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Comparison and Optimization of Pyrolysis Bio-Oil Composition from Sewage Sludge and Spirulina Microalgae

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ABSTRACT

The abundant presence of spirulina microalgae and sewage sludge led to the researchers pay attention to recycling and economical conversion into valuable materials. This study investigated the simultaneous pyrolysis composition of two materials, spirulina microalgae and sewage sludge and also the factors affecting of the production of bio-oil from them. The effect of temperature, weight ratio of spirulina to SS, and the heating rate was investigated. Optimal conditions for pyrolysis was obtained at 519.3 °C, the weight ratio of 0.73 and heating rate of 17.9 °C/min and bio-oil production yield also was obtained 69.35%. The heat value of bio-oil was obtained at 25.52 MJ/kg and its energy efficiency was 66.3%. The results showed that with increasing in the temperature, the amount of aromatic substances that enhance the heat value were increased. Also, by directing the reaction to optimal conditions, the oxygenated and nitrogenous compounds detected in the bio-oil were reduced. The highest bio-oil yield was obtained at 69.09% and 450 °C, the weight ratio of (spirulina /SS) 0.5 and heating rate of 20 °C/min. The simultaneous combination of spirulina and SS increases the number of aromatic substances and decreases oxygenated and nitrogenous group spirulina in bio-oils.

Introduction

The increasing global population and the industrial growth along with the advancement of technology, have increased the consumption of fossil fuels. But fossil fuels are limited and made pollution, so attention to new energy sources and more economical methods has increased. Waste is one of the most important materials. Any type of solid, gas, and liquid that is directly or indirectly obtained from human activity and is considered as waste. Due to the widespread use of plastics in human life, the consumption of plastics has increased dramatically [1]. The entry of a huge amount of spirulina microalgae into nature has harmful effects on the

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environment, and proper management of spirulina microalgae can play an effective role in preserving the environment.

Hazardous waste and sludge make it difficult to manage and bury. Unlike effluents from treatment plants, which have usually good quality for discharge to nature. Sludge, which is the result of the concentration of existing pollutants, is in no way allowed to enter the environment in its raw and untreated form. Researchers in recent years have studied alternative methods for optimal treatment of these materials as well as energy and fuel production from them in this regard [2].

Sludge management from these treatment plants is the main part of wastewater management. Doing so requires a lot of money and constant effort [3]. Spirulina microalgae is rich in protein and low in fat and therefore is a good feed for the pyrolysis process and the production of valuable aromatic substances such as solvents. Low-lipid microalgae strains such as spirulina can easily adapt to the culture medium and grow faster than high-lipid strains in wastewater. Spirulina is one of the most famous green-blue algal strains grown on a large scale. This strain is used as a dietary supplement due to its gamma linoleic acid and carotenes. Some research, in the rapid pyrolysis of chlorella with zeolite catalyst and weight ratio of 1:9, were declared the yield of aromatic hydrocarbons of 25%, and the amount of monoaromatic aromatics (such as BTX) in aromatic products was higher [2-4].

These amounts of waste due to their toxicity, stability, and high concentration include a wide range of environmental, economic, and health effects. The upward trend in population growth is increasing the need for energy, and in this regard, the vast and relatively cheap sources of nonrenewable fuels such as oil and natural gas are declining. Therefore, removal and transformation into materials with appropriate economic value, and the invention of up-to-date methods to use the energy of spirulina microalgae waste, have been considered [5].

Waste incineration and landfilling methods are relatively obsolete and simple and cannot be used due to environmental problems. Incineration of sewage sludge causes the release of gases such as CO, NOX, NH3, and PbO [6-8]. An alternative method to remove these values is chemical recycling [9]. Among the available solutions for chemical recycling, the pyrolysis process is in focus due to its low cost, process safety. It breaks long chains into smaller, less complex molecules through heat and pressure. This process requires high heat in a short time in the absence of oxygen. The pyrolysis process is mainly classified into fast and slow. The rapid pyrolysis method is used to increase the production of liquid products. At present, the tendency to rapid pyrolysis with an average temperature of 450 - 600 °C and a residence time of a few seconds, and a high heating rate has been considered in recent years [10]. Pyrolysis is a flexible process and its parameters can be optimized based on the product. The products of this process include bio-oil, gas, and biochar, all three of which are recyclable for energy production. The liquid product can be used in multiple ways and has spirulina microalgae aplications such as consumption in furnaces, boilers, turbines, and diesel engines without the need for updating or refining. About half of the organic matter in the sludge can be converted into useful bioenergy (in the form of gas and liquid) and the rest remains stabilized in the solid, the solid can also be used to increase soil quality [11]. The most limiting factor in the use of this method is the solids produced in this process, because it may contain heavy metals and some unsuitable organic and inorganic compounds. The resulting liquids contain organic compounds include acids, alcohols, aldehydes, ketones, esters, cyclic compounds, and phenolic compounds [12]. Research on the thermal decomposition of activated sludge spirulina microalgae has been conducted, in which acrylamide addition complicates the pyrolysis process and causes turbulence in the process, and increases the process energy [13]. The pyrolysis process was used to dispose of food waste, which had good results, which increased the conversion from 0.1 to 0.9, 90% of the material was completely decomposed after the pyrolysis process [14]. Naqvi et al. have also discussed recent developments in the pyrolysis of wastewater sludge and its kinetics, resource recovery, thermogravimetric platforms, and innovative perspectives that use thermogravimetric techniques and other kinetic models to analyze sludge [15].

Sewage sludge is currently considered unsuitable waste, its entry into the environment is associated with adverse effects and its disposal management is associated with high cost. Therefore, a solution that can reduce the volume of this material virtually is viable economically and considered by urban management and waste management. Pyrolysis of sewage sludge is difficult due to high ash content, but its combination with a substance that has high volatile substances and produces high bio-oil improves the overall process. Therefore, in this research, the combination of sewage sludge and spirulina microalgae biomass was used. So far, the combination of these two substances has not been studied simultaneously. The purpose of this study is to investigate the simultaneous pyrolysis of two spirulina microalgae and sewage sludge. One of the goals of combining the two feeds for pyrolysis is to improve the amount of oil produced.

Experimental

Materials

Pure spirulina was purchased from Sina algae Company. SS was prepared from the Islamshahr sewage sludge treatment plant. The dichloromethane solvent was purchased with purity 99% wt from Dr. Mojllali's company and nitrogen gas are also used.

By placing the SS in a dry environment for 48 hours, its moisture was taken and obtained by passing a sieve of particles with dimensions of 1-3 mm. These materials were stored in the refrigerator and in plastic bags.

Experimental Pyrolysis Method

First, a certain amount of SS with spirulina was weighed according to their weight ratio in each test, and after combining, it was poured and placed in a pyrolysis reactor. Before starting the test, nitrogen gas with a flow rate of 0.5 L/min was introduced into the vessel for 30 min to completely remove oxygen from the reactor medium. After reaching the desired temperature, the reactor temperature was kept constant for 30 min to complete the decomposition of the pyrolysis compound. The device was then switched off and after reaching the ambient temperature, the solid waste remaining in the pyrolysis reactor was collected as bio-char. Also, the liquid collected in the falcon weighed as bio-oil. DCM solvent was used to wash all components at each time. By measuring the amount of bio-oil, coal, and gas obtained, the yield of each product was calculated from Eqs. 1 and 2 [16].

$$\mathrm{Bio-oilyield;\ wt:\%} = \frac{\mathrm{mass\ of\ bio\_oil(g)}}{\mathrm{massoffeed(g)}} \times 100 \quad (1)$$

$$\mathrm{Biocharyield;\ wt:\%} = \frac{\mathrm{massofbio\_char(g)}}{\mathrm{mass\ of\ feed(g)}} \quad (2)$$

Characterization Methods

After testing and obtaining bio-oil, elemental analysis (Truspec is manufactured by the LECO, USA), thermal weighing analysis (TGA) (Q600 machine made by TA company, USA) [17], and gas-mass chromatography (GC-MS) were performed to determine the product specifications [18]. Also, after performing pyrolysis tests and production of bio-oil under optimal conditions, the bio-oil sample is tested for elemental analysis. The high heat value (HHV) of the feed and bio-oil produced can be calculated according to Eq. 3 [16]:

$$HHV(MJ/Kg) = 0.338 * C + 1.428 * (H - O/8) + 0.095 \times S \quad (3)$$

In this regard, C, H, O, and S are the weight percentages of carbon, hydrogen, oxygen, and sulphur. With the help of Eq.4, the energy efficiency for the bio-oil can be calculated [15]:

$$\text{Energy Recovery (ER)} = (\text{HHVbiooil} \times \text{mbiooil})/(\text{HHVbiomass} \times \text{mbiomass}) \quad (4)$$

GC-MS analysis for samples was performeed under optimal conditions, in which helium with a volume flow of 50 ml/min is used as the carrier gas, and the samples are filtered before injection to remove solids. The amount of injection in each step is half a microliter. The samples are kept at 40 °C for one hour before injection. The injection temperature is 40 °C. The temperature increases at a rate of 40 °C/min to 300 °C and is kept at this temperature for half an hour. The characteristics of the column are 30 m, 0.25 mm, and 0.25 µm thick (5975C machine, UA-5 column type, made by Agilent Technologies, Singapore) [19].

Experimental Design

In this research, Design Expert.11 software and the CCD test design method have been used. The experimental variables are temperature (T: °C), heating rate H: °C/min, and the input ratio of two substances in the feed (R). The temperature variation range is between (350-550) °C, the heating rate is 10-20 °C/min and the weight ratio of spirulina to SS in the feed is 0.2-0.8. Finally, the test design table was presented as Table 1.

Table1. Experimental design results with software Design Expert.11

Number of levels	Temperature (°C)	The weight ratio	Heating speed (°C/min)	Bio-Oil yield	Bio-Char yield
1	550	0.5	20	28.33	69.09
2	450	0.5	15	28.55	68.42
3	450	0.5	20	28.7	68.46
4	550	0.2	20	47.5	46.53
5	350	0.8	20	25.62	64.05
6	450	0.5	15	28.06	68.46
7	450	0.8	15	27.5	68.76
8	450	0.2	15	47.86	47.97
9	550	0.5	15	27.79	66.41
10	550	0.8	10	25.8	66.17
11	550	0.2	10	46.14	45.36
12	350	0.2	10	45.96	41.87
13	350	0.8	10	25.58	62.65
14	550	0.8	20	26.87	67.18
15	450	0.5	15	26.6	68.45
16	450	0.5	15	26.03	68.51

Results

Elemental and Proximate Analysis

The results of elemental analysis and spirulina microalgae, approximation of spirulina and SS waste are shown in Table 2. Due to the small amounts of nitrogen and sulfur elements in the feed, the number of SO_x and NO_x in pyrolyzed bio-oil samples will be less. The HHV of most microalge biomass compared to other masses such as SS is due to the high amount of carbon in these materials. Volatiles in SS and spirulina are predicted to be 66.3% and 80.9%, respectively.

Volatiles contain organic compounds that decompose at high temperatures. The relatively high number of volatiles in SS and spirulina with a high percentage of purity increases the bio-oil production and also increases the HHV of the pyrolyzed sample.

Table 2. Proximate analysis of raw feeds and their heat value

Food	C	H	N	S	O	FC	Humidity	VM	Ash	HHV (MJ/kg)
Spirulina	47.45	7.14	10.64	1.2	33.55	6.05	5.4	80.9	7.65	22.42
Sewage sludge	28.8	4.4	4.5	1.5	33.6	0.2	6.3	66.3	27.2	10.16

Thermal Gravimetric Analysis

Figs. 1 and 2 show the TGA and DTG diagrams of spirulina and SS. The weight loss versus temperature curve with a linear heating rate of 15 °C/min for thermal decomposition of spirulina is shown in Fig.1. As can be seen, decomposition is a one-step process with a final temperature about 420 °C. The curve in Fig.1 shows that the greatest weight loss is related to the decomposition at 408 °C temperature. Also, 90.98% of weight loss occurs in the temperature range between 250 to 450 °C. The residual weight is 9.02% and remains constant up to 800 °C. Fig.2 shows the TGA and DTGA curves of SS. The total weight loss of SS up to 900 ℃ temperature reaches about 51.67%. Three distinct areas with different peaks are shown. The first peak is predicted to be about 5%, which is related to the removal of water, the highest rate of this weight loss occurs at 78.2 °C temperature. The second area of weight loss occurs in the temperature range between 150-500 °C, which is about 40% of the total weight loss [20]. This temperature range is related to the decomposition of volatile substances and the main decomposition occurs in this temperature range. In this range, there are two main peaks at 147.2 °C and 304.6 °C temperatures related to this major weight loss, and it seems that in these two peaks, two volatile organics are produced. The reason, is the presence of components such as proteins and carboxylic functional group in the spirulina and SS About 5% weight loss is also observed in the temperature range of 500-900 °C. According to the researchers' report on the presence of large amounts of inorganic substances such as calcium in SS, with a high spirulina microalgae aproximation, this weight change in this temperature range is due to the decomposition of inorganic substances such as calcium carbonate [21].

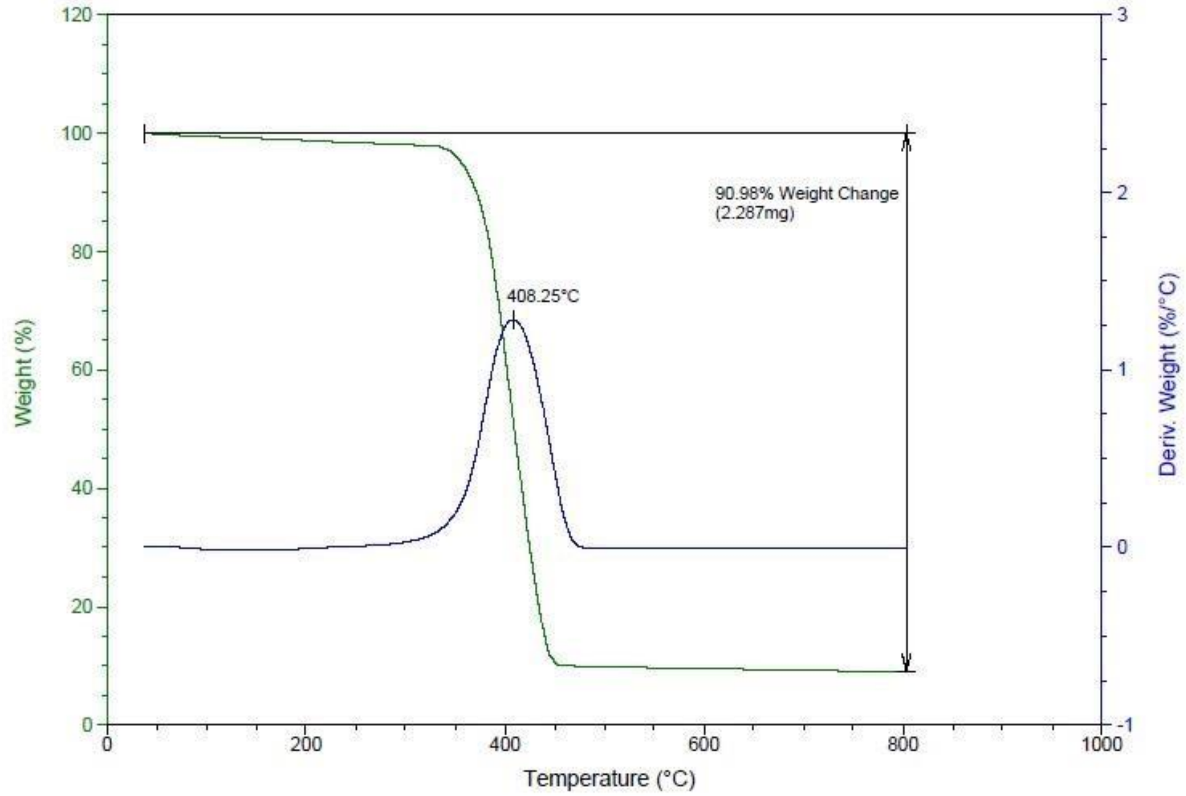

Fig. 1. Thermal weighing analysis and derivative of thermal weighing analysis of spirulina

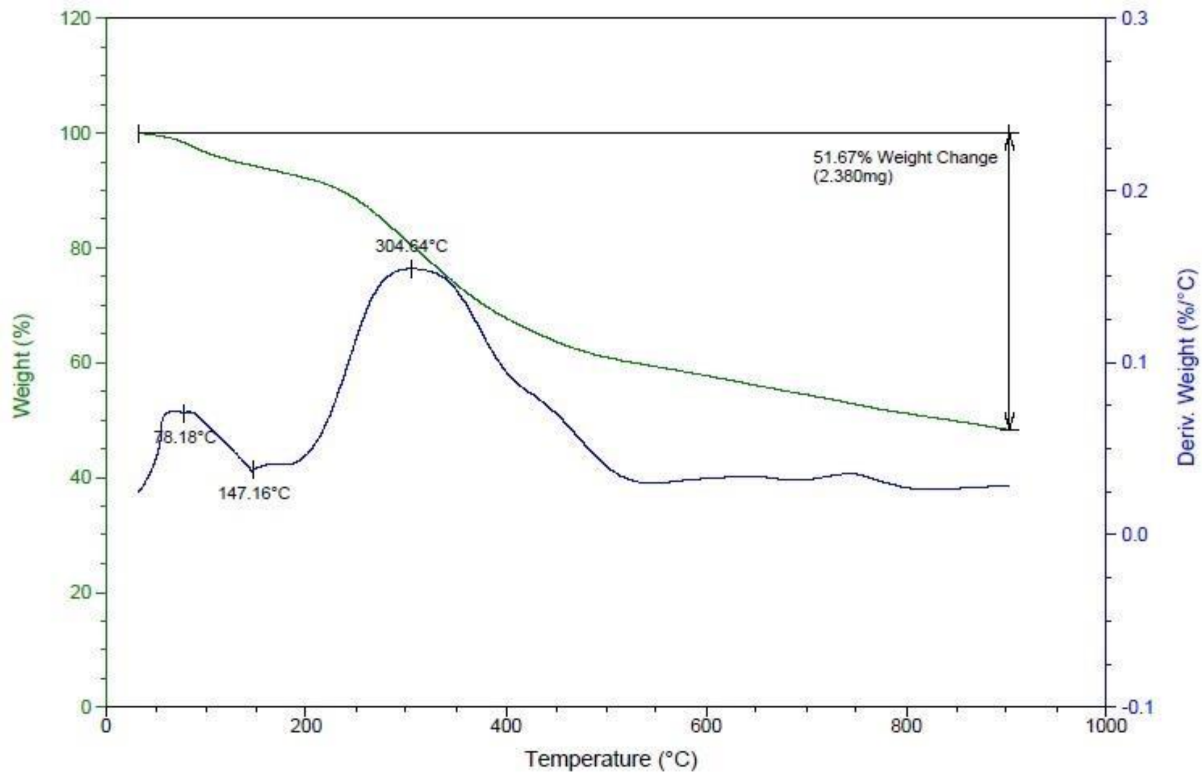

Fig. 2. Thermal weighing analysis and derivative of thermal weighing analysis of Sewage sludge

3.3. Analysis of variance

The software has proposed a quadratic model for the yield of bio-oil (including quadratic expressions), including linear expressions, binary interaction expressions, and squared expressions. Value and the criterion are R^2. The default value of p-value to confirm the accuracy of the models in the software was obtained for $p < 0.05$. The criterion p-value also indicates the importance of the equation terms of the presented models. So that the value of $p < 0.1$ indicates the importance of the term is in model equation. Therefore, in this model, all expressions except (TR) and (RH), and (TH) are important [22]. The coefficient column in Table 3 indicates the effect coefficients of the model terms. The absolute value of the coefficient indicates the magnitude of the effect of that term. For modeling, the temperature parameter (T) had the greatest impact on increasing the bio-oil yield production. The weight ratio parameter (R) and the heating rate parameter (H) have an increasing effect on the bio-oil yield production, But due to the fact that the coefficient related to the parameter (R) is larger than the heating rate parameter (H), it is assumed that this parameter is more effective.

Table 3. Results of data analysis of variance

Parameter (Coefficient)	**Bio-oil yield % Coefficient**	**Bio-oil yield % p-value**
Intercept	68.41	<0.0001
A (Temperature)	1.69	<0.0001
B (Ratio)	1.38	<0.0001
C (Heat rate)	0.6750	<0.0001
AB (TR)	-0.0125	0.7880
AC (TH)	-0.0775	0.1167
BC (RH)	-0.02	0.6679
A2T2	-3.67	<0.0001
$B^2(R^2)$	-9.98	<0.0001
$C^2(H^2)$	-0.1391	0.1017

The Overall Impact of the Parameters

Diagrams of the effect of temperature on bio-oil yield are shown in Fig.3. The dashed line in this chart is the spirulina microalgae and confidence limit are less than 95%. When the temperature increases, the bio-oil yield increases and then decreases after reaching a maximum. The effect of the weight ratio parameter on the two feeds is similar to the temperature parameter, so that by increasing this amount, the content of produced bio-oil increases to optimal conditions and then decreases with a gentle slope. The reason is that in the low weight ratio, the amount of spirulina in the composition became low and the available SS is high, according to the research, pyrolysis of the composition with a higher amount of sewage sludge leads to a decrease in the percentage of bio-oil production [23]. Also, the bio-oil yield increases almost linearly with a gentle slope with heating rate.

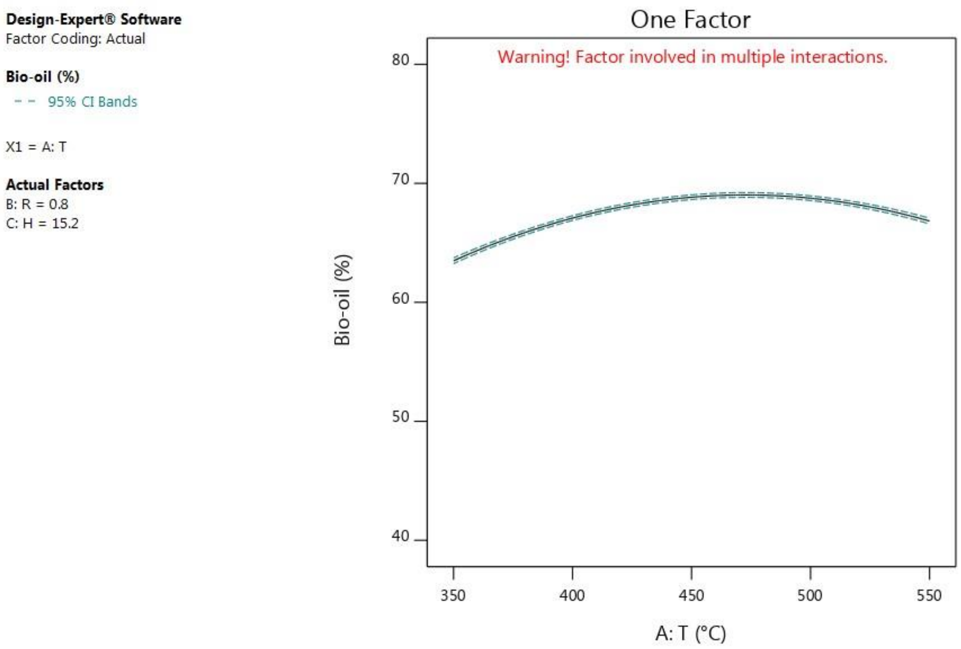

Fig. 3. Diagram of the general effect of temperature parameter on bio-oil yield production

Statistical models

The coded equation and the real equation of the proposed models for bio-oil yield are in the form of Eqs.5 and 6 [24]:

$$\text{Bio} - \text{oil yield (Coded)} = 67.55 + 1.5 \times T + 10.30 \times R + 0.8 \times H - 0.25 \times TH - 0.25 \times RH - 3.86 \times T2 - 9.86 \times R2 + 0.6364 \times H2$$

$$\text{Yield (Actual)} = -60.8 + 0.370227 \times T + 141.41929 \times R - 0.461970 \times H0.0005 \times T \times H + 0.16666 \times R \times H - 0.000382 \times T2 - 109.59R2 + 0.025455 \times H2 \quad (6)$$

Due to the good agreement of the model prediction with the experimental data, the obtained statistical model has good accuracy, and also the laboratory results are reproducible.

Response Level Diagrams

Response level diagrams are a graphical representation of the effect of experimental parameters on the response quantity, in which the simultaneous effect of two parameters on the response are displayed while the third parameter is considered at a fixed central point. The surface and procedure diagrams for the pyrolysis compound are shown in Fig.4. The color guide of the graphs shows that the closer value of the parameters to the red range, are the higher response value. For response level diagrams, the bio-oil yield in terms of T and H is observed that by increasing the temperature the effect of heating rate increases; In other words, the increasing effect of heating rate on bio-oil yield at high temperatures is greater than this effect at low temperatures. The interaction between feed weight and temperature is such that at low temperatures, with an increasing weight ratio of feed, bio-oil yield increases and finally reaches a maximum value and continues along the path. At higher temperatures, increasing the weight ratio of the two feeds has a less positive effect on the bio-oil yield and takes a downward trend chart. The increase in bio-oil yield has been biomass, while the highest value of this yield has been obtained in average T values around 450 °C. Three-dimensional methods also confirm this fact for pyrolysis samples.

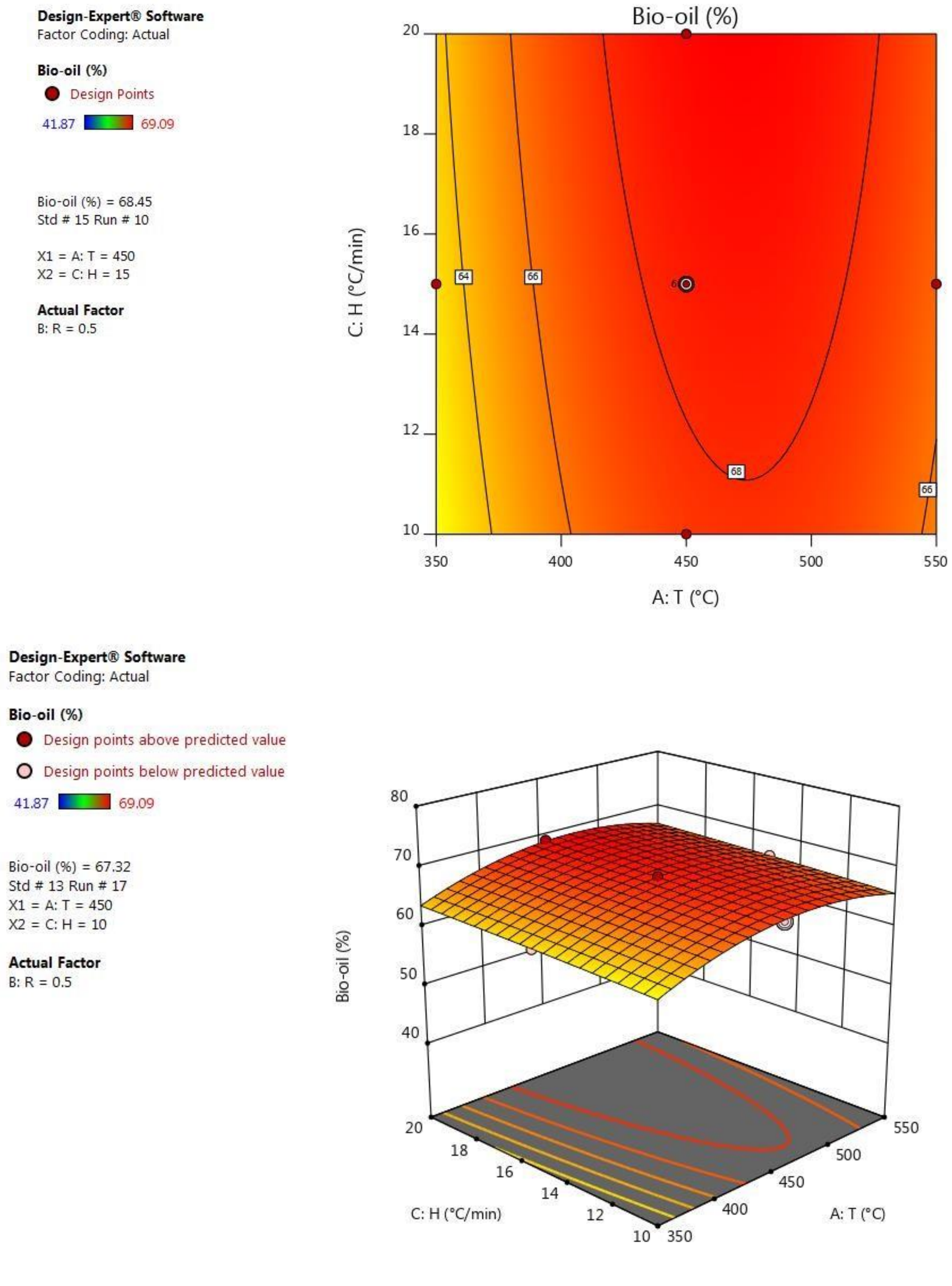

Fig.4. Two-dimensional and three-dimensional diagrams of bio-oil yield production in terms of T and H

Optimization

Using the proposed mathematical model for bio-oil yield, optimal conditions were obtained to achieve the maximum amount of bio-oil production for the pyrolyzed combination of SS and spirulina. Also, to check the accuracy of the optimal conditions obtained by the model, pyrolysis of the desired compound was performed under the optimal conditions of the model. The optimum pyrolysis conditions for the combination of SS and spirulina were 519.3 °C temperature, the weight ratio of the two feeds was obtained 0.73 and the heating rate was obtained 17.9 °C/min. Under these conditions, the highest yield of bio-oil was predicted about 70.17%, which according to the error of 1.16% in predicting the optimal value, shows that the model has been able to predict the optimal value with great accuracy.

Miandad et al. Investigated the effect of temperature and residence time parameters of direct spirulina pyrolysis in a batch reactor. So that the yield of bio-oil production in this process reached 76%, the optimum temperature and optimal time of this process were obtained 450 °C and 75 minutes, respectively. The HHV of bio-oil produced by this process was obtained 41.6 MJ/kg [25]. The produced bio-oil in the pyrolysis process of wastewater sludge contains significant sources of light aromatics such as benzene, toluene, and xylene. The outstanding bio-oil product of this process, which contains a weight percentage between 30 and 40%, was obtained at temperatures of spirulina microalgae aproximately 424 to 575°C [26].

Table 4. Compounds in the dark phase of pyrolysis bio-oil at 450 °C

No.	Formula	Component	Wt. %
1	$C_2H_4O_2$	Methyl formate	0.36
2	C_6H_6	Benzene	0.34
3	C_7H_8	Toluene	5.1
4	C_8H_{10}	Ethylbenzene	4.27
5	C_8H_8	1,3,5,7-Cyclooctatetraene	18.82
6	C_9H_{12}	Benzene, (1-methylethyl)-	0.21
7	C_9H_{10}	Benzene, 1-propeny-l	0.19
8	C_7H_6O	Benzaldehyde	3.54
9	C_9H_{10}	Alpha-methylstyrene	4.92
10	C_9H_{10}	benzene, 2-propenyl-	0.86
11	$C_{10}H_{14}$	Benzene, (1-methylpropyl)-	0.62
12	C_8H_8O	Acetophenone	1.58
13	$C_{10}H_8$	Naphthalene	0.21
14	$C_9H_{12}O$	Benzeneethanol, β-methyl-	1.02
15	$C_{14}H_{14}O_2$	Benzene,1,1’-[1,2-ethanediyl]bis-	2.60
16	$C_{15}H_{16}$	Benzene1,1'-(1-methyl-1,2-ethanediyl)bis-	1.07
17	$C_{11}H_{14}$	Bicyclo[4.2.1]nona-2,4,7-triene,\7-ethyl-	1.31
18	$C_{11}H_{14}O_2$	Benzeneacetic acid, α-ethyl-, methyl ester	0.55
19	$C_{15}H_{16}$	Benzene, 1,1'-(1,3-propanediyl)bis-	3.51
20	$C_9H_9N_3$	1-Benzyl-1,2,3-triazole	14.5
21	$C_{16}H_{18}$	Benzene, 1,1'-(1,4-butanediyl)bis-	0.8
22	$C_{16}H_{16}$	Naphthalene1,2,3,4-tetrahydro-1-phenyl-	1.32
23	$C_{15}H_{10}O$	5H-Dibenzo[a,d]cyclohepten-5-one	1.51
24	$C_{15}H_{13}N$	1-Phenyl-3,4-dihydro isoquinoline	2.97
25	$C_{15}H_{14}O$	Benzene,1,1’-[1,2-ethanediyl]bis-	1.01
26	$C_{16}H_{12}$	Anthracene, 9-ethenyl-	1.84
27	$C_{18}H_{18}$	2,5-Diphenyl-1,5-hexadiene	1.55
28	$C_{12}H_{14}O_2$	3(2H)-Furanone,dihydro-2,2-dimethyl-5-phenyl-	1.14
29	$C_{16}H_{12}$	Naphthalene, 2-phenyl-	7.80
30	$C_{17}H_{16}O$	1,5-Diphenyl-4-penten-1-one	1.62
31	$C_{14}H_{22}O_6$	2-Propenoicacid,2-methyl-,1,2-ethanediylbis(oxy-2,1-ethanediyl) ester	1.36
32	$C_{17}H_{14}$	Naphthalene, 2-(phenyl methyl)-	0.66
33	$C_{15}H_{13}N$	Benzonitrile, m-phenethyl-	3.95
34	$C_{24}H_{38}O_4$	1,3-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester	2.00

GC-MS Analysis

The bio-oil compounds were examined in dark and light phases. Also Pyrolysis samples were tested at 450 and 550 °C temperature with the same heating rate (15 °C/min) and a constant weight ratio of 0.5 (spirulina /SS). This is done to investigate the changes in bio-oil compounds in the process by increasing temperature. Table 5 illustrates information about the comparison of the percentage of compounds in bio-oil at two temperatures of 450 °C and 550 °C with heating rate and percentage of the same weight composition in the dark phase.

Based on the results of GC-MS analysis, important hybrid group spirulina and their values can be identified. These group spirulina include aromatic compounds, oxygenated compounds, and nitrogenous compounds in the dark phase. As can be seen in Table 5, the highest amount of group compounds in the dark phase of pyrolysis bio-oil at both temperatures is related to aromatic compounds.

Table 5. Comparison of the percentage of compounds in bio-oil at two temperatures of 450 °C and 550 °C with heating rate and percentage of the same weight composition in the dark phase

Group type	Bio-oil at 450 °C (%)	Bio-oil at 550 °C (%)
Percentage of aromatic compounds	60.29	70.02
Percentage of oxygenated compounds	18.29	11.24
Percentage of nitrogenous compounds	21.42	10.79

In the case of aromatic compounds, the higher amount of these compounds, have the higher HHV of the fuel. Aromatic compounds improve the HHV of the fuel to some extent, but in amounts greater than 50% can slightly increase the pollutant compounds. It was also observed, due to the increase in pyrolysis temperature, the HHV of the bio-oil has increased to some extent. The percentage of nitrogenous compounds indicates the amount of fuel pollution produced, so higher amount of nitrogenous compounds, due to the more fuel pollution. Nitrogen-containing compounds are carcinogenic and their high levels in the fuel can be life-threatening for humans and other organisms by causing environmental pollution [27]. Finally, oxygenated compounds reduce the HHV [28]. Therefore, according to Table 5, increasing in temperature increases the HHV of the desired bio-oil, and also cause reduction in the values of oxygenated and nitrogenous group in spirulina, consequently the bio-oil will be lower and environmental reliability will be higher. Table 6 examines and compares the percentage changes of spirulina functional group in terms of the combination and non-combination of spirulina and pyrolysis SS.

Table 6. Comparison of aromatic, oxygenated, and nitrogenous compounds for both combining and non-combining states of spirulina and pyrolysis sewage sludge

Group type	Pyrolyzed bio-oil Total SS and spirulina (%) (without simultaneous combination)	Petroleum biopyrolyzed at 450 °C with pure SS(%)	Petroleum, biopyrolysis at 450 °C with spirulina (%)	Petroleum biofilm with a combination of spirulina and SS at 450 °C(%)
percentage of aromatic compounds	35.6	16.88	54.33	60.29
Percenta ge of oxygenated compounds	37.7	29.8	45.67	18.29
Percentage of nitrogen-containing compounds	26.66	53.32	0	21.42

It can be seen that the simultaneous combination of spirulina and SS in pyrolysis has advantages over separate pyrolysis of feed with the same weight ratios. Whereas the weight ratio of the two substances for pyrolysis at 450 °C is considered at 0.5, it is possible to take the average percentage of the identified spirulina functional group of each feed in the pyrolysis mode individually, to review and compare the desired categories. Considering that the percentage of aromatic compounds in the combined state of two feeds is higher than the average state of pyrolysis of two components in the single state and also the percentage of oxygenated and nitrogenous compounds are lower than the average state, so it is concluded that the simultaneous combination of these two materials is effective for pyrolysis and also more effective than the average in terms of the fuel HHV and environmental criteria. Therefore increasing the temperature up to 450 °C causes this amount increases to 66.82% (Fig.5). As a result, the amount of substances such as monocyclic aromatics has increased [29]. For example, the amount of toluene at 450 °C compared to 550 °C increased from 3.54% to 4.64%. Further studies show that the identified aromatic mono-ring materials have the highest amounts, which are obtained at 550 °C temprature and have a relatively significant increase compared to the pyrolysis temperature at 450 °C temprature. Liu et al. reported that the formation of aromatic monolayers by lateral suction in product formation increased with increasing temperature. At high temperatures, dehydrogenation reactions are reduced, and also the reactions such as the density of aromatic rings to form polychromatic materials are reduced. For this reason, with increasing temperature, the amount of mono-ring aromatic substances in the clear phase of pyrolysis petroleum has increased [30].

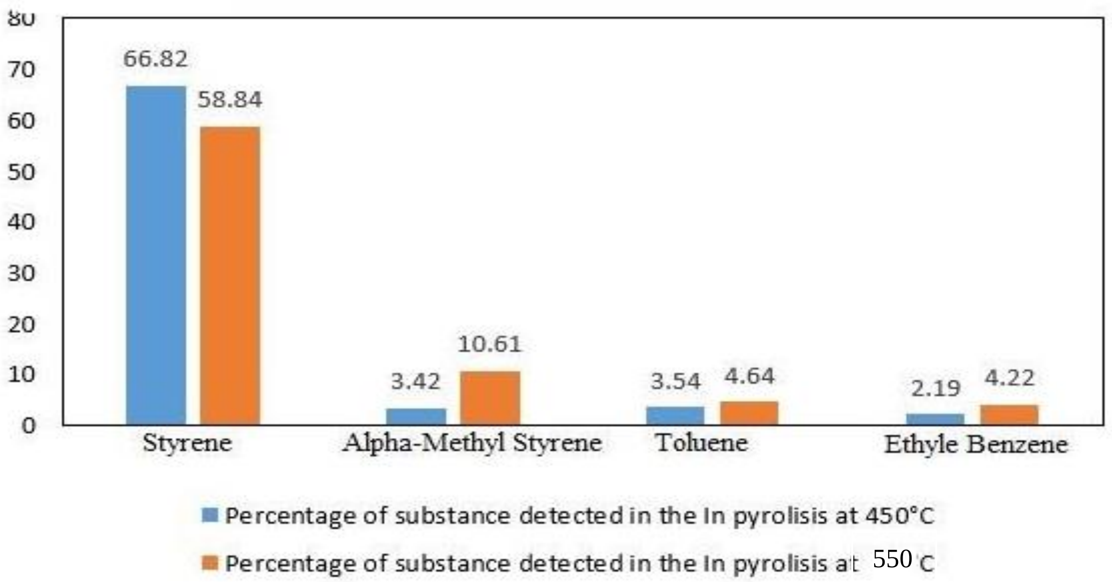

Fig. 5. Changes in the percentage of materials detected at two different temperatures of the pyrolysis process in the clear phase

Conclusions

The results of pyrolysis of a combination of spirulina and SS are as follows:

- The highest bio-oil yield for this compound was obtained by amount 69.09% at 450 °C temprature, the weight ratio of (spirulina/SS) (0.5 and heating rate of 20 °C/min). Under the same conditions and with pure spirulina feed 76% was reported. The project can be concluded that the combination of these two materials with different operating conditions has improved the yield of bio-oil and is effective in converting the waste of this material into usable fuel with relatively low pollution.
- According to the results of the analysis of variance, it was found that all three parameters, temperature, the weight ratio of spirulina to SS, and heating rate are

effective in bio-oil yield and increase the conversion of waste into fuel. As predicted, the temperature parameter has the most positive effect on this process.

- According to the GC-MS analysis performed for bio-oil from pyrolysis of the desired compound at 450°C and 550 °C temprature, it was concluded that by increasing the temperature and moving the reaction conditions to the defined optimal conditions, the percentage of aromatic compounds increased, which increases the high heat value of the bio-oil and also reduces the percentage of nitrogenous compounds that increase fuel pollution. The presence of spirulina oxygenated group in petroleum reduces the HHV, whereas by increasing temperature, the amount of these compounds in the bio-oil has decreased, and also HHV of the bio-oil improves.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationshis that could have to influence the work reported in this paper.

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