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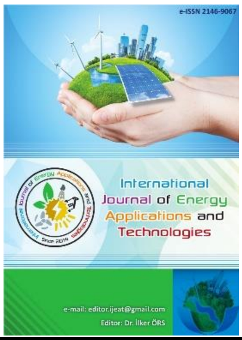

Original Research Article

Detecting chemicals with high yield in pyrolytic liquid of spirulina sp. microalgae via GC-MS

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ABSTRACT

Pyrolysis of *Spirulina* sp. Microalgae was carried out in a semi-batch glass reactor system. Effect of temperature on the yields of pyrolytic products (gaseous, liquid and solid residue) and chemical composition of the liquid products were investigated. All experiments were performed in 25 mL/min nitrogen atmosphere with 15 g feedstock which was dry and powder form of *Spirulina*. Temperature was varied from 470 to 620 °C with 50 °C break by utilizing PID controller which was setted 10 °C/min heating rate. The aqueous phase and bio-oil (organic phase) of the liquid products were characterized by GC-MS. Maximum yields of bio-oil and aqueous phase were obtained approximately as 30 wt. % at 520 °C and as 20 wt. % at 470 °C. It was detected that bio-oil composed of aliphatic and cyclic hydrocarbons (such as toluene and heptadecane), oxygenated components (such as phenol, o-cresol and nonadecanol), nitrogenous components (such as hexadecaneamide and 3-Methyl-1H-indole). Unlike bio-oil, hydrocarbons like toluene, ethyl benzene, styrene and alkanes were not detected in aqueous phase.

Keywords: Biomass; Bio-oil; Green Chemicals; Microalgae; Pyrolysis

1. Introduction

Due to run out of fossil fuels, researchers have studied on renewable and sustainable energy sources that are wind, solar, tide, waste and biomass. Plants, algae, animal wastes are in biomass class [1–3]. Biofuel (bioethanol, biodiesel, biogas) are obtained from biomass [4–6]. Besides that, biomass can be used for produce green chemicals, adsorbent and catalyst by pyrolysis [7–9].

Invaluable liquids which can be fuel or the source of green chemicals produce from biomass by using thermochemical or biochemical processes. Biochemical processes are required to hazardous chemicals like methanol and sodium hydroxide and energy [10]. In addition, they include many steps [11]. But, thermochemical process especially pyrolysis is a process which are preferred a lot. Because, it can be obtained solid, liquid and gaseous product simultaneously in one step at short time with pyrolysis [12,13]. Pyrolytic products yields depend on several factors. Biomass type, reaction conditions (temperature, heating rate, duration time), reactor configuration and catalyst using are these factors. The most important ones are temperature and heating rate [14,15]. Biomass feedstock amount don't affect pyrolytic product yields.

Microalgae as a biomass source of pyrolysis can be cultivated in wastewater and barren fields in a short span of time. Additionally microalgae are carbon-neutral, i.e., carbon dioxide was taken by them from the atmosphere during photosynthesis is equal to released carbon dioxide when they are used for whatever purpose [16,17].

Liquid product of microalgae pyrolysis includes two phases that are called aqueous phase and bio-oil. These two phases can be separated from each other easily [18]. There was too many researches about obtaining microalgal bio-oil.

Chaiwong et al. (2013), fulfilled pyrolysis of *Spirulina* as a microalgae in fixed bed reactor at 450-600 °C. They obtained maximum bio-oil yield at 550 °C and determined the main components of bio-oil are heptadecane, toluene, ethylbenzene and indole as a result of GC-MS analysis [19]. Chen et al. (2017), carried out pyrolysis for three different types of microalgae in fixed bed reactor at 400-800 °C. They obtained that peak area of aromatic hydrocarbons in bio-oil increased with temperature for all types of microalgae as a result of GC-MS analysis [20]. Andrade et al. (2018), worked between 450 and 750 °C for a microalgae. They determined that cyclic hydrocarbons and toluene increased with temperature [21].

Arthrospira platensis (Spirulina platensis) has been known as scientific name of Spirulina
microalgae. Spirulina which belongs to the blue green algae class has cultivated in a large
scale on the world [22]. For example, in China Spirulina production is approximately 10,000 Tons per year [23]. Spirulina has the highest product yield among microalgae species [24]. It has high carotenes and gamma-linolenic acid content, so the most popular application area of Spirulina has been food supplement sector [22]. Bio-oil production has been another application area of Spirulina. Bio-oil has thought alternative fuel to diesel. While low quality bio-oil can be obtained from lignocellulosic biomass sources, Spirulina supplies bio-oil whose features are stable, improved high heating value (HHV) and low oxygen content. These properties arise from lipid and protein content. Undesired linear hydrocarbons which decrease the bio-oil quality occur from lipid degradation in biomass. Spirulina has low lipid content. Besides that, its high protein content promotes aromatic hydrocarbon production which increases bio-oil quality as well [25]. On dry basis, Spirulina's weight comprises of approximately 60 % protein and 10 % lipid [26]. Compared to other biomass types (land and coastal types), Li et. al. decided that Spirulina has low activation energy for total conversion and therefore it should be prefer thermochemical conversion [24]. Apart from these important properties, Spirulina has high atomic nitrogen (N) content, so it can be possible to see nitrogenous compounds in its bio-oil which results from thermal degradation of the biomass [22].Thermal degradation of Spirulina originates from three steps which are dehydration, de volatilization and carbonization. Firstly, up to 140 ºC moisture of the microalgae evaporates. Secondly, up to 550 ºC carbohydrates, lipids and proteins in the biomass degrades to main pyrolysis products and mass loss of biomass is high (65 %). Above 550 ºC, carbonization takes place and mass loss of the microalgae is low (9%) [25]. After 600 ºC, it has been known that Spirulina amount almost don't change [22].

In this research, we aimed to observe temperature (470, 520, 570, 620 °C) effect on the product (bio-char, liquid, gaseous) yields and the liquid composition by carrying out pyrolysis of *Spirulina* sp. microalgae. Bio-oils were analyzed by GC-MS comprehensively. In addition, unlike other researches in literature, we examined aqueous phase composition as well.

2. Materials and Methods

2.1. Characterization of sample

Spirulina in powder form was bought from a local herbalist. Particle size measurement of the Spirulina was made by using Malvern Mastersizer 2000 Particle Size Analyzer. According to the analysis results, average particle size of the sample was detected 37 µm by volume. Elemental analysis of *Spirulina* was performed by utilizing Leco brand and CHN628 model with Sulfur add-on module equipment. Result of the analysis was shown in Table 1.

Table 1. Elemental composition of microalgae (wt. %, ash free and dry basis)

C	H	N	S	O*
46.69	6.22	10.76	1.55	34.78

*by difference

2.2. Pyrolysis of microalgae

Thermal experiments were made as the following. It was used that tubular pyrex glass reactor has 4 cm diameter and 33 cm length. Reactor which had fulled of 15 g feedstock was settled vertically in handmade ceramic furnace. Furnace temperature and heating rate were controlled by Protherm brand PID controller. Inner temperature of the reactor was measured by Elimko brand 2000 M model digital display device linkes NiCr-Ni thermocouple. The scheme of reactor in furnace was shown in Fig. 1. Firstly, PID controller temperature was adjusted to desired temperature (T1) with a heating rate. Secondly, temperature increasing in furnace was seemed on PID screen (T2) with taking signals from furnace to PID. At the same time, reactor temperature can be read on digital display (T3).

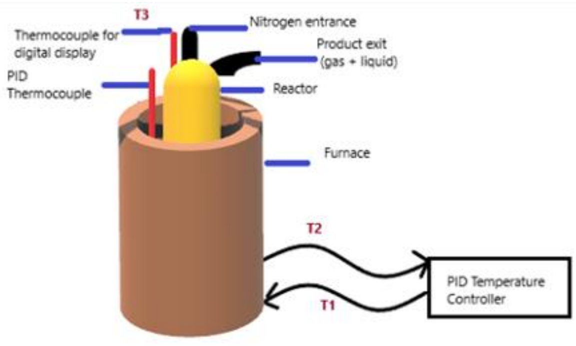

Fig. 1. Reactor in furnace

Reactor was used in experiments was operated at temperature range which is 470-620 °C during 60 min. Its heating rate was chosen as 10 °C/min. Throughout the experiments nitrogen gas had 25 mL/min flowrate was passed through glass setup which has a gap is open to the atmosphere. Products moved away the reactor in gas form gattered after they had passed a condenser. Non-collecting ones were released to atmosphere. Condensing liquid was mono ethyleneglycol and it held 0 °C by PolyScience brand circulator.

Product yields were calculated by using Equ. 1-4. The setup was shown in Fig. 2.

Bio-char yield (%) = (rae, g-empty reactor, g)/(fie, g) (1)

rae: reactor after experiment
fir: feedstock in the reactor

Liquid yield (%) = (tlgee, g)/(fir, g) (2)
tlgee: total liquid in glass equipments after experiment

Gaseous yield (%) = 100 – (Bio-char yield + liquid yield) (3)

Total conversion (%) = liquid yield + gaseous yield (4)

Reactor configuration was selected to compare other researches about microalgae. For example, Chaiwong et al. (2013) worked with 6 cm inner diameter fixed bed reactor and under 30 mL/min N_2 flowrate [27]. Thus, Velocity of the swept gas of our study (2 cm/min) is same as this study (1.1 cm/min). Besides that, small reactor diameter is important for removing volatile matters in reactor quickly [28].

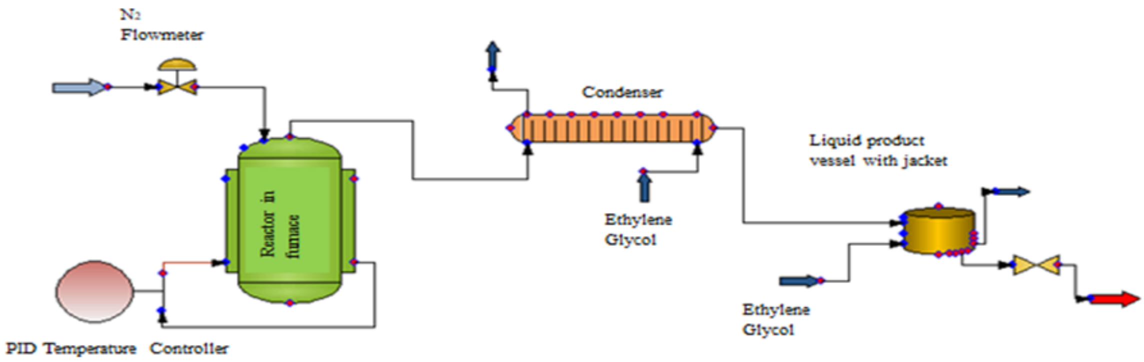

Fig. 2. Chemcad drawing of the experimental setup

2.3. GC-MS analysis of pyrolytic liquid

Compositions of bio-oil and aqueous phase were analyzed by utilized GC-MS whose brand and model were Thermo Finnigan and DSQ 250 respectively. Capillary column whose brand and model were Zebron and ZB-1MS respectively was found in the equipment. The column whose inner diameter was 0.25 mm had 60 m length. The column was able to operate between 30 and 370 ºC. Analysis conditions were as follows. Sample volume was chosen as 0.5 µL. Ion source temperature was adjusted to 220 ºC. Column temperature was increased gradually. Firstly, the column was held 45 ºC for 4 min. After that, its temperature was risen to 280 ºC. Within that period, heating rate was determined as 3ºC/min. Run of the total analysis was maintained at 102 min.

3. Results and Discussion

3.1. Yields of pyrolysis products

Effect of temperature on the product yields and total conversion (gaseous + liquid product yield) was given in Fig. 3. Liquid product yield was obtained as nearly 45% at 470ºC. After that, it increased to about 55% at 520ºC. %. It was seemed that this amount was high by comparing other studies. For example, Chaiwong et al. (2013) found liquid yield as 45% at 520 ºC [19]. Liquid product yield stood at 55% till 620 ºC. At that temperature, liquid product yield decreased from 55% to 50%. In brief, maximum liquid product yield was obtained between 520 and 570 ˚C for *Spirulina*'s conventional pyrolysis under our specific conditions in the study. That data was compatible with other studies. For example, Chen et al. (2017), obtained maximum liquid product yield at between 500 and 600 ºC for *Spirulina*'s pyrolysis [20].

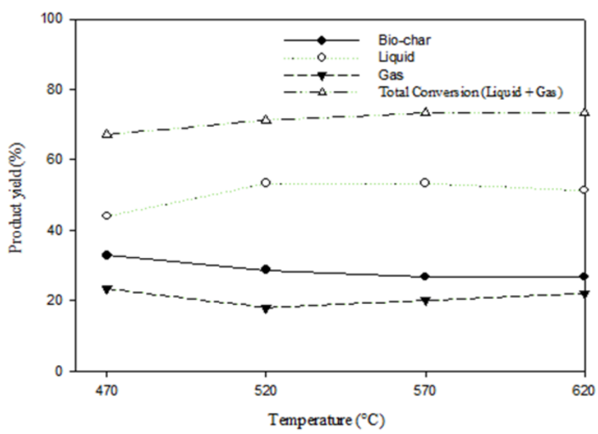

Fig. 3. Change in product yields with temperature

Effect of temperature on the bio-oil and aqueous phase yields was presented in Fig. 4. Bio-oil product yield was obtained as nearly 20% at 470ºC. After that, it increased to about 40%. And it stood at that value till 620 °C. At that temperature, liquid product yield decreased from 40% to 30%. Aqueous phase yield was obtained as around 20% at all temperatures. It was obtained as 20% at 470ºC. And then, it stood nearly 15% till 620 ºC. At that temperature, aqueous phase yield increased from 15% to 18%. In summary, maximum bio-oil and aqueous phase yield were achieved at 520 and 470 ˚C respectively. That finding was compatible with other studies. Pan et al. (2010), were observed maximum bio-oil and aqueous phase yield were approximately 30 wt. % and 20 wt. % respectively as a result of their slow pyrolysis research for *Nannochloropsis* sp. Microalgae [29].

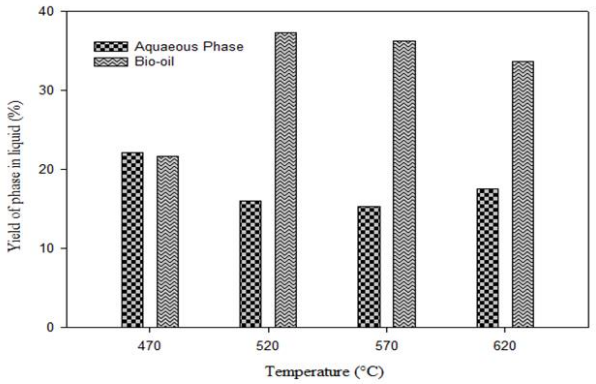

Fig. 4. Change in bio-oil and aqueous phase yield with temperature

3.2. Chemical composition of liquid product

Chromatogram for bio-oil were shown in Fig. 5. Structure of some components which were found in bio-oil was added to the chromatogram with respect to their retention times. Considering that, it was deduced that bio-oil composed of aliphatic and cyclic hydrocarbons (such as toluene and heptadecane), oxygenated components (such as phenol, o-cresol and nonadecanol), nitrogenous components (such as hexadecane amide and 3-Methyl-1H-indole). Retention times and peak areas of each component in bio-oil were taken place in Table 2. It was understood that oxygenated compounds (43%) formed the main part of bio-oil. Nitrogenous compounds (26%) and hydrocarbons (19%) were also found in bio-oil highly. Samely, Dai et. al. (2019) found that oxygenated compounds and nitrogenous compounds were comprised of nearly 40 % and 25% of bio-oil at 600 ºC [30] . It was determined also other compounds (12%) in bio-oil which composed of both nitrogen and oxygen such as piperidone and hexadecane amide. It must be noted that while it was forming that table, it was regarded only 40% of the total peak area. Because it was determined that bio-oil composed of other several components which had long name and low peak area percentage. In Fig. 6, change in peak area of some component with temperature was given. It was seemed that rise in temperature had positive effect on the amount of pyrrole and hexadecane amide while phenol and toluene amount decreased with increasing temperature.

It was detected that peak area of some compounds in bio-oil were higher than other researches. For example, Anand et al. (2016) has found that peak area percentage of pyrrole and phenol were 0.6 and 1.93 respectively at 600 ºC [22]. Chaiwong et. al. (2013), has obtained bio-oil that comprised of 0.37 % toluene and 1.14 % phenol at 550 ºC [27].

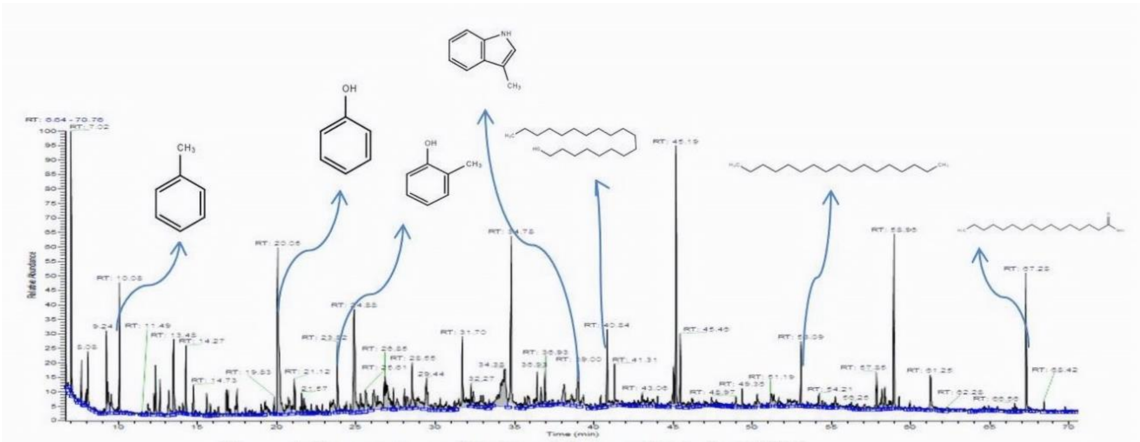

Fig. 5. Chromatogram of the bio-oil that was obtained at 520 ºC

Aqueous phase components in the liquid product were determined in the same approach. Retention times and peak areas of each component in aqueous phase were taken place in Table 3. Unlike bio-oil, hydrocarbons like toluene, ethyl benzene, styrene and alkanes were not detected in aqueous phase. It was understood that oxygenated compounds (45%) formed the main part of aqueous phase and nitrogenous compounds (28%) followed that. At that time, amount of other compounds (27%) which had both nitrogen and oxygen was high compared to bio-oil. These compounds occurs because of protein degradation in Spirulina [31]. These differences was shown in the aqueous phase chromatogram also (Fig. 7). To the best of our knowledge, there have been little information about aqueous phase composition of Spirulina in literature. Jena and Das (2011), obtained aqueous phase which included acetic acid and some nitrogenous compounds such as pyrazine and amids at 350 ºC [31].

Table 2. Components in bio-oil of *Spirulina* that was obtained at 520 ºC

Retention time, min	Component	Formula	Peak Area, %	Retention time, min	Component	Formula	Peak Area, %
3.92	octanal	$C_8H_{16}O$	1.47	17.49	1H-pyrazole, 3,5-dimethyl-	$C_5H_8N_2$	0.53
4.14	acetic acid, hydroxy-	$C_2H_4O_3$	2.81	18.04	2-ethyl-furan	C_6H_8O	0.13
4.44	acetic acid, cyano-	$C_3H_3NO_2$	1.87	18.33	2,3-dimethyl-1H-pyrrole	C_6H_9N	0.12
5.23	Cyclobutanecarbonitrile	C_5H_7N	0.31	19.26	Octanenitrile, 2-methylene-	$C_9H_{15}N$	0.52
6.86	benzene	C_6H_6	0.06	20.05	phenol	C_6H_6O	4.54
7.02	furan tetrahydro-2-methyl-	$C_5H_{10}O$	1.98	20.75	4-aminopyridine	$C_5H_6N_2$	0.76
8.08	Butanenitrile, 3-methyl-	C_5H_9N	0.81	21.12	furan, 2-ethyl, 5-methyl-	$C_7H_{10}O$	0.85
9.24	pyrrole	C_4H_5N	1.7	21.57	nonanol	$C_9H_{20}O$	0.33
9.56	Pentanenitrile	C_5H_9N	0.51	22.18	tetradecane	$C_{14}H_{30}$	0.12
10.08	toluene	C_7H_8	1.45	22.52	benzene, 1-propenyl-	C_9H_{10}	0.24
10.55	2-Methylpentane	C_6H_{14}	0.06	22.88	3-pyridinemethanol	C_6H_7NO	0.17
11.73	3-Methylpyridine	C_6H_7N	0.05	23.82	o-cresol	C_7H_8O	1.12
11.87	octane	C_8H_{18}	0.33	24.88	m-cresol	C_7H_8O	2.78
12.34	Pentanenitrile, 4-methyl-	$C_6H_{11}N$	0.73	40.43	nonadecane	$C_{19}H_{40}$	2.78
12.62	2-methyl-1H-pyrrole	C_5H_7N	0.44	40.84	nonadecanol	$C_{19}H_{40}O$	1.24
13.19	Pyrazine	$C_4H_4N_2$	0.59	49.36	hexadecane	$C_{16}H_{34}$	0.29
13.48	2-piperidone	C_5H_9NO	1.09	53.09	heptadecane	$C_{17}H_{36}$	0.82
14.07	Hexanenitrile	$C_6H_{11}N$	0.14	54.21	dodecane	$C_{12}H_{26}$	0.22
14.27	N-Methylaniline	C_7H_9N	0.73	57.85	oleic acid	$C_{18}H_{34}O_2$	0.63
14.73	o-xylene	C_8H_{10}	0.46	58.17	cyclododecane	$C_{12}H_{24}$	0.56
15.09	2,5-dimethylpyridine	C_7H_9N	0.08	58.96	hexadecane nitrile	$C_{16}H_{31}N$	2.24
15.56	styrene	C_8H_8	0.28	59.26	cyclopentadecanone, 2-hydroxy-	$C_{15}H_{28}O_2$	0.16
15.81	ethylbenzene	C_8H_{10}	0.18	61.25	N-hexadecanoic acid	$C_{16}H_{32}O_2$	0.79
16.81	2-methyl-1H-pyrrole	C_5H_7N	0.66	67.28	hexadecane amide	$C_{16}H_{33}NO$	1.93

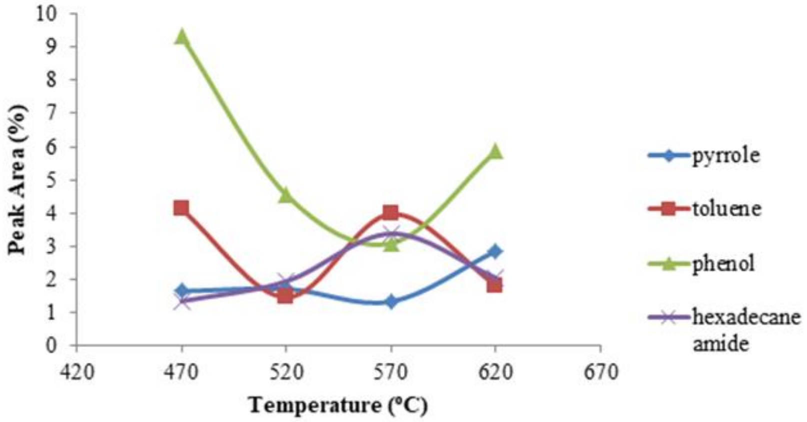

Fig. 6. Component distribution of bio-oil with temperature

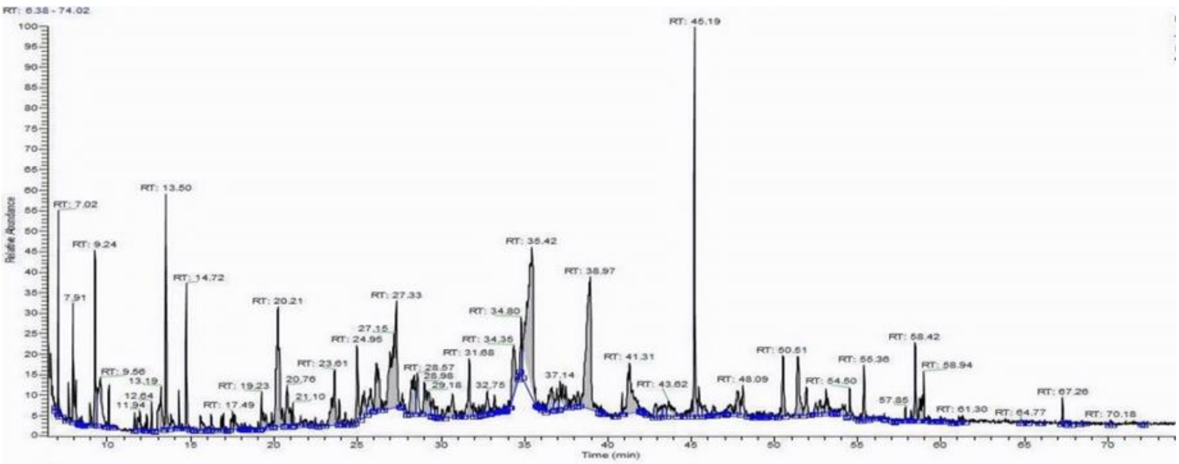

Fig. 7. Chromatogram of the aqueous phase that was obtained at 520 ºC

Table 3. Components in aqueous phase of *Spirulina* that was obtained at 520 ºC

Retention time, min	Component	Formula	Peak area, %
4.14	acetic acid, hydroxy-	$C_2H_4O_3$	7.48
4.44	acetic acid, cyano-	$C_3H_3NO_2$	5.9
5.23	Cyclobutanecarbonitrile	C_5H_7N	0.78
7.02	furan tetrahydro-2-methyl-	$C_5H_{10}O$	0.91
9.24	pyrrole	C_4H_5N	1.75
9.56	Pentanenitrile	C_5H_9N	1.38
12.25	Pentanenitrile, 4-methyl-	$C_6H_{11}N$	0.05
12.64	2-methyl-1H-pyrrole	C_5H_7N	0.2
13.19	Pyrazine	$C_4H_4N_2$	1.12
13.5	2-piperidone	C_5H_9NO	1.97
13.78	Hexanenitrile	$C_6H_{11}N$	0.28
17.49	1H-pyrazole, 3,5-dimethyl-	$C_5H_8N_2$	0.54
18.03	2-ethyl-furan	C_6H_8O	0.05
18.22	2,3-dimethyl-1H-pyrrole	C_6H_9N	0.05
19.23	Octanenitrile, 2-methylene-	$C_9H_{15}N$	0.66
20.21	phenol	C_6H_6O	3.25
20.76	4-aminopyridine	$C_5H_6N_2$	0.92
21.1	furan, 2-ethyl, 5-methyl-	$C_7H_{10}O$	0.19
21.57	nonanol	$C_9H_{20}O$	0.06
22.89	3-pyridinemethanol	C_6H_7NO	0.1
23.61	o-cresol	C_7H_8O	1.5
40.86	nonadecanol	$C_{19}H_{40}O$	0.15
57.85	oleic acid	$C_{18}H_{34}O_2$	0.12
58.94	hexadecane nitrile	$C_{16}H_{31}N$	0.88
59.24	cyclopentadecanone, 2-hydroxy-	$C_{15}H_{28}O_2$	0.09
67.26	hexadecane amide	$C_{16}H_{33}NO$	0.25

4. Conclusions

Pyrolysis of Spirulina sp. microalgae was carried out. First of all, elemental analysis of *Spirulina* showed that the microalgae had high carbon and oxygen content. For thermal pyrolysis of *Spirulina*, maximum liquid product was obtained at 520 and 570 °C as 55 %. By comparing other studies, this amount was found high. It was detected that bio-oil of *Spirulina* composed of hydrocarbons, oxygenated and nitrogenous compounds. Specifically, hydrocarbons were found in the form of alkanes and aromatic compounds like benzene, styrene, toluene and ethyl benzene. It was detected that peak area of some compounds like phenol, pyrrole and toluene in bio-oil were higher than other researches. Unlike bio-oil, hydrocarbons like toluene, ethyl benzene, styrene and alkanes were not detected in aqueous phase. But reached percentage of oxygenated and nitrogenous compounds in the aqueous phase was nearly same as bio-oil. This reserarch was showed that liquid phase of microalgae especially bio-oil can be used as carbon-neutral fuel after advanced upgrading techniques.

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