300-380 °C (weight loss approximately 20 wt.%), which corresponds to the degradation of impurities such as fatty acids methyl esters [23]. The third stage was at 420-460 °C (weight loss approximately 10 wt.%), due the continuous degradation of residual impurities, coke, and ash [23]. The residual mass of crude glycerol was around 2 wt.%; the residue of algae biomass was much higher (20 wt.%).

Figure 8 shows the TG and DTG curves for LBOs obtained from water- and co-solvent HTL at 310°C for 30 min. LBO from IPA-HTL had a similar boiling point distribution compared to that from water-HTL; both LBO samples had higher residue rate (5.0%) than LBO from GLY-HTL (2.80%) and ethanol-HTL (2.31%). The first weight loss peak temperatures of water-LBO, EtOH-LBO, IPA-LBO, and GLY-LBO were 243 °C, 241 °C, 258 °C and 227 °C, respectively, and EtOH-LBO had strong second (408 °C) and third (623 °C) peak temperatures while the others LBO samples did not. The two main coke oil types of the LBO were diesel oils and lubricating oils (Table 3). EtOH-LBO and IPA-LBO contained fewer low-boiling-point (<250 °C) compounds than water-LBO, while GLY-LBO produced more low-boiling-point compounds. The addition of CGLY increased the fraction of high-boiling-point compounds. As shown in Tableb4, the two main coke oil types of LBOs were diesel oils and lubricating oils. EtOH-LBO and IPA-LBO contained a less fraction of low-boiling-point (<250°C) compounds than water-LBO, which occupied 37.88%, 44.11% and 50.31% respectively, whereas GLY-LBO had more low-boiling-point compounds (63.65%). On the contrary, the addition of crude glycerol increased the high-boiling-point compounds. The LBO of WWT G.s with crude glycerol at 350C contained 41.53% low-boiling-point compounds.
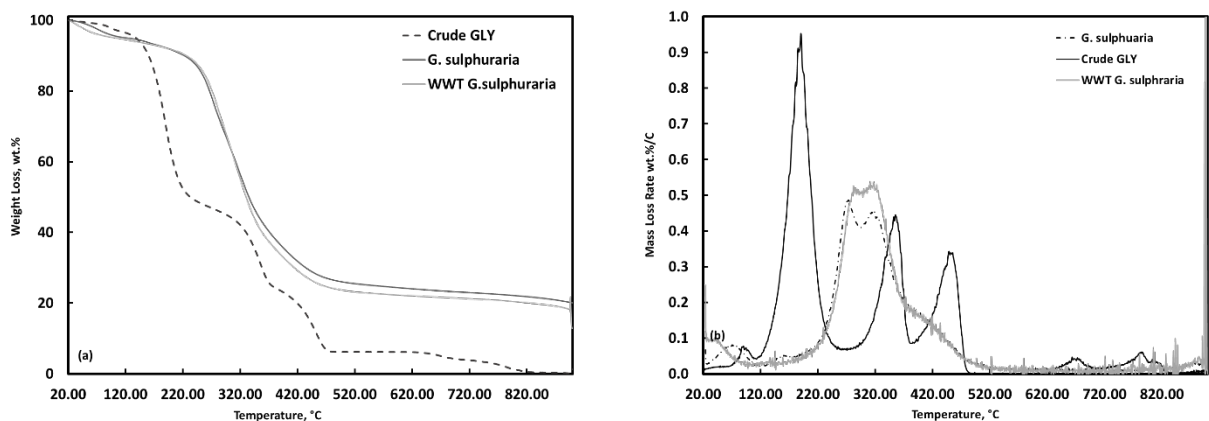
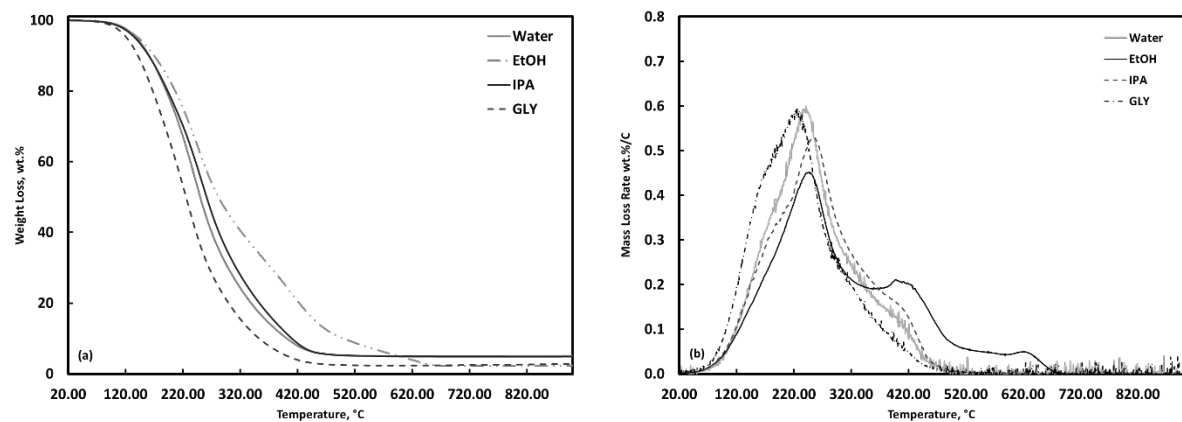**Figure 7: TG (a)/DTG (b) curves of algae biomass and crude glycerol.**

Figure 8: TG (a)/DTG (b) curves of LBO obtained from pure water/ 40% EtOH/ 40% IPA/ 40%GLY at 310°C for 30min

Table 4: Boiling temperature distribution of light bio-crude oils

	Boiling Temperature Distribution wt.%						
Temperature range (°C)	**IBP-70**	**70-120**	**120-170**	**170-250**	**250-500**	**500-600**	**600+**
Carbon number	**C1-C9**	**C5-C10**	**C10-C16**	**C14-C20**	**C20-C50**	**C20-C70**	**>C70**
Coke oil type	**Gases + Naptha**	**Gasoline**	**Kerosene**	**Diesel oils**	**Lubricating oils**	**Fuel oils**	**residue**
G. sulphuraria							
5, Water, 310, 30	0.27	2.14	10.43	37.48	44.48	0.25	4.96
5, 40% Ethanol, 310, 30	0.23	2.19	7.70	27.74	52.19	5.08	4.85
5, 40% IPA, 310, 30	0.26	2.45	9.84	31.55	50.62	0.28	4.99
5, 40% GLY, 310, 30	0.43	4.20	16.68	42.35	33.85	0.12	2.38
5, 40% GLY, 330, 30	0.53	5.38	17.71	35.74	38.22	0.15	2.28
5, 40% GLY, 350, 30	0.72	7.09	22.01	37.62	30.87	0.04	1.64

5, 40% GLY, 350, 5	0.44	5.25	18.73	37.48	35.16	0.12	2.83
WWT G. sulphuraria							
0, CGLY, 350,30	0.16	0.80	2.88	27.73	64.00	0.10	4.33
5, CGLY, 350,30	0.14	0.85	4.61	35.94	52.08	0.12	6.27
10, CGLY, 350,30	0.81	3.46	6.27	24.65	60.36	0.19	4.26

Conclusion

The HTL product distribution demonstrates that co-solvent addition effectively improves bio-crude oil production. At low HTL temperatures (310 °C), IPA and GLY achieved the highest LBO yield (24.9 wt.%). The decrease of nitrogen recovery in the aqueous phase suggests that co-solvents promote the transfer of organic compounds into the oil phase. With 40 wt.% glycerol, the highest yield of LBO (73.2% as dry algae basis) was observed at 350 °C for 30 min. Glycerol plays the same role as reduced sugar in Maillard reactions, besides degradation to provide H^+. The disadvantage of co-solvents is that all the added alcohols cannot be recycled after HTL. The absolute mass of LBO reached was 214 g out of 327 g feedstock wastewater treatment algae and crude glycerol. This suggested that around 66 wt.% organic compounds in both algae biomass and crude glycerol were converted into bio-crude oil, which has potential to be upgraded into advanced biofuels. The type of co-solvent influences the chemical compositions of the produced bio-crude oils.

6. Provide a paragraph on who will benefit from your research results. Include any water agency that could use your results.

    This research provides information about downstream energy recovery of microalgae, and microalgae has a promising ability on wastewater treatment. So that a complete energy recovery will be built up from upstream wastewater treatment by microalgae to downstream bio-crude oil production.

7. Describe how you have spent your grant funds. Also provide your budget balance and how you will use any remaining funds. If you anticipate any funds remaining after May 15, 2019, please contact Carolina Mijares immediately. (575-646-7991; mijares@nmsu.edu)

Description	Amount Spent To Date
Undergraduate Assistant Salary	$2,049
Undergraduate Assistant Fringe	$22
Travel (TCS Conference, Mag Lab Visit)	$1,849
Registration Fee for TCS Conference	$350
Supplies/Chemicals/Analytical Instrument Use Fees	$1765
Poster Printing	$70
Compressed Gas Cylinder Rentals	$241
Balance: $154	

For remaining funding

Travel for Mag Lab Visit (reimbursement in process)	$154

8. List presentations you have made related to the project.

"Role of Co-Solvents in Hydrothermal Liquefaction of Algae", Oral presentation.
Thermal & Catalytic Sciences Symposium (TCS) 2018 – Oct. 8-10, Auburn, AL.
"Roles of Co-solvents in Hydrothermal Liquefaction of Protein-Rich Algae", Conference paper.
2019 ASABE Annual International Meeting July 7–10, 2019 - Boston, Massachusetts.

9. List publications or reports, if any, that you are preparing. Remember to acknowledge the NM WRRI funding in any presentation or report that you prepare.

Preparing a manuscript of "Role of Co-Solvents in Hydrothermal Liquefaction of Algae" for publication.

10. List any other students or faculty members who have assisted you with your project.

Umakanta Jena (Assistant Professor), Feng Cheng (Postdoc) Tianbai Tang (MS), Huilin Wang (MS), Cesar Martinez Bejarano, Jacob Usrey, Nicholas Soliz, Nicolas Carrera-Little, April Wright (undergraduate students), Chemical & Materials Engineering
Barry Dungan (Senior Ag Research Assistant), Jacqueline Jarvis (Research Assistant Professor), Omar Holguin (Assistant Professor), Plant and Environmental Sciences

11. Provide special recognition awards or notable achievements as a result of the research including any publicity such as newspaper articles, or similar.

None to date

12. Provide information on degree completion and future career plans. Funding for student grants comes from the New Mexico Legislature and legislators are interested in whether recipients of these grants go on to complete academic degrees and work in a water-related field in New Mexico or elsewhere.

I passed the comprehensive exam in summer 2018 and I plan to graduate Spring 2020.

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