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ABSTRACT

In this work, Pyrolysis experiments of biomass of Scenedesmus & Spirogyra (SSB) were carried out in a pyrolysis reactor to detect different hydrocarbons and compounds present in SSB. GC-MS analysis and IR has been done of bio-oil obtained from pyrolysis of SSB and a simple process of converting of algal biomass to bio-oil through pyrolysis is explained with the help of graphs and tables. The bio-oil was obtained in single step pyrolysis in which temperature of the system was kept 25ºC and then increased up to 650ºC time by time. Pyrolysis is a thermal process for converting various biomasses, residues and wastes to produce high-energy-density fuels. After pyrolysis the obtained bio-oil was introduced to fractional distillation and then analyzed by gas chromatography/mass spectrometry (GC-MS) and IR. Different hydrocarbons and other compounds were detected.

Keywords: Biomass, Bio-oil, Pyrolysis, GC-MS, FT-IR.

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INTRODUCTION

With the increasing stringent environmental legislations and growing energy demand, researchers are looking for environment friendly alternative energy sources among which biodiesel is one potential candidate. Biodiesel refers to the fatty acid alkyl esters (FAAEs), mainly methyl esters which are derived from lipid substances originated from oils, fats, waste greases, recycled oils etc [1, 2, 3]. Recently biodiesel are getting more and more importance as an engine fuels and one of the most promising alternative energy. biodiesel or bio-oil are becoming more attractive for the users in all over the word because of their usefulness for the people and environment around us, Biodiesel is an oxygenated fuel consisting of long chain fatty acid which contain 10–15% oxygen by weight to find and develop an alternative energy is a major issue to our environment due to the depletion of fossil fuel [4-6]. Among many kinds of alternative energies, biodiesel can be directly applied to nowadays diesel engines with benefits low pollutions, high environmental friendliness and sustainability. and it contains neither sulfur, nor aroma. These facts lead biodiesel to enhance more complete combustion and less emission of particulate matter [7]. Recently, catalytic pyrolysis has aroused a great interest for the advantages of operating at atmospheric pressure and the lack of need for hydrogen [8], which has been demonstrated by many researchers. The experiments on catalytic pyrolysis of biomass were generally carried out in a fixed bed reactor or fluidized bed [9, 10]. On the other hand biodiesel has higher molecular weight, density, viscosity and pour point than conventional diesel fuel [11,12]. Higher molecular weight and viscosity of biodiesel causes low volatility and poor fuel atomization, injector coking, piston ring sticking and leading incomplete combustion [13] as well as it has cold flow property which is a barrier to use it in cold or chill weather [14]. Anyhow the best benefit of Bio-oils is that they are preparing from renewable sources like corpse, plants, trees and residues etc. approximately 100 years ago, Rudolf Diesel tested Bio oil as the fuel for his engine that was available with him [15, 16] Soybean oil was transesterified into ethyl and methylesters, and comparisons of the performances of the fuels with diesel were made.[17,18].Also, methylesters have been prepared from palm oil by transesterification using methanol in the presence of a catalyst (NaOH) or (KOH) in a batch reactor [19]. Ethan oils a preferred alcohol in the transesterification process compared to methanol because it is derived from natural agricultural products and is renewable and biologically less objectionable in the environment. The success of rapeseed ethylester production would mean that biodiesel`s two main raw materials would be agriculturally produced, renewable and environmentally friendly [20]. Methyl, ethyl, 2-propyl and butyl esters were prepared from canola and linseed oils through transesterification using KOH and/or sodium alkoxides as catalysts. In addition, methyl and ethylesters were prepared from rapeseed and sunflower oils using the same catalysts [21, 22] Biomass is a renewable source which has received attention due to various characteristics, particularly its low cost and wide availability. Biomass can be converted into bio-fuel by means of different processes, e.g., reductive combustion, liquefaction, pyrolysis and gasification [23]. The use of biomass is particularly interesting when it involves waste products such as waste vegetable oil, fruit seeds, sugarcane bagasse, sugarcane straw, rice husks, coconut fibers, and coffee grounds, which are also potential sources of energy [24]. Taking into account that bio-oil from pyrolysis contains a very complex mixture of products, its chromatographic analyses requires the coupling of these instruments with a mass selective detector to aid the identification of eluted products [25].The mass spectrum, sometimes, is not sufficient to identify unknown compounds, due to the similarity of their spectra, thus the use of reference compounds may be an aid to overcome this problem. Furthermore, the use of analytical standards may allow quick quantification through one of several techniques, such as the internal standard method [23, 26]. However bio-oils from pyrolysis may include up to several hundred of compounds [27-30]. Although fast pyrolysis can produce considerable amount of bio-oils, for example a yield up 56.8%was reported in domestic research, their direct applications as fuels are limited by the problems of high viscosity, high oxygen content and corrosion, as well as their thermal instability. Therefore, bio-oils should be upgraded using proper methods before they can be used in diesel or gasoline engines [31].

RESULT & DISCUSSION

Theoretical bases of the pyrolysis of Biomass/SSB

SSB is a cellulosic biomass of Blue green algae which consider as third generation bio-fuel. It is used for the preparation of liquid and gaseous fuel. It contains small quantity of the lignin and its growth and multiplication is very rapid. The pyrolysis of the cellulosic biomass gives water soluble oxygenated compounds. It is thought that the cellulosic biomass may manufacture methanol, anhydrosugars, furans and aldehydes compounds. These can be used as fuel if appropriately utilized. These products are formed along with large quantity of water therefore need some treatments like removal of some heavy species as phenol and ketones to use as engine fuel. Important compounds like phenol and ketones can be recovered from these oils. The product of pyrolysis also contain oil like liquid which is believed as composed of compounds containing less oxygen contents. These are partly soluble in the aqueous mixture. Different pretreatment procedures were used to increase the oil products and to decrease the contents of organic acids and aldehydes as well as other reactive compounds, as oxygenated and nitrogenated species because they not only lead to high corrosiveness and acidity, but also set up many obstacles to applications.

Catalytic optimization

To choose a suitable amount or ratio of catalyst with biomass at which maximum amount of oil while minimum amount of residue and non-condensable gases are obtained. For this purpose numerous reaction were carried out in which the amount of catalyst was changed in each reaction with same amount of biomass. At different ratio of catalyst and biomass the pyrolysis reaction was carried out and finally 1:10 of catalyst and biomass respectively was found proper for maximum product yield of pyrolysis.

EXPERIMENTAL

Biomass of Scenedesmus & Spirogyra (SSB)

The SSB was first dried in fresh air and sunlight for 7days until a little bit moisture (5% approximately) remained and then it was converted into small size (powder form) the fine powder SSB was introduced to pyrolysis in the presence of catalyst calcium oxide (CaO).

Production of bio-oil from SSB

The bio-oil was produced from the pyrolysis of SSB. the weight of the sample was kept 300grams also some amount of sand was added to the mixture for some purposes (as heat resistant), after preparation of the sample it was kept inside a stainless steel reactor of pyrolysis system which is further connected to other condensation chambers which are shown in figure 1. Temperature of the reactor was increased from 25°C-650°C, through which biomass was converted to biogas and then the biogas was condensed in condensation chambers to bio-oil. The condensed fractions from this chamber was collected and introduced to fractional distillation. The obtained bio-oil was separated into two fractions and residues using distillation. It was carefully watched to accurately separate the two fractions and residue. These fractions were found in the temperature range of 65-200°**C** and the residue of distillation. The first fraction was obtained in the temperature range of 65-150°**C**, the second fraction was collected in the range 150-200°**C**.

Biomass pyrolysis system:

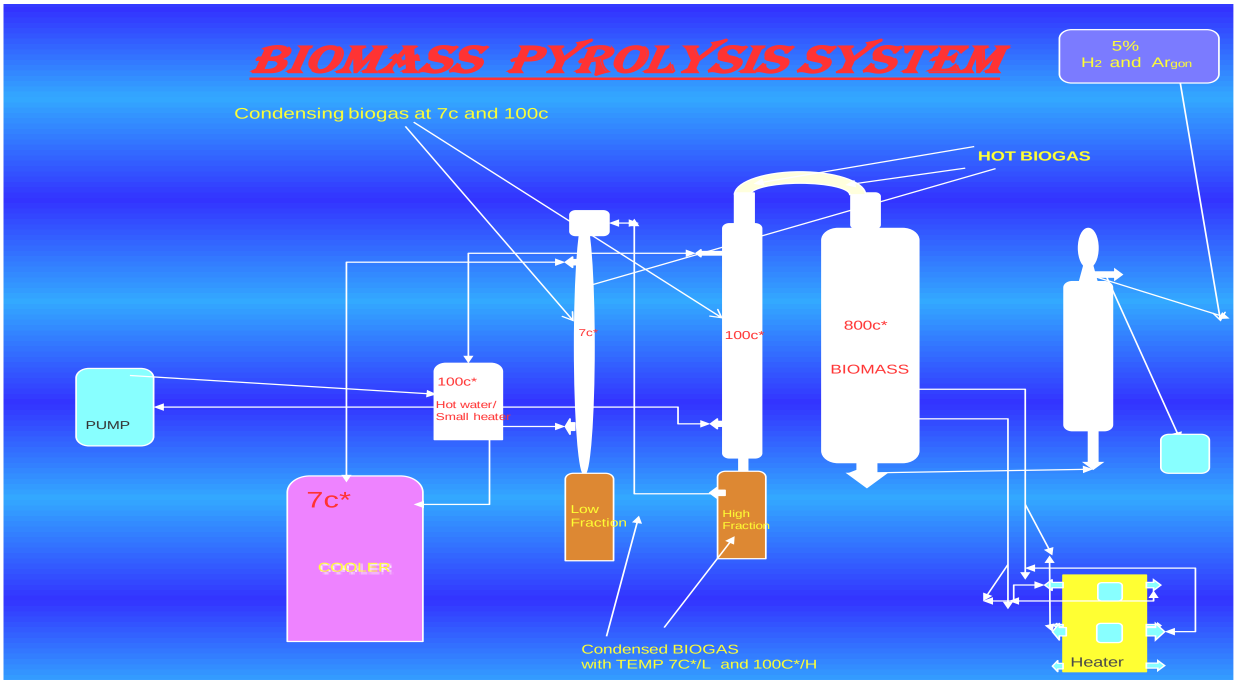


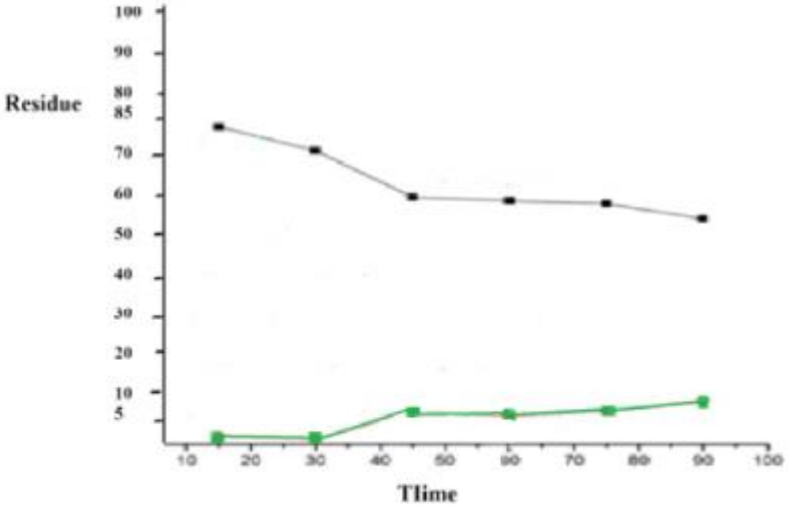
Fig 1.The biomass pyrolysis system

Table 1. Important data of Temperature for Pyrolysis of SSB

S.NO	Temperature	Biomass	% Liquid	% Gases	% Residue

	(^{0}C)	(g)	(Bio-oil)	(Non-condensable part)	(Ash + Sand)
1	250	300	7.01	0.103	92.89
2	350	300	20.11	9.66	70.23
3	450	300	25.99	11.24	62.77
4	550	300	26.97	15.93	57.10
5	650	300	34.16	12.84	53.10

Fig 2. below graph shows the relationship between Residues and time.



GC/MS chromatogram of SSB

The GC/MS analysis was carried out in order to find out the hydrocarbons and other compounds present in the bio-oil. The obtained bio-oil from pyrolysis was analyzed by GC/MS. The main peaks identification of compounds has been performed by using NIST mass spectral data base. The SSB bio-oil which obtained from pyrolysis was complex mixture and contained different class of hydrocarbons and other groups which are shown in the table. 2.

Chromatographic conditions were as follows

Injection volume of 0.2 µL, oven at 40°C (1 min) 6°C min−1 up to 300°C (10/Min) split mode with a ratio of 100:1 and injection temperature of 290 °C. Time taken was 54.3 minutes, He (helium) as carrier gas with a flow rate of 2.9 mL min−1.

GC-MS Chromatogram

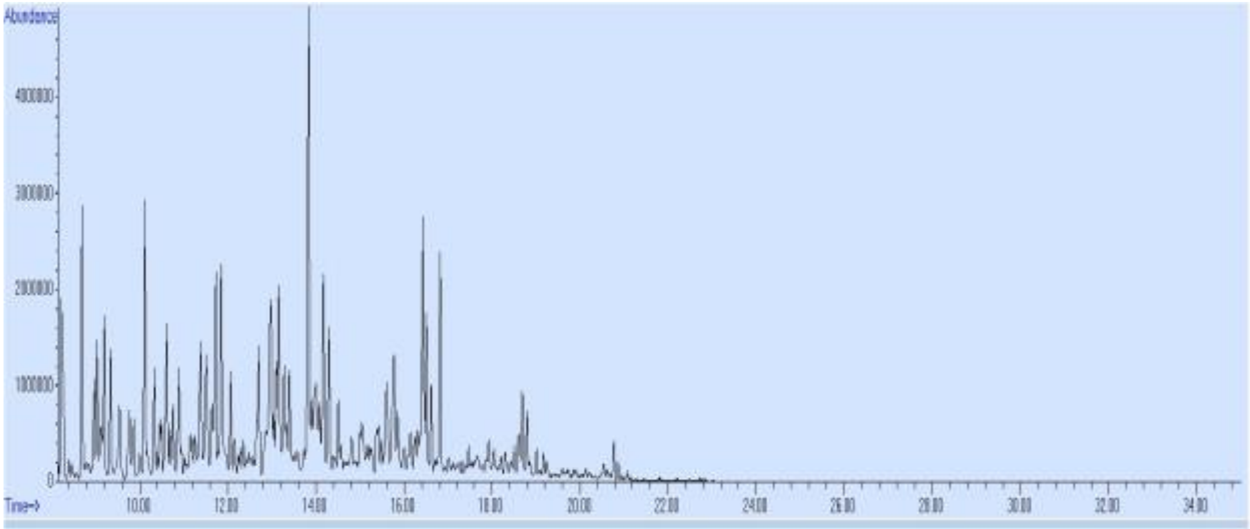


Fig 3, GC/MS CHROMATOGRAM OF THE SSB BIO-OIL AFTER PYROLYSIS.

Table. 2. Main compounds identified in the bio-oil product by GC-MS analysis.

S.NO	Name of compounds	Compound's Formula	Retention Time	% composition
1	2,2-dimethylpropiophenone	$C_{11}H_{14}O$	2.12	2.05
2	Isobutyronitrile	C_4H_7N	2.34	1.00

3	2-pyrrilidinone	C_4H_7NO	2.41	8.05
4	3,4,5- tri-methyl pyrazole	$C_6H_{10}N_2$	2.97	10.09
5	1-H-imidazole1,2,4,5-tetramethyl	$C_7H_{12}N$	3.43	8.25
6	3-methylbutanenitrile	C_5H_9N	3.75	2.10
7	2,3,4-trimethyl-d-xylose	$C_8H_{16}O_5$	3.93	9.09
8	Pyridine	C_5H_5N	4.02	1.65
9	Benzonitrile, 4-methyl	C_8H_7N	4.35	5.16
10	Pyrrole	C_4H_5N	4.45	2.05
11	Methylbenzene	C_7H_8	4.56	2.01
12	2-Methylpyrazine	$C_5H_6N_2$	5.91	2.10
13	Pentadecane	$C_{15}H_{32}$	6.21	5.10
14	Benzenamine,N-(1-methyl-2-propyl)	$C_9H_{13}N$	6.35	5.23
15	1,4-Pentadien-3-one	C_5H_6O	6.45	2.11
16	Ethylbenzene	C_8H_{10}	6.84	2.80

17	Benzocyclobuten	C_8H_8	7.52	2.04
18	Phenol	C_6H_6O	9.75	2.13
19	2-hexadecene3,7,11,15-tetramethyl	$C_{20}H_{40}$	9.92	4.09
20	Hexadecanenitrile	$C_{16}H_{31}N$	10.59	9.02
21	2-methoxy-3H-azepine	C_7H_9NO	11.07	2.15
22	1-chloro-3-fluorobenzene	C_6H_4ClF	12.55	2.11
23	2-Methyl-2-Phenylpropanenitrile	$C_{10}H_{11}N$	13.87	2.10
24	1-Tridecene	$C_{13}H_{26}$	14.47	2.76
25	5-Methylindole	C_9H_9N	15.96	2.00

Table **2.** is the SSB bio-oil table which contain different hydrocarbons and compounds. The sample GC/MS result indicate the presence of different classes of hydrocarbons which includes azole, aromatic amines and nitriles, carbohydrate, alkenes, ‘and alkane. The most abundant compound 2, 3, 5-trimethyl pyrazole 10.09 % accounted for the total oil. The azoles including 3, 4, 5-trimethyl-pyrazole, pyrrolidinone etc and aromatic amine and nitrile these compounds were assumed to be derived from protein degradation. While the 2, 3, 4-trimethyl-d-xylose derived from the hydrolysis of cellulose. The alkenes class compound 3, 7, 11, 15-tetramethyl-2-Hexadecene is probably generated from the conversion of unsaturated fatty acid in algal cell. Long chain compound Pentadecane accounted 5.10 % correspondingly of the total oil.

FT-IR spectrum of the SSB bio-oil sample

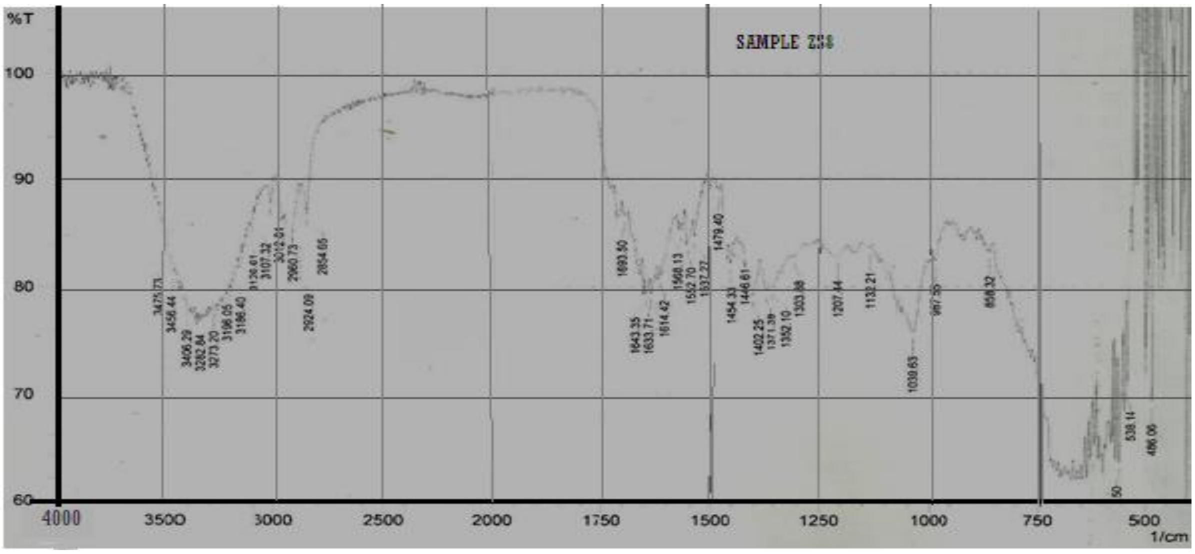


Fig.4. above FTIR spectrum of the SSB bio-oil.

Table.3. Characteristics IR Absorption frequencies of organic functional groups of SSB

Functional group	Type of vibration	Characteristics Absorption (Cm^{-1})	Intensity
C-H (alkane)	Stretch	2928.10	Strong
-C-H	Bending	1370.12	Variable
C=C (alkene)	Stretch	1647.30	Variable
C=C	Stretch	1560.15	Medium-weak, multiple bands.
C-O (Ether)	Stretch	1240.33	Strong
=C-H	Stretch	3081.16	medium
O-H (Alcohol)	Stretch (H-	3455.22	Strong, broad

Infrared spectroscopy (IR) result of SSB bio-oil sample

The table 3. Result of SSB oil sample indicates that (C-H) Alkane stretching at 2928.10 cm^{-1} and intense broad peak and axial at 3000 cm^{-1}.While alkane bending at 1370.12 $cm-^{1}$ occur and the peak intensity is variable. The (O-H) is also a weak broad peak is due to the presence of water content in bio-oil or may be due to alcohol which appears at 3455.12 cm^{-1}. The strong intensity due to stretching vibration of ether appears at 1240.33 cm^{-1}. The aromatic C=C stretching at 1560.15 $cm-^{1}$ so its intensity is medium weak multiple band and The alkenes =C-H stretching at 3081.16 cm^{-1} its intensity is medium while the alkenes stretching occur at 1647.30 cm^{-1} and the intensity of peak is variable. The presence of different functional groups in SSB bio-oil sample indicates the presence of hydrocarbons in the bio-oil and also the (O-H) broad peak indicates the presence of alcohol and water contents. The broad O-H peak was due to the interaction (hydrogen bonding) among the water contents. The bio-oil sample consists of Alkane, Alkenes, ether, alcohol and aromatics.

CONCLUSION

SSB was found one of the most promising biomass for pyrolysis yield. It has a great development potential around the world. Due to the advantages in economic problems and environmental protection, bio-oil as a new substitute of fossil fuels, has acquired extensive recognition globally. Researches demonstrated that pyrolysis bio-oil could be upgraded using various approaches, such as hydrogenation, hydrodeoxygenation, catalytic pyrolysis, catalytic cracking, steam reforming, molecular distillation, supercritical fluids, esterification and emulsification. On one hand, the pyrolysis bio-oil has many advantages in properties, such as less toxic, good lubricity and stronger biodegradation and so on. On the other hand, it also has lots of disadvantages in characteristics, for example, high contents of water, oxygen, ash and solids, low pH value, high viscosity, chemical and thermal instability, low heating value, and poor ignition and combustion properties but still we can use the upgraded bio-oil as alternative fuel of boiler and internal combustion engine. In this work, studies of The GC-MS peaks showed that the obtained bio-oil was mostly composed of hydrocarbons but also has many other important compounds and our future work will be the recovery of important compounds like phenols and ketones from SSB bio-oil.

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