Effect of Extractive Solvents on Bio – oil Production From Microalgae via Hydrothermal Liquefaction

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Abstract

Bio–oil from spirulina sp. is complicated mixture with valued chemicals. The hydrothermal liquefaction (HTL) converts directly the spirulina microalgae into liquid oil at reaction temperature 300°C with heating rate 10°C /min,100 bars pressure and 30 min. reaction time eight different organic solvents with different polarities were applied to extract the bio – oil from these chemicals. The order of bio–oil extraction yield of the eight solvents from high to low were as follow tetrahydrofuran (THF) > dichloromethane (DCM) > acetone (ACE) > chloroform (CHL) > methanol (MeOH)> ethyl-acetate (EAC) > hexane (HEX) >toluene (TOL).The results obtained from single stage extraction process showed that maximum percentage oil yield was (26.55%). with rather high heating value (HHV ≈ 30 MJ/kg). The combination of THF, EAC and n-hexane was selected to extract and separate the bio – oil into three fraction heavy oil (48.9%) mid weight oil (37.8%) and light oil (62.2%). These three oils were characterized using gas chromatography mass spectrum (GC – mass).

Keywords:- Bio–oil , extractives, hydrothermal , liquefaction, micro- algae.

1. Introduction

Development of bio – energy has become a must to overcome global depletion of fossil fuel and decreasing environmental pollution (Wang et al., 2011). Biomass is taken a big interest as a renewable energy source due to its advantages of renewal and abundance. Currently, first generation bio-fuels are derived from food crops. Using agricultural residues for energy production can be a good solution for waste disposal. Therefore it is necessary to develop second generation bio-fuels that are not based on food crops (Liu et al., 2013). Many studies and investigations have focused on various technologies such as pyrolysis, gasification and mechanical extraction with esterification have been used for biomass conversion to bio-fuel. Hydrothermal liquefaction (HTL) is the third-generation method for biomass utilization (Liu et al., 2012 and Ye et al., 2012).Previous studies on HTL of algae were conducted either in batch or continuously operated HTL reactors under similar processing conditions (Biller et al., 2011 and Jazrawi et al., 2013). One of the important objectives of previous HTL experimental works was to detect the reaction conditions i.e. temperature, holding time and solids content for maximum bio-crude recovery (Valdez et al., 2012 and Jena et al., 2011). The maximum bio-crude recovery was mostly achieved with feed-stocks containing ~20 % w/v solids at subcritical conditions with the use of water as a reaction medium (Brown et al., 2010). Maximum bio-crude yield was recorded at temperatures close to critical point of water, with long reaction time about 60min.(Biller et al., 2011).

Nowadays, scientists are focusing on reaching maximum bio-crude recovery at relatively short reaction times e.g. 1 to 5 min. (Faeth et al., 2013 and Alba et al., 2012). To produce purest fuel with highest yield, lowest possible cost and under optimum environmental conditions, separation processes requires detailed knowledge about the solute reactions in the aqueous and organic phases (Jokovic et al., 2013 and Yang et al., 2014). In this paper, the extraction yield was computed and the composition of bio – oil was analyzed using nine organic solvents(THF) ,(DCM), (ACE), (CHL), (MeOH), (EAC),(HEX) and (TOL)with different polarities to select the optimum solvent. Solvent polarity is an indication for all salvation capability of reactants, activated complexes and molecules in the ground and excite cites. Moreover, it was salvation polarizability expression of refractive index (Katritzky et al., 2014). Also a novel combination of solvent was selected to sequentially extract and separate bio – oil into three fractions. The main objective of the present study is to determine facile and an efficient solvent combination (nine solvents) with multistep extraction to enhance bio-oil extraction and separation.

2. Experimental

2.1. Materials

Solvents used in this investigation were all of analytical grade and were purchased from El Nasr pharmaceutical Chemicals Co. The biomass used is dried and milled spirulina sp. That was collected from center, EGYPT. Elemental analysis of the biomass was carried out by an Elemental Viro- El, Germany analyzer.

2.2. Hydrothermal Liquefaction (HTL) process

HTL experiments have been carried out in a 400 ml auto-calve from Parr Co. Applying optimum HTL conditions (300°C – 30 min., 20% w/v solid to liquid ratio and about 100 bars pressure to prepare the bio-crude oil as shown in Figure 1 (Hawash et al., 2014 and Li et al., 2013)

The bio–oil was extracted from bio – crude which was the solid phase of HTL process after filtration(Yang et al., 2014).

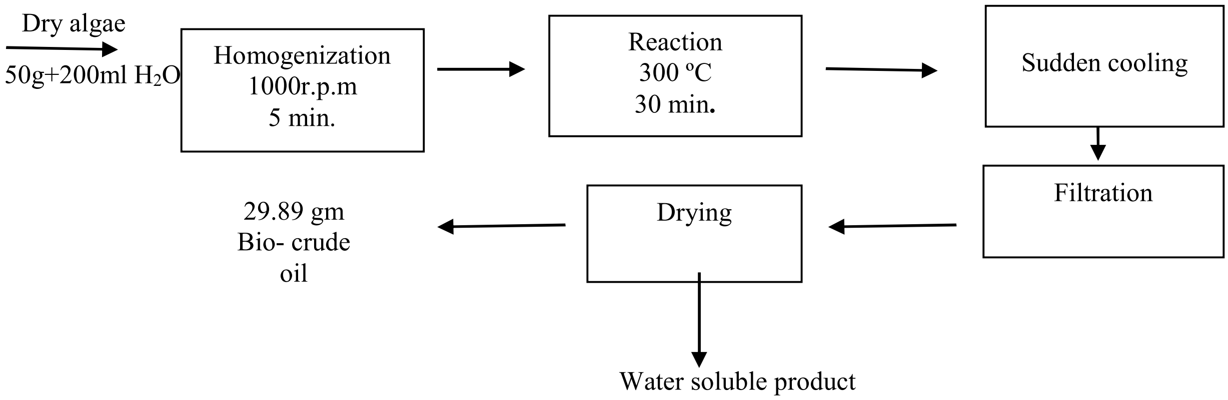

Figure 1. Hydrothermal Liquefaction of Microalgae

2.3 Single Stage extraction procedure

Extraction process was done using ultrasonic irradiation (USI) in an ice bath for 20 min. followed by filtration (Li et al., 2013). The filtrate was collected and dried from water using anhydrous sodium sulfate then the solvent was evaporated using Rota evaporated under vacuum. The residue after evaporation was considered bio- oil. The extrability of bio–oil was determined using the following equation(Yang et al., 2014).

$$\%\ \text{Extrability of Bio–oil} = \frac{\text{Mass of bio–oil}}{\text{Mass of bio–crude from HTL}} \times 100$$

Eight different organic solvents of different polarities were studied.

2.4Multistep extraction

Certain weight of the bio–crude was extracted by definite volume of solvent under ultrasound irradiation bath (USI) for 20 min. and filtered. Extraction and filtration process were repeated twice to ensure complete extraction then the solvent was evaporated from the filtrate. THF was added to the bio-crude for extraction then after filtration and drying the filtrate known as THF extracted oil (TEO). The TEO was extracted using EAC through the same pervious procedure to obtain the heavy oil (HO) which the EAC – insoluble solid. While the dry filtrate which is EAC – extracted oil (EEO) was further extracted with n-HEX to obtain the n-HEX insoluble solid (mid- weight oil, MO) and n-HEX- extracted oil is the light oil (LO).

2.5 Analytical technique

2.5.1 Elemental analysis for (HHV) Calculation

The bio- oil extracted by the nine solvents was subjected to elemental analysis for HHV calculation. An elemental analyzer (Elemental Vero- El, Germany) was used for CHNOS determination. Bio–oil produced from Spirulina species, was subjected to elemental analysis based on C, H, N, O and S calculation. The effective H/C ratio is the indication of biomass potential as a feedstock for fuel production. The effective H/C ratio is calculated from the following equation (Vennestrom et al., 2011).

$$\frac{H}{C} = \frac{N(H) - 3N(O)}{N(C)} \qquad (2)$$

Where N(H), N(C) & N(O) were estimated by dividing the compositional value of each element by its atomic weight. The more negative value suggests that the feed stock has a small heating value due to excessive oxidation or hydration. Each sample was analyzed for elemental composition and the data from elemental composition were used to estimate the higher heating value according to the Dulong equation (Brown et al., 2010) as follows:

$$\text{HHV (MJ kg}^{-1}) = 0.3383\,C + 1.422(H - O/8) + 0.095S \qquad (3)$$

Where C, H, O is the mass percentages of carbon, hydrogen and oxygen respectively.

2.5.2 Gas chromatography mass (GC/MS)

Gas chromatography Mass (GC/MS) of the extracts was performed using a Thermo Scientific, Trace GC Ultra / ISQ Single Quadruple MS, TG-5MS fused silica capillary column (30m, 0.251mm, 0.1mm film thickness).For GC/MS detection, an electron ionization system with ionization energy of 70 EV (electron volt) was used. Helium gas was used as the carrier gas at a constant flow rate of 1mL/min. The injector and MS transfer line temperature was set at 280 ^{0}C. The oven temperature was programmed at an initial temperature 40 ^{0}C (hold 3 min.) to 280 ^{0}C as a final temperature at an increasing rate of 5 ^{0}C /min.

3. Results and Discussion

3.1 Single Stage Extraction

Results of bio – oil extraction yield versus the applying nine solvents at different polarities are shown in Figure 2

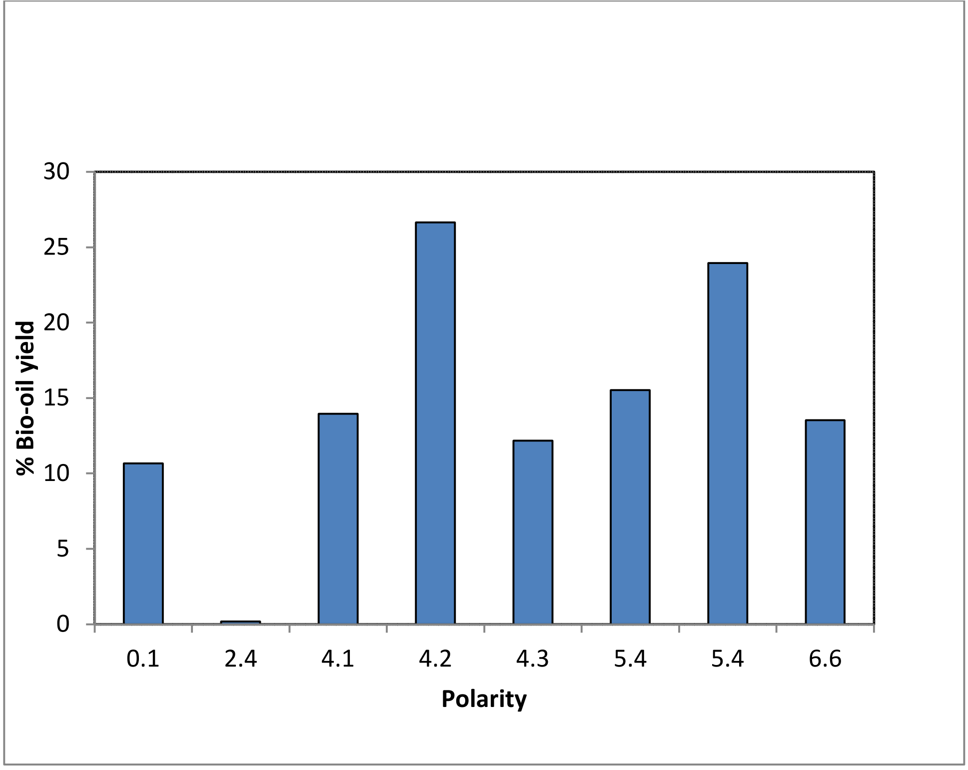

Figure 2. Bio–oil Extraction Yields of Solvents with Different Polarities

It is clear that the bio–oil extraction yield ranged from 26.55% to 0.18%. It is obvious that the percent bio – oil extraction yield varied with solvent polarity. The maximum extraction yield (26.55%) of oil was obtained using THF as a solvent. DCM also had rather high extraction yield of bio – oil. ACE,CHL, Me OH, EAC and n-HEX had bio–oil extraction yield ranged from 11% to 15.5% .While, TOL gave only an extraction yield 0.18%. Variation of the polarity of solvent on the extracted bio – oil yield is not linearly but fluctuated up and down. It seems to mountain – like peaks which indicate that the bio – oil contain both high and low polarity compounds. Comments of the effect of polarity on extraction bio – oil yield are illustrated in Table1. They are in good agreements with previous studies(Hneito office 2011).

Table 1.The effect of solvent polarity on extraction yield

solvent	**polarity**	**Yield %**	**Comments**
THF	4.2	26.55	Highest yield, highly viscous product
DCM	3.4	23.95	" """""
ACE	5.4	15.52	Moderate yield, highly viscous product
CHL	4.1	13.95	""""""
Me OH	6.6	13.53	""""""
EAC	4.3	12.18	""""""
HEX	0.1	10.66	""""""
TOL	2.4	0.18	Low yield, highly viscous product

3.1.1. Elemental composition and HHV calculation

The yield of extracted bio –oil did not vary linearly with the polarity of the solvents and is fluctuated as illustrated in Table 2.

Table 2. Elemental composition and properties of extracted Bio-oils

Ultimate Analysis%	**Me OH**	**CHL**	**ACE**	**EAC**	**TOL**	**THF**	**DCM**	**n-HEX**	**Spirulina Sp.**
N	3.97	4.55	5.58	4.5	4.23	5.05	4.1	2.33	8.88
C	56.25	68.9	70.87	73.15	74.26	73.73	66.32	74.6	40.54
S	0.46	0.65	0.455	0.31	0.29	27.62	30.92	0.33	6.54
H	4.19	5.72	6.42	6.13	6.57	3.32	3.15	6.2	7.01
O	35.13	20.18	16.67	15.91	14.65	10.88	22.51	16.54	37.69
H/C Molar ratio	0.89	1.003	1.09	1.005	1.06	0.54	0.57	1.996	2.075
O/C Molar ratio	0.47	0.11	0.18	0.16	0.15	0.11	0.25	0.17	0.697
HHV (MJ/kg^{-1})	18.77	27.9	30.18	30.67	31.89	30.28	25.82	31.14	17.33

3.1.1.1 Feedstock analysis

The elemental and biochemical composition of spirulina sp. used in the present study is presented in Table2. Compared with the other micro algal strains, the carbon content of spiralina pt. was low. Therefore the higher heating value of this strain was less than the other microalgae strains. However, spirulina sp. used in this study had a higher hydrogen to carbon ratio (H/C), atomic ratio (2.075) which leads to more energy upon combustion of the feedstock. Also, it was found from the calculated effective hydrogen to carbon ratio (-0.018, less negative) that spirulina sp. is more suitable feedstock for liquid transportation (Vennestrom et al., 2011).

3.1.1.2 Bio-oil analysis

The resultant bio-oil after each extraction and drying was dark in color and viscous. The HHV of bio oil obtained after each solvent extraction was higher than that original feedstock (17.33 MJ/kg). Generally, as shown in Table 2 bio–oil produced had a higher carbon and hydrogen content and the sulfur content was relatively low. The content of nitrogen is ranged from 2.3 to 5.58% w/w, mostly this is attributed to higher protein content in microalgae (Barreiro et al., 2013; Faeth et al., 2013; Jena et al., 2011 and Jena et al., 2011).Furthermore, bio-oil associated with a high oxygen are regarded as poor quality as they exhibited low energy value and poor storage stability (Jena et al., 2011). The comparison of the estimated carbon to nitrogen and carbon to hydrogen ratios of this study to previous studies showed a good similarity which is suggesting that spirulina sp. as a potential feedstock for bio-oil production. The heating value for bio–crude oil extracted with different solvents was around 30 MJ kg^{-1} except that produced by methanol which was low but nearly close to that of the micro- algae feedstock (~ 17 MJkg^{-1}).By comparing polarity and HHV for each solvent, it was found that methanol which is of highest polarity (6.6) gave low HHV due to the presence of high oxygen content (35.13%)

which leads to poor quality of bio – oil also it exhibits low energy and poor stability. It is clear that, n – hexane solvent with low polarity (0.1) and oxygen content 16.54%, it gave high HHV (31.14MJkg^{-1}), which means that the HHV depends on oxygen content more than its dependence on solvent polarity.

3.2 Muti steps extraction

Steps of heavy, mid and light oils extraction are shown in Figure 3 on which also results of multi steps extraction are illustrated.

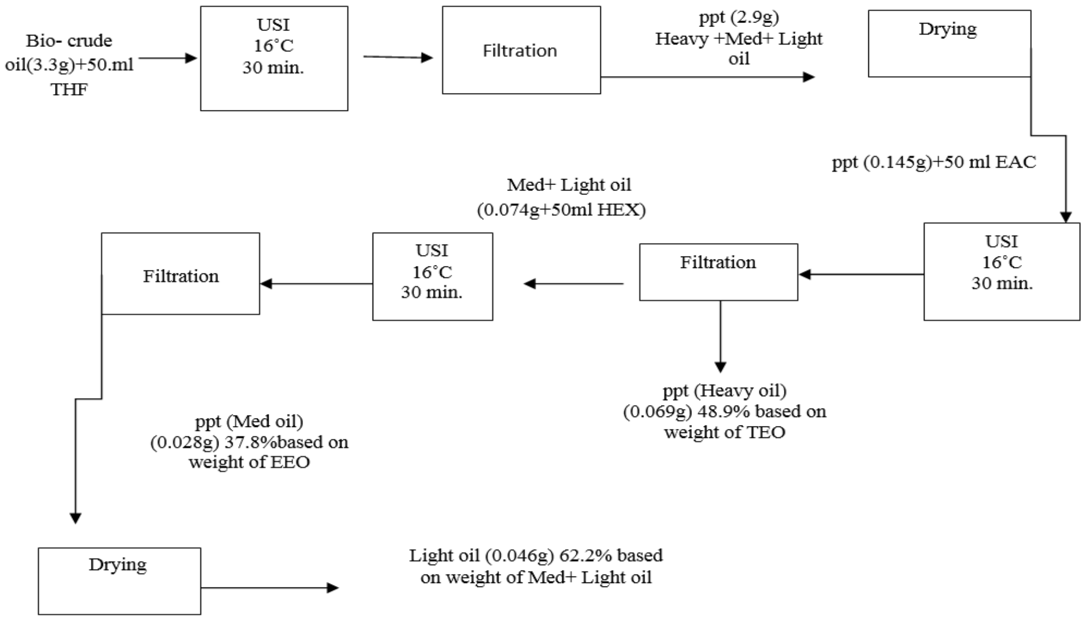

Figure 3. Multistep Solvent Extraction

3.2.1 GC/Mass analysis results

Bio-crude oil from spirulina sp was divided into light oil, mid-weight oil, heavy oil and residue by multistep extraction. From GC/MS analysis the constituents and % area of light oil, mid-weight oil, and heavy oil are listed in Table 3, 4, 5. Crude oil is considered "heavy" if it has long hydrocarbon chains, or "light" if it has short hydrocarbon chains: an API gravity (an inverse measure of petroleum liquid's density relative to that of water) of 34 or higher is "light", between 31-33 is "medium", and 30 or below is "heavy". Light Crude oil is liquid petroleum that has low density and that flows freely at room temperature. It has low viscosity, low specific gravity and high API gravity due to the presence of a high proportion of light hydrocarbon fractions. It usually contains higher levels of naphtha (gasoline-range hydrocarbons) with predominately volatile paraffinic hydrocarbons, which can be processed readily to produce gasoline and are considered “light” crude. As seen in Table 3 light crude is composed of a high number of paraffin, which are straight and branched chain hydrocarbon. It generally has low wax content. Also, light crude oil receives a higher price than heavy crude oil on commodity markets because it produces a higher percentage of gasoline and diesel fuel when converted into products by an oil refinery. On the other hand, heavy crude oil (48.9%) has more negative impact on the environment than its light (62. 2%) counterpart since its refinement requires the use of more advanced techniques and the use of contaminants. Heavy oil differ from light oils by their high viscosity (resistance to flow) at reservoir temperatures, high density (low API gravity) (http://www.petrolium.co.uk/light-oil, 2015). Heavy crude oils and mid- weight oil (37.8)are usually rich in aromatics and tend to contain more residual material, e.g. asphaltenes, and heterocyclics, e.g. sulfur, nitrogen, oxygen-containing hydrocarbon analogs as shown in Table 5(The American petroleum institute 2011).

Table 3. Components of Light oil

Compound	M.wt	Area%	Molecular formula
n.Octyl acetate	172	15.86	$C_{10}H_{20}O_2$
Acetic acid, 2 methyl propyl Ester	116	8.77	$C_6H_{12}O_2$
1Butanol, 3methyl, acetate	130	21.27	$C_7H_{14}O_2$
Acetic acid, pentyl ester	130	21.27	$C_7H_{14}O_2$
1Butanol, 3methyl, acetate	130	21.27	$C_7H_{14}O_2$

Table 4. Components of mid-weight oil

Compound	M.wt	Area%	Molecular formula
Benzeneethanol	150	7.24	$C_{10}H_{14}O$
Benzene	162	7.24	$C_{12}H_{18}$
Acetic acid, 1,2ethanediyl ester	210	15.84	$C_6H_{10}O_4S_2$
Mannosamine, alcohol	179	15.84	$C_6H_{13}NO_5$
3,3Diphenyl1methy Lidenecyclobutane	220	31.59	$C_{17}H_{16}$

Table 5. Components of heavy oil

Compound	M.wt	Area%	Molecular formula
Methyl commate A C	500	5.47	$C_{32}H_{52}O_4$
Methyl4,4,7trimethyl4,7d hydroindan6carboxylate	220	73.46	$C_{14}H_{20}O_2$
3(2,2dimethylpropylidene)bicyclo[3.3.1]nonane2,4dion	220	73.46	$C_{14}H_{20}O_2$
2H1Benzopyran, 6,7dimethoxy2,2dimethyl	220	73.46	$C_{13}H_{16}O_3$
Pregnane3,11,20,21tetrol, cyclic20,21(butylboronate)	418	2.96	$C_{25}H_{43}BO_4$
6,6'Dimethyl5,5', 8,8'tetrahydroxy2,2' Binaphthalene1,1',4,4'tetrone	406	2.96	$C_{22}H_{14}O_8$
6,6'Dimethyl5,5',8,8'tetrahydroxy2,2'Binaphthalene1,1',4,4'tetrone	406	2.96	$C_{22}H_{14}O_8$
Spirost8en11one,3hydroxy	428	2.57	$C_{27}H_{40}O_4$
2,3bis[(trimethylsilyl) oxypropyl ester	498	2.53	$C_{27}H_{54}O_4Si_2$
2,3bis[(trimethylsilyl) oxypropyl ester	496	1.88	$C_{27}H_{52}O_4Si_2$
2,3bis[(trimethylsilyl) oxypropyl ester	498	2.27	$C_{27}H_{54}O_4Si_2$

3.2.2 Elemental results and HHV calculations of light , mid and heavy oils

Bio-crude oil from HTL process is divided into LO , MO and HO using multistep extraction. The appearance of the three oils are quite different. LO was light yellow , while HO looked black and thick. According to elemental analyses results shown in Table 6 , it is concluded that , due to the high content of carbon and hydrogen in LO composition , so it is estimated HHV of about 36 MJL/ kg .

Table 6. Elemental analysis result of LO & MO

Parameter	N%	C%	S%	H%	O%	HHV (MJ/kg)
LO	7.36	77.666	1.89	7.35	5.7	35.83
MO	7.13	61.81	1.04	2.2	27.8	19.28

4. Conclusions

This study confirms that – spirulina sp. is an ideal feedstock for bio – oil production. During studying the single step extraction using nine different solvents, it seems that: THF is the most convenient solvent because it gave the highest yield of oil extraction and higher heating value (HHV) than the others, while n-HEX gave the lowest yield. Multistep extraction method provided a potential separation of bio – oil into fractions light, mid and heavy oil. Investigating the multistage solvent extraction using THF, EAC and n-HEX gave us highest yield of LO, MO and HO. Mid – weight oil is rich in aromatic compounds which can be a pro missing candidate for partial substitutes for petroleum and asphalt binder while heavy oil was found to be rich in ester.

LO with higher HV (35.83MJ/kg), high number of paraffin and low wax content produces higher percentage of gasoline and diesel fuel when converted into products by an oil refinery.

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