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MICROWAVE ASSISTED PYROLYSIS OF POLYSTYRENE AND ALGAL BIOMASS FOR RESOURCE AND ENERGY RECOVERY

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Abstract

The first part of this study was to study the microwave pyrolysis of polystyrene for resource and energy recovery and the second part was to study the effect of torrefaction and solvent pretreatment on biofuel obtained via microwave assisted pyrolysis of *Spirulina*. The synergy of catalyst (KOH) and polystyrene (PS) quantities on product yields and pyrolysis operating parameters were focused. The average heating rates were in the range of 30-50°C/min. The maximum yield of pyrolysis oil was found to be 95 wt.%, which was obtained with a feed to catalyst ratio of 27.5 g: 7.5 g. The oil yield increased from 80-95 wt.% when the mass of the catalyst increased from 5-7.5 g and thereafter oil yield decreased with an increase in catalyst quantity. It can be concluded that initially the catalyst addition increased the temperature rise rates of polystyrene. The presence of catalyst not only affected the temperature evolution of polystyrene but also changed the pyrolytic product distribution and gas composition. The second part of research looks at the process of microwave-assisted pyrolysis (MAP) for the purpose of producing bio-oil from both fresh and torrefied *Spirulina* (algal biomass).Fresh algae with solvent soaking produced yield of bio-oil 56.11 wt% with conversion 86.48 % and pyrolysis index of 93.27, whereas torrefied algae with solvent pretreatment further enhanced yield of bio oil to 59.24 wt% and pyrolysis index of 96.00 with reducing time and temperature.The MW energy consumption reduced from 688 - 513 KJ and higher heating value (HHV) was observed (36.4 MJ/Kg) with torrefaction and solvent pretreatment. The bio oil properties were characterized with Gas Chromatography Mass Spectrometry (GC-MS) and Fourier Transform Infrared Spectroscopy (FTIR) analysis.

Keywords: Microwave pyrolysis; Graphite; Polystyrene; KOH; Heating rate. *Spirulina,* Torrefaction, Solvent pretreatment, GC-MS, FTIR.

1. Introduction

Polystyrene is one of the most used thermoplastic materials (Zhang et al., 2014). It is largely employed in packaging, as composite for case of computers or inner parts of cars, for thermal isolation and for the production of a lot of commodities. PS is also used for fine applications like production of new materials such as thermo-responsive polymers, energy storage mediums or composites (Prathiba Rex et al., 2021). In the last years PS production is increased constantly and management of PS wastes is a great public, economic and environmental problem (Peng et al., 2022). Due to its high stability and low density it causes a rapid filling of landfills. For these reasons an efficient disposal of wastes PS through recycling processes is becoming mandatory. The main recycling process involves the direct remanufacturing through milling, washing, drying, and molding but this is not possible for contaminated or degraded waste because they cannot be directly reintroduced in the production cycle. Degraded or contaminated PS or composite containing PS may be disposed through thermal degradation (Verma et al., 2020). In recent years, technologies such as combustion, pyrolysis, and cracking on acid catalysts has been developed. Within these processes, pyrolysis was investigated with the aim to dispose waste PS and collect valuable chemicals, among which styrene was the main compound. In the course of time various methods have been proposed using different reactors and conditions. Also pyrolysis of contaminated PS or PS containing composites such as poly(acrylonitrile–butadiene–styrene) (ABS) or other copolymers between styrene and other olefins or different materials were reported (Zhang et al., 2017).

In the last few years microwave assisted pyrolysis (MAP) has gained interest as a new and sometimes complementary pyrolytic method . MAP is a fast and green approach to pyrolysis and it was employed to process a large variety of different material (Prathiba et al., 2018; DadiV.Suriapparao et al., 2018; Lopez et al., 2017; Suriapparao et al., 2020).

On the other hand, Among the various alternative energy sources, biomass has become a key focus in energy policy discussions, particularly within the European Union. Major biomass sources include agricultural and forestry residues (such as wood industry waste like shavings and sawdust), animal waste from livestock farms, sewage, algae, and aquatic crops. *Spirulina* has an impressive biomass productivity rate, capable of producing 20 to 400 times more protein than food sources like soybeans, corn, and beef (Varma et al., 2024; Wang et al., 2020). It can be cultivated in chemical-based or seawater-based culture media. During the cultivation stage, *Spirulina* requires CO_2 for photosynthesis, which helps reduce the carbon footprint in the atmosphere. Additionally, *Spirulina* is rich in protein and low in fat, making it an ideal feedstock for pyrolysis, which produces valuable aromatic substances like solvents. This application offers solutions to global issues such as wastewater management and climate change by contributing to carbon footprint reduction (Varma et al., 2025).Torrefaction or mild pyrolysis is a thermal pretreatment for biomass, which reaches temperatures between 200 ºC and 300 ºC and generally in the absence of oxygen (Wang et al., 2019).

Torrefaction of biomasses promotes an increase in ash and fixed carbon content as well as a reduction in volatile matter content, the latter being the primary source of bio-oil for pyrolysis. From an elementarypoint of view, the main principle of torrefaction is the removal of oxygen from biomass. Besides, torrefaction can effectively decrease the moisture content of biomass, increase its heating value, and decrease the acidity of bio-oil later obtained by pyrolysis (i.e. stepwise pyrolysis) (Bhatia et al., 2020). Pre-treatment stands as a crucial step in economically converting biomass into biofuels (Kumar & Sharma, 2017). Organic solvent treatment of algae is a technique commonly used to extract valuable compounds, such as lipids, pigments, and bioactive compounds, from algal biomass, along with facile solvent recovery and reuse. Torrefaction and solvent soaking of fresh tea waste powder had positive effect on bio char and bio oil yields has been reported in earlier studies (TalibHamzah et al., 2022).

In the first part of this study, microwave assisted pyrolysis of polystyrene (PS) was conducted, and the effects of microwave power, susceptor, and PS to catalyst ratio on (i) temperature and heating rate profiles, (ii) overall oil, gas and char yields, and (iii) composition of oil and gas, were evaluated.The second part of the study aims to fill a knowledge gap in microwave-assisted pyrolysis (MAP) of fresh and torrefied Spirulina algal biomass.It examines how torrefaction and solvent soaking with benzene, acetone, and ethanol affect product formation and energy consumption during MAP. This research focuses on evaluating the role of pretreatment in biomass processing, with pyrolysis products analyzed using GC-MS and FTIR.

2. **Materials and methods**

2.1 Materials selection and analysis

Commercial grade polystyrene (PS) was procured from the plastic supply vendor. Microalgal biomass, more especially "*Spirulina*," sourced from Delhi-based Lavanya Agro Industries, serves as the principal feedstock for this investigation. The elemental carbon and hydrogen contents were analyzed using an elemental analyzer (ElementarVario EL III). The calorific value was measured using a standard bomb calorimeter (Model: IKA C2000).

2.2. Torrefaction &Chemical Solvent soaking pre-treatment of algae

The fresh and torrefied algae (carried out at different temperatures of 150, 175 & 200 ^{0}C) were soaked in acetone, benzene, and ethanol as part of the chemical pre-treatment process. During the soaking process, the feedstock was moved to a glass beaker and the solvent was added. To ensure that the feedstock particles were dispersed entirely, a solvent was added. To enhance the solvent diffusion into the feedstock, the soaking solution containing the feedstock was constantly agitated for 24 hours. To stop solvent vaporization a loss during the soaking phase, aluminum foil was placed on top of the beaker. Filtration separated the feedstock from the solvent once the soaking process was finished. To remove the solvent, the filtered feedstock was dried for one hour in an oven set at 100 °C. The pyrolysis studies utilized pre-treated algae and graphite powder as susceptors. For subsequent usage in thermal characterization, feedstock preparation, and pyrolysis tests, the samples for the pre-treatment were placed within an airtight zip-lock bag.

2.3 Experimental methodology

A laboratory-grade multimode microwave oven (Model: RG34L1500, RAGA'S Scientific Microwave Systems, Ragatech, Pune, India) was adapted into a pyrolysis reactor for research purposes. The magnetron in the oven emits microwaves ranging from 300 J/s to 1500 J/s, maintaining a steady wave frequency of 2.45 GHz. MAP experiments were conducted using a modified multimode microwave oven. The top side of the oven cavity was machine drilled to provide a circular opening. This opening was provided for gas purging pipe, temperature sensor and vapor collection. A borosilicate flat bottom flask having a capacity of 500 ml was used to place the feedstock and susceptor mixture. In each experiment, feedstock and susceptor were mixed thoroughly for the uniform spreading of susceptor particles within feedstock. A contact-type temperature sensor (Chromel Alumel thermocouple) was inserted into the borosilicate flask to monitor the feedstock temperature during the pyrolysis. The thermocouple sensor can measure the temperature with an accuracy of $\pm$ 2 ^{0}C. The sensor was placed in a hollow cylindrical metallic tube to minimize microwaves interferences. The cold junction of the thermocouple was connected to a digital temperature indicator. The borosilicate flask was connected to a vapor condensation and gas collection system. Nitrogen gas purging at 50 ml/min for 10 min was also provided before each experiment to remove the atmospheric oxygen present in the feedstock mixture. After keeping the borosilicate flask with feedstock and susceptor in the oven cavity. It was covered with ceramic wool insulation and the flask top was connected to oil collection and temperature measurement. The, microwave oven front door was closed and set the microwave power and time provided on the panel. In each Experiment the temperature was recorded for every 30 s and the microwaves delivery was stopped once the pyrolysis temperature reached up to 450 ^{0}C. The oven front door was opened to cool down the temperature and the borosilicate flask was removed once the temperature was ambient. The flask was weighed to know the char yield and the condensers along with the oil collection flaks was measured to know the oil yield. (**Figure 1).**

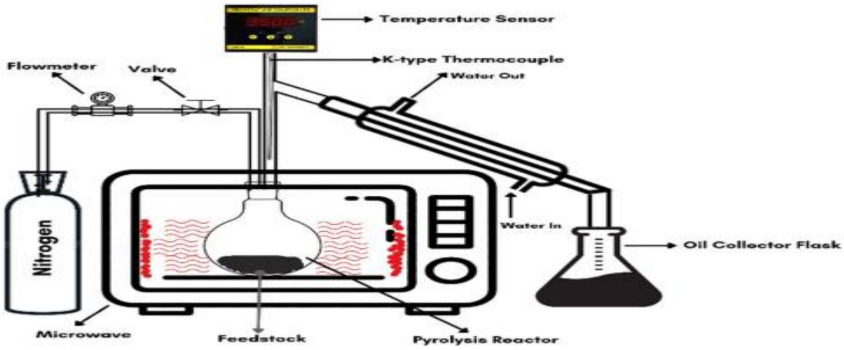


Figure-1: Microwave pyrolysis setup

2.4 Pyrolysis Product Analysis

The majorproducts, which included both bio-oil and bio-oil, were measured and collected. The formulas determine the biochar and bio-oil product yields [22] (Equations 1 to 3).

$$W_S(\%) = \frac{M_S}{M} \times 100 \text{ ---------------------------- } (1)$$

$$W_B(\%) = \frac{M_B}{M} \times 100 \text{ ------------------------- } (2)$$

$$W_G(\%) = 100\% - W_S - W_B \text{------------------- } (3)$$

Where W_S, W_B, and W_G stand for the relative yields of biochar, bio-oil and gas. (M is the weight of the pyrolysis sample; M_S and M_B are the weights of the biochar and bio-oil, respectively.

2.5GC-MS & FTIR analysis of product oil

GC/MS, Agilent 7890, 5975C was used to analyze the composition of the product oil that was recovered from MAP of torrefied and ethanol pretreated algae. The sample injector, which was kept at 220 ^{0}C, was used to inject 0.25 µL of the oil sample for this experiment. At a non-isothermal heating rate of 5 ^{0}C/min, the GC oven was preheated to 350 ^{0}C and maintained at that temperature for 30 minutes. As a carrier gas, 2.0 mL min^{-1} of high-purity helium gas was employed. A conventional Rxi-5Sil MS column (30 m length X 0.25 mm i.d. X 0.25 µm film thickness) was employed for compound separation. A mass spectrometer was used to obtain the mass spectra of the oil to examine its chemical composition. Isothermal temperatures of 220 ^{0}C and 175 ^{0}C were maintained for the ion source and detectors, respectively. There was a 70 eV potential for electron ionization in the MS ion source. Most relevant compounds in the m/z range of 50 to 500 Da were scanned using a typical threshold of 100. For this study, substances whose spectra had a match factor of more than 80% were evaluated compared to the NIST library. The bio-oil compounds' chromatogram and their complete inventory are available in the supplementary materials. The chemicals were evaluated based on findings.

Liquid samples of MWP bio-oil were analyzed for functional groups using a Thermo Scientific Nicolet IS-5 FT-IR spectroscopy system. The samples included both fresh and torrefied algae that had been soaked in solvent. The sample spectra were obtained with a resolution of 4 cm^{-1} within the wave number range of 4000 to 500 cm^{-1}, averaging 32 scans per sample. FTIR analysis was used to learn about the pre-treatment conversion of hemicellulose, cellulose, and lignin (Oumer et al., 2018).

3. Results and Discussions

3.1. Feedstock characterization

3.1.1 Proximate and elemental analysis of the feedstocks

The proximate and elemental analyses of the feedstocks are provided in **Table 1**. The commercial polymer PS, contain very high volatile matter (> 90 wt%) with low fixed carbon (0.5) and zero ash, which is expected. The low oxygen content in the polymers (2 wt%) can be due to the presence of additives like plasticizers and colorants. The low oxygen content in the polymers (2 wt%) can be due to the presence of additives like plasticizers and colorants (Prathiba Rex et al., 2021).

Table -1Proximate and elemental analysis of the feedstocks on dry basis.

Feedstock	Proximate analysis (wt%)			Elemental analysis (wt%)				
	VM	FC	Ash	C	H	N	S	O
PS	99.5	0.5	0.0	89.5	8.5	0.0	0.0	2.0

Proximate analysis was carried out according to IS 1350-1 (1984). The proximate analysis of polystyrene yielded 0.01 wt.% of moisture content, 1.07 wt.% fixed carbon and 95.87 wt.% volatile matter, offering greater possibility to pyrolyse the plastic and to recover the volatile content as oil. The high ash content of 3.05 wt.% is associated with the inorganic matter in the material. The accumulation of the inorganic material in the plastic is due to two reasons, (1) atmospheric dust which consists of major earth elements like Si, Fe and Al that could have been accidentally incor- porated in the polymeric products, (2) clay earth pigments like talc [$Mg_3Si_4O_{10}(OH)_2$] and calcium carbonate [$CaCO_3$] as additives.

3.1.2 FTIR analysis of char recovered from microwave pyrolysis of PS

Figures (2 (a &b)) shows the FTIR spectrum before and after microwave assisted pyrolisis of char (solid) at 5gm of PS + 7.5 gm of KOH. The surface functional groups of PS can be quantitatively analysed by FTIR. The FTIR analysis result shows that a lot of number of peaks were detected, informing the complex structure of the material. In the single bond area (2500-4000 cm^{-1}), several peaks were detected. A broad absorption band in the range of between 3650 and 3250 cm^{-1}, indicates hydrogen bond. This band confirms the existence of hydrate (H_2O), hydroxyl (-OH), ammonium, or amino. For hydroxyl compound, it should be followed by the presence of spectra at frequencies of 1600–1300, 1200–1000 and 800–600 cm^{-1}. The sharp intensity absorption in the absorption areas of 3670 and 3550 cm^{-1} , allows the compound to contain an oxygen related group, such as alcohol or phenol that illustrates the absence of hydrogen bonding. The narrow band at above 3000 cm^{-1}, indicates unsaturated compounds or aromatic rings. The narrow band at below 3000 cm^{-1}, shows the presence of aliphatic compounds. The peak at 1591 cm^{-1} is aromatic C=C functional group. The peaks of fingerprint region can be observed in 600-1500 $cm-^{1}$. No specific peak for aldehyde has been found at between 2700 and 2800 cm^{-1}. Aromatic ring structures are identified in the region as C-H 1,2-Disubstitution (ortho) in 770–735 cm^{-1}, C-H 1,3-Disubstitution (meta) 810–750 cm^{-1} C-H 1,4-Disubstitution (para) 860–800 cm^{-1}. Similar report was also obtained from the studied conducted by Liet al., 2018.

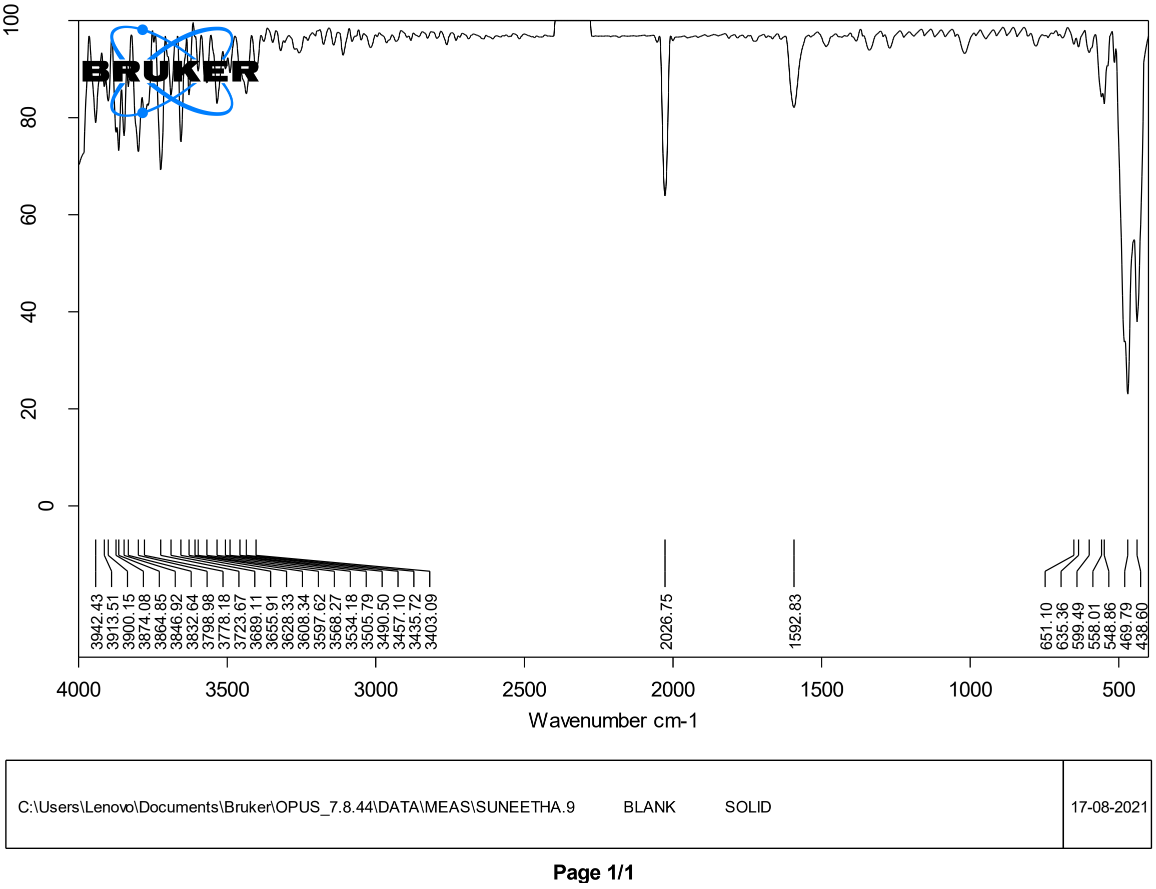


Figure-2 (a) FTIR analysis of char (solid) before microwave assisted pyrolysis

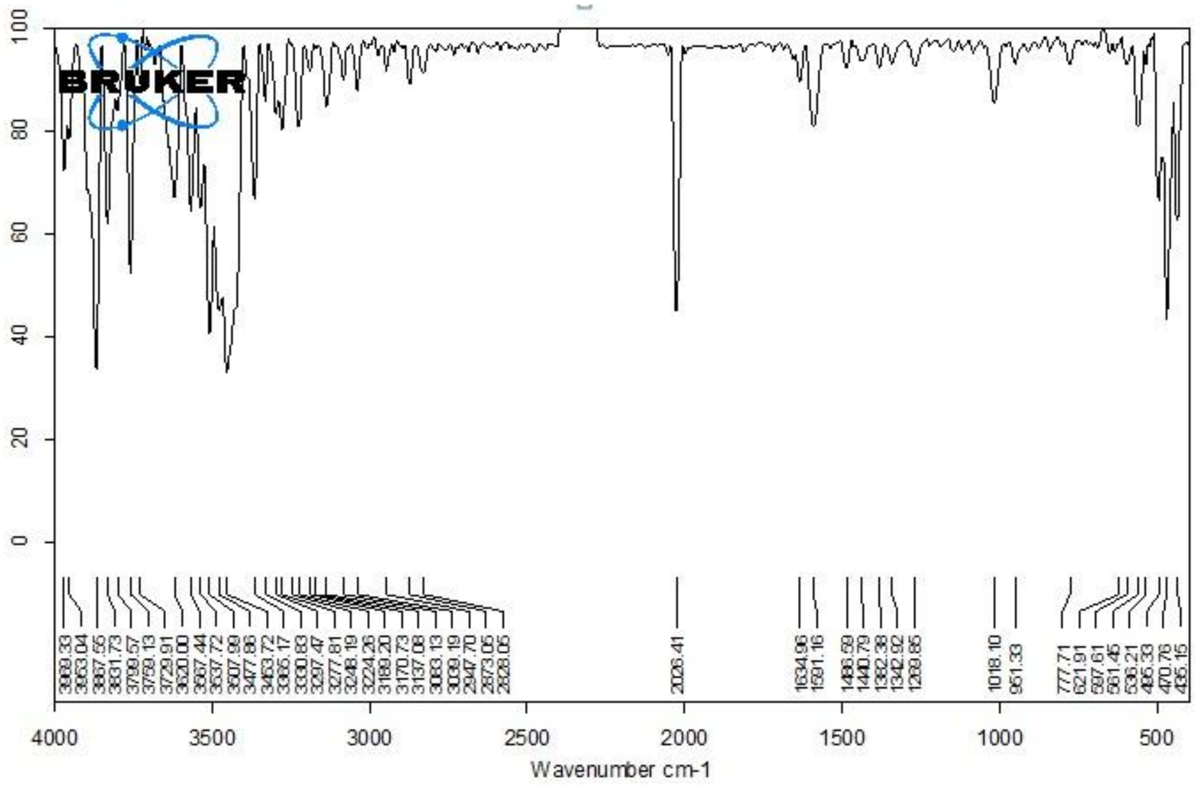


Figure-2 (b) FTIR analysis of char (solid) after microwave assisted pyrolysis

3.1.3 *Yield of pyrolysis oil at different feedstock and catalyst ratios*

Pyrolysis oil yields at various PS + KOH compositions under a constant microwave power of 450 W, using 10 g of graphite as a susceptor, are illustrated in **Figure 3.** The maximum oil yield of 94.9 wt.% was achieved with 27.5 g of polystyrene and 7.5 g of KOH within a shorter pyrolysis time of 12 minutes, indicating efficient catalytic activity. In contrast, the minimum oil yield of 80 wt.% was obtained with 5 g of polystyrene and 10 g of KOH over a longer duration of 15 minutes, suggesting suboptimal feed-to-catalyst ratio. These findings highlight the importance of composition optimization and are consistent with earlier reports by Veluru Sridevi et al. (2022).

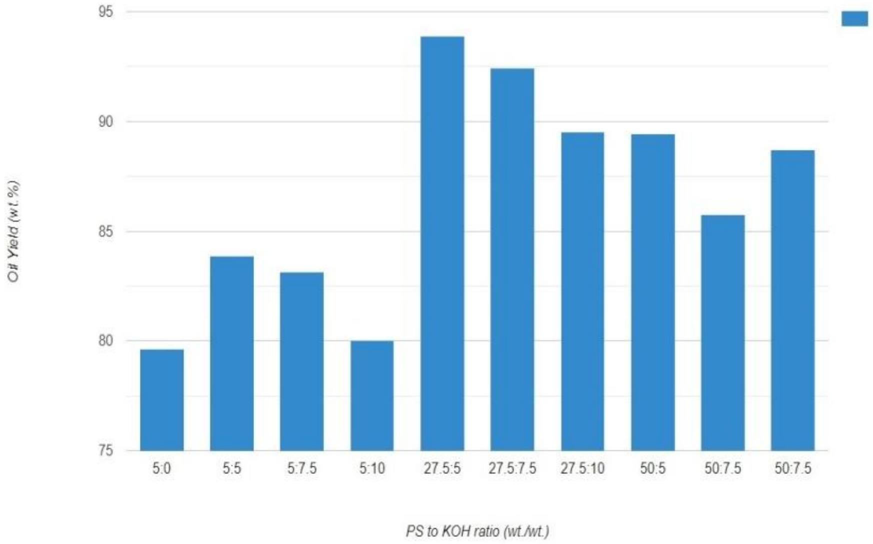


Figure 3 Yield of pyrolysis oil obtained at different PS + KOH compositions

Table-2 shows Heating rates, product yield, energy yield and oil physiochemical properties obtained in catalytic pyrolysis of PS.

$$\text{Energy yield (\%)} = \left(\frac{\text{HHV}_{\text{bio-oil}} \times \text{Bio-oil yield}}{\text{HHV}_{\text{feed}}}\right) \times 100\% \qquad 1$$

$$\text{Energy efficiency (\%)} = \left(\frac{\text{Total energy of products (in J)}}{\text{Total energy of feed (in J)} + \text{Microwave energy (in J)}}\right) \times 100\% \qquad 2$$

Where,

$$\text{Total energy of products} = \sum_{i=\text{oil,gas,char}} \text{HHV}_i \times \text{mass}_i$$ 3

$$\text{Total energy of feed} = \text{HHV}_{\text{feed}} \times \text{mass (20 g)}$$

4

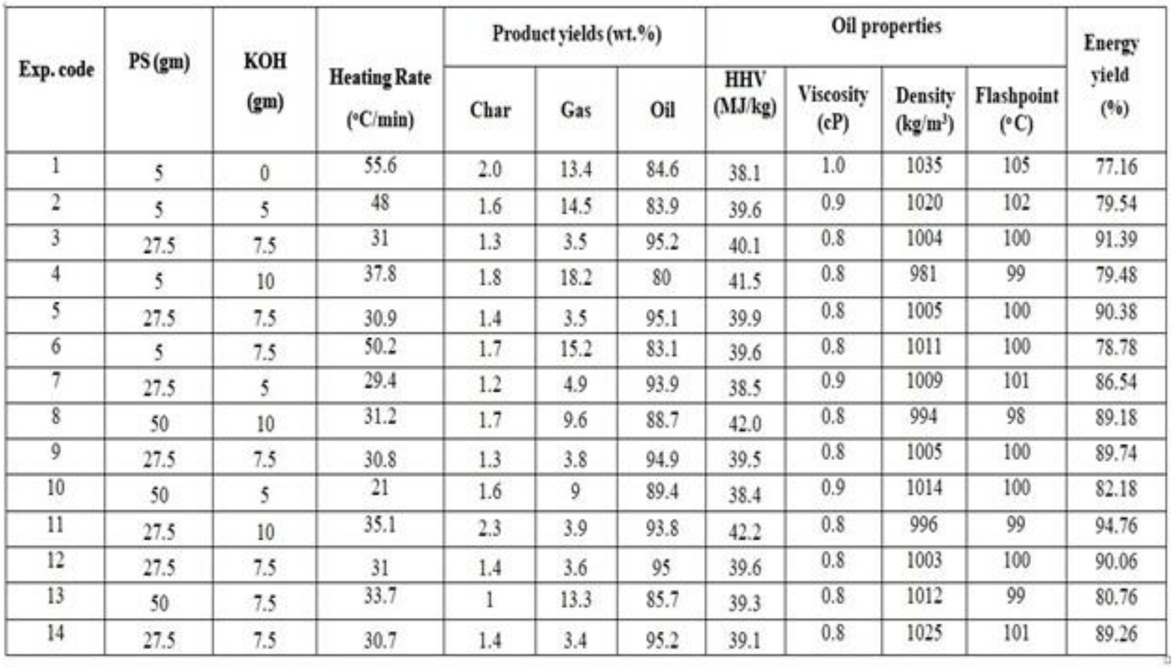
$$\text{Microwave energy} = 450\ \text{W} \times \text{Total pyrolysis time}$$

Process Conditions:-

*Microwave Power – 450 W, Graphite:10 g, Pyrolysis temp: 600°C 5

*Feed – Graphite (G) + Polystyrene (PS) + KOH

Table-2 Heating rates, product yield, energy yield and oil physiochemical properties obtained in catalytic pyrolysis of PS



Exp. code	PS (gm)	KOH (gm)	Heating Rate (°C/min)	Product yields (wt.%)			Oil properties				Energy yield (%)
				Char	Gas	Oil	HHV (MJ/kg)	Viscosity (cP)	Density (kg/m³)	Flashpoint (°C)	
1	5	0	55.6	2.0	13.4	84.6	38.1	1.0	1035	105	77.16
2	5	5	48	1.6	14.5	83.9	39.6	0.9	1020	102	79.54
3	27.5	7.5	31	1.3	3.5	95.2	40.1	0.8	1004	100	91.39
4	5	10	37.8	1.8	18.2	80	41.5	0.8	981	99	79.48
5	27.5	7.5	30.9	1.4	3.5	95.1	39.9	0.8	1005	100	90.38
6	5	7.5	50.2	1.7	15.2	83.1	39.6	0.8	1011	100	78.78
7	27.5	5	29.4	1.2	4.9	93.9	38.5	0.9	1009	101	86.54
8	50	10	31.2	1.7	9.6	88.7	42.0	0.8	994	98	89.18
9	27.5	7.5	30.8	1.3	3.8	94.9	39.5	0.8	1005	100	89.74
10	50	5	21	1.6	9	89.4	38.4	0.9	1014	100	82.18
11	27.5	10	35.1	2.3	3.9	93.8	42.2	0.8	996	99	94.76
12	27.5	7.5	31	1.4	3.6	95	39.6	0.8	1003	100	90.06
13	50	7.5	33.7	1	13.3	85.7	39.3	0.8	1012	99	80.76
14	27.5	7.5	30.7	1.4	3.4	95.2	39.1	0.8	1025	101	89.26

3.1.4 GC-MS analysis for product oil

The product oil was analyzed to examine the composition of various hydrocarbons present in it. From GC-MS analysis, the oil consists of the following compounds as shown in **Table 3.(a)** shows the analysis in the absence of catalyst, whereas **Table 3. (b)** shows the analysis in the presence of catalyst. GC-MS analysis shows, the oil consists of 92.8% of aromatic content in the absence of catalyst and 93.8% aromatic content in the presence of catalyst. It is due to polystyrene present in the polymer. The liquid oil in absence of catalyst analysis consists of single ring aromatics such as styrene (45.6%), ethylbenzene (1.9%), Naphthalene (0.6),in the presence of catalyst styrene (37.2 %), ethylbenzene (2.8%), Naphthalene (0.4). Styrene is formed by unzipping reactions or end chain b-scission reactions (D. V. Suriapparao et al., 2020).

Table – 3. (a) Gas chromatography-mass spectrometry analysis (GC-MS) without catalyst

SL No.	Compound Name	Area%
1	Styrene	45.6
2	(cyclopropylmethyl)benzene	21.2
3	Benzene, 1,1',1'',1'''-(1,3,4,6-Hexanetetrayl)Tetrakis	8.4
4	Benzene, (1-Methylethenyl)	4.5
5	Benzene, 1,1'-(1,3-Propanediyl)Bis	3.0
6	Benzene, Ethyl	1.9
8	Benzene, 1,1'-(1,2-Ethanediyl)Bis	1.0
9	Benzene, (1,3-Dimethyl-3-Butenyl)	1.5
10	Bicyclonona-2,4,7-Triene, 7-Phenyl	1.1
11	1-(4-Methylphenyl)-4-Phenylbut-1,3-Dien	1.5
12	Naphthalene, 2-Phenyl	0.8
13	Benzene, 1,1'-(1-Methyl-1,2-Ethanediyl)Bis	0.7
14	(1-Methylene-4-Phenyl-4-Pentenyl)Benzene	0.4
15	Benzene, 1,1'-(1,2-Ethenediyl)Bis	0.4
16	Benzene, 1,1'-(1-Butene-1,4-Diyl)Bis	0.2
17	Naphthalene	0.6
18	1-(4-Methylphenyl)-4-Phenylbuta-1,3-Diene	0.4
19	1,1':3',1''-Terphenyl, 5'-Phenyl	0.5
20	1h-Indene	0.7
21	Benzene, 1-Ethenyl-2-Methyl	0.2
22	2,3-Dihydro-1h-Cyclopenta[L]Phenanthrene	0.2
23	Benzene, 1,1'-(1,2-Cyclopentanediyl)Bis-	0.1
24	9-Vinylanthracene	0.4

25	Phenanthrene	0.1
26	Benzene, 1,1'-(3-Methyl-1-Propene-1,3-Diyl)Bis	0.4
27	M-Terphenyl	0.5
28	Ethylene, 1,1-Diphenyl	0.3
29	1-(4-Methylphenyl)-4-Phenylbuta-1,3-Diene	0.3
30	Benzene, 1,1',1"-[5-Methyl-1-Pentene-1,3,5-Triyl]Tris	0.6
31	Benzene, 2-Propenyl	0.4
32	Naphthalene, 1,2,3,4-Tetrahydro-1-Phenyl	0.1
33	1,2-Dihydro-3-Phenylnaphthalene	0.4
34	4-Phenyl-1,3-Butadienyl]Benzene	0.3
35	Diphenylmethane	0.3
36	Bicyclo[4.2.1]Nona-2,4,7-Triene, 7-Phenyl	0.4
37	Benzene, 1,1'-(1-Methyl-1,3-Propanediyl)Bis	0.3
38	1,1'-Biphenyl	0.3

Table – 4. (b) Gas Chromatography-Mass Spectrometry Analysis (GC-MS) With Catalyst

SL No.	Compound Name	Area%
1	Styrene	37.2
2	(Cyclopropylmethyl)Benzene	12.3
3	Benzene, 1,1',1",1'"-(1,3,4,6-Hexanetetrayl)Tetrakis	6.4
4	Benzene, (1-Methylethenyl)	3.9
5	Benzene, 1,1'-(1,3-Propanediyl)Bis	1.9
6	Benzene, Ethyl	2.8
8	Benzene, 1,1'-(1,2-Ethanediyl)Bis	2.6
9	Benzene, (1,3-Dimethyl-3-Butenyl)	3.1
10	Bicyclo[4.2.1]Nona-2,4,7-Triene, 7-Phenyl	1.8
11	1-(4-Methylphenyl)-4-Phenylbut-1,3-Dien	1.7
12	Naphthalene, 2-Phenyl	1.5
13	Benzene, 1,1'-(1-Methyl-1,2-Ethanediyl)Bis	0.6

14	(1-Methylene-4-Phenyl-4-Pentenyl)Benzene	0.4
15	Benzene, 1,1'-(1,2-Ethenediyl)Bis	0.5
16	Benzene, 1,1'-(1-Butene-1,4-Diyl)Bis	0.3
17	Naphthalene	0.4
18	1-(4-Methylphenyl)-4-Phenylbuta-1,3-Diene	0.4
19	1,1':3',1''-Terphenyl, 5'-Phenyl	0.3
20	1h-Indene	0.4
21	Benzene, 1-Ethenyl-2-Methyl	0.6
22	2,3-Dihydro-1h-Cyclopenta[L]Phenanthrene	0.8
23	Benzene, 1,1'-(1,2-Cyclopentanediyl)Bis	0.9
24	9-Vinylanthracene	2.1
25	Phenanthrene	1.1
26	Benzene, 1,1'-(3-Methyl-1-Propene-1,3-Diyl)Bis	0.7
27	M-Terphenyl	0.8
28	Ethylene, 1,1-Diphenyl	1.9
29	1-(4-Methylphenyl)-4-Phenylbuta-1,3-Diene	2.0
30	Benzene, 1,1',1''-[5-Methyl-1-Pentene-1,3,5-Triyl]Tris	3.2
31	Benzene, 2-Propenyl	2.5
32	Naphthalene, 1,2,3,4-Tetrahydro-1-Phenyl	0.7
33	1,2-Dihydro-3-Phenylnaphthalene	1.3
34	[(1e,3e)-4-Phenyl-1,3-Butadienyl]Benzene	0.4
35	Diphenylmethane	0.5
36	Bicyclo[4.2.1]Nona-2,4,7-Triene, 7-Phenyl	0.7
37	Benzene, 1,1'-(1-Methyl-1,3-Propanediyl)Bis	1.1
38	1,1'-Biphenyl	0.2

3.2 Feedstock characterization of *Spirulina*

In the second part of the study, the proximate and elemental analyses of algae were conducted based on dry-weight measurements. For algae, the analysis revealed a fixed carbon content of 12.7 wt. %, volatile matter of 78.7 wt. %, 7.7wt. % ash, and the remaining moisture content. Elemental analysis indicated carbon, hydrogen, nitrogen, sulphur, and oxygen compositions as 48.1wt. %, 7 wt. %, 10.1 wt. %, 0.9 wt. %, and 26.2 wt. % respectively. These results are presented in **Table 5**. Notably, carbon content was higher in algae, while the opposite was observed for fixed carbon. The feedstocks' carbon-to-hydrogen (C/H) ratio reveals that algae, due to its lower C/H ratio, is more favorable for higher oil and gas yields (Hu et al., 2019).

Table 5 Proximate and Ultimate Analysis of algae

Analysis	Content	*Spirulina*
Ultimate Analysis	**C**	48.1 *wt. %.*
	H	7 *wt. %.*
	C/H Ratio	6.8 mol/mol
	O/C Ratio	0.55 mol/mol
	N	10.1*wt. %.*
	S	0.9*wt. %.*
	O	33.9 *wt. %.*
Proximate Analysis	**Ash**	7.7 wt. %.
	Volatiles	78.7 wt. %.
	Fixed Carbon	12.7 wt. %.
	Moisture	0.9 wt. %.

3.3 Impact of torrefaction and solvent pretreatment on product yield

This technique was employed at a microwave power of 450 W to reach 600 °C. All experiments were conducted under uniform conditions, with consistent feed utilized throughout. The condensed bio-oil underwent phase separation, resulting in two distinct fractions: light and heavy. The dark, light fraction, resembling water in appearance, is commonly referred to as the aqueous phase, while the brownish, heavy fraction constitutes the organic phase, referred to as tar(Zhou et al., 2019). The bio-oil yields from the experiments involving fresh and torrefied algae were 49.20 and 57.67 wt. % respectively. Conversely, the bio-oil yields from fresh algae with acetone; benzene; ethanol pretreated were 42.77; 48.06; 56.11 wt%. The bio oil yields of torrefied algae at 150 ^{0}C treated with the same solvents were: 59.04; 54.55; 59.24 wt %. The resulting yields of torrefied algae with solvents soaking are mentioned in the **Figure 4.** The highest bio-oil yields were observed with torrefied algae treated with ethanol and acetone. It was observed that while during experiments with torrefied algae treated with benzene vapours released at earlier stage (24 ^{0}C) and stopped at 276 ^{0}C compared to other solvents. Because benzene is non polar and shows positive impact in decomposition of algal biomass in shorter pyrolysis time. Benzene is a non-polar solvent, which might interact differently with the algal biomass compared to acetone and ethanol a polar solvents. The polarity affects the dissolution and extraction of different biomass components (Zhou et al., 2016).

Boateng & Mullen, 2013 confirmed that fast pyrolysis of torrefied biomass produces less bio-oil and more biochar; however, bio-oil from torrefied biomass shows an improvement in some characteristics. Alvarez et al., 2014 and Chen et al., 2016; Chen et al., 2019 have demonstrated that the highest production of bio-oil is at temperatures around 500 ^{0}C. With increasing temperatures, there is a higher production of gas.

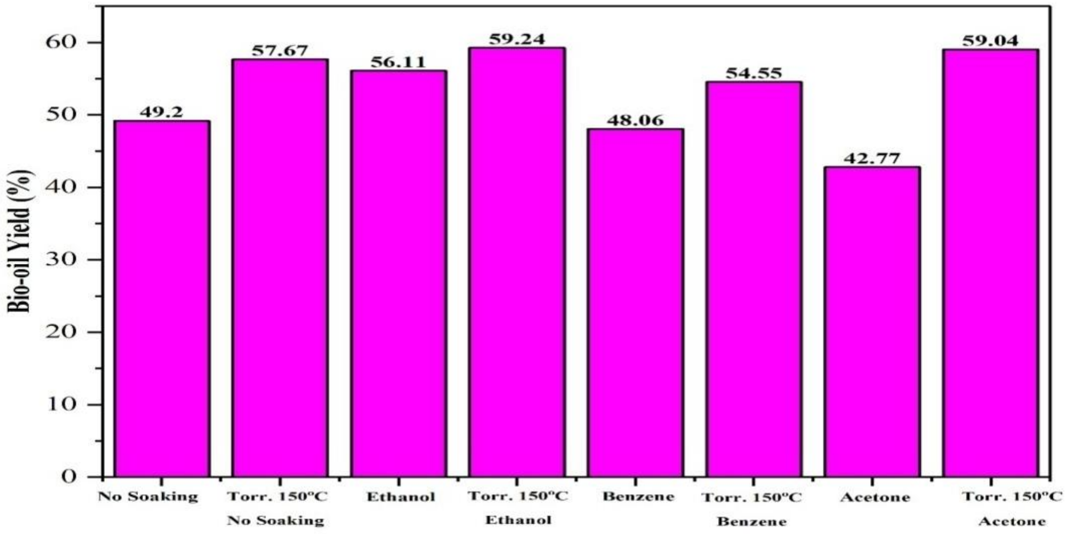


Figure 4 Product yields of MAP of torrefied& solvent soaking algae

3.4 FTIR analysis of fresh &torrefied algae soaked in solvents.

Figure 5 shows the FTIR analysis of fresh algae powder and **Figure 6** shows the torrefied algae powder with solvent soaking. Infrared spectroscopy (IR) is a powerful analysis tool used in identifying functional groups within organic molecules based on absorption of infrared light at specific wavelengths. For this reason, in the fingerprint region, 500-1800 cm^{-1}, we can identify a few major functional groups: the C-H bending vibrations for alkanes (1350-1470 cm^{-1}), the C=O stretching vibrations for carbonyl compounds, such as ketones, aldehydes, and carboxylic acids (1680-1750 cm^{-1}), and the C=C stretching vibrations for alkenes (1620-1680 cm^{-1}). In addition, aromatic compounds have characteristic C=C stretching vibrations between 1450 and 1600 cm^-1. We have the stretching vibrations of X-

H bonds in the region of 2300-4000 cm^{-1}: O-H stretches for alcohols and carboxylic acids (3200-3550 cm^{-1}), N-H stretches for amines and amides (3300-3500 cm^{-1}), and C-H stretches for alkanes, alkenes, and alkynes (2850-3300 cm^{-1}). This high-energy range is important in making the identification of the presence of these functional groups in organic molecules.Withtorrefaction with solvent soaking gives more vibrations, the appearance of functional groups is clear, peaks are widen and strong bonding that enhanced the properties of the bio oil (Hong et al., 2017).

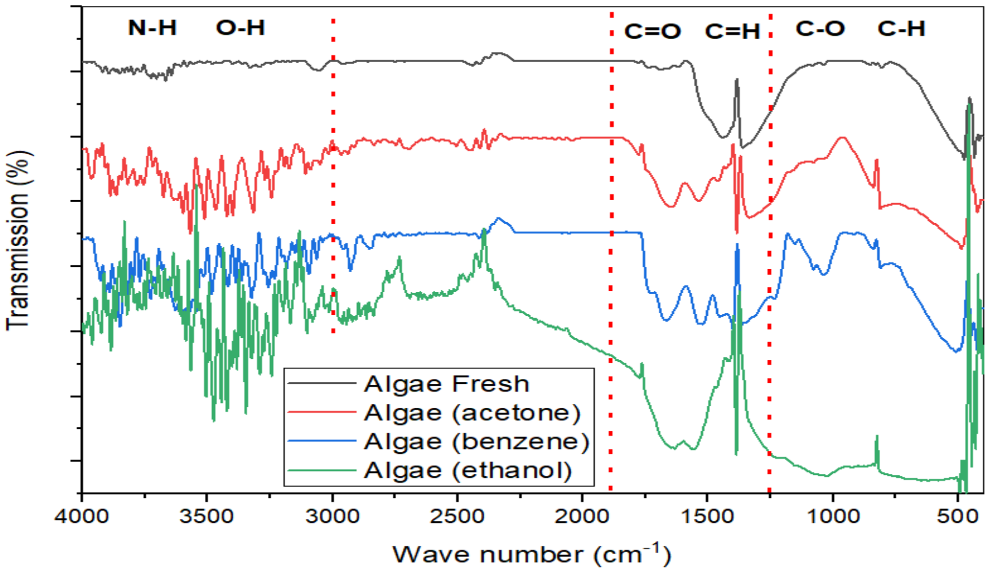


Figure 5FTIR analysis of fresh algae powder soaked with solvents.

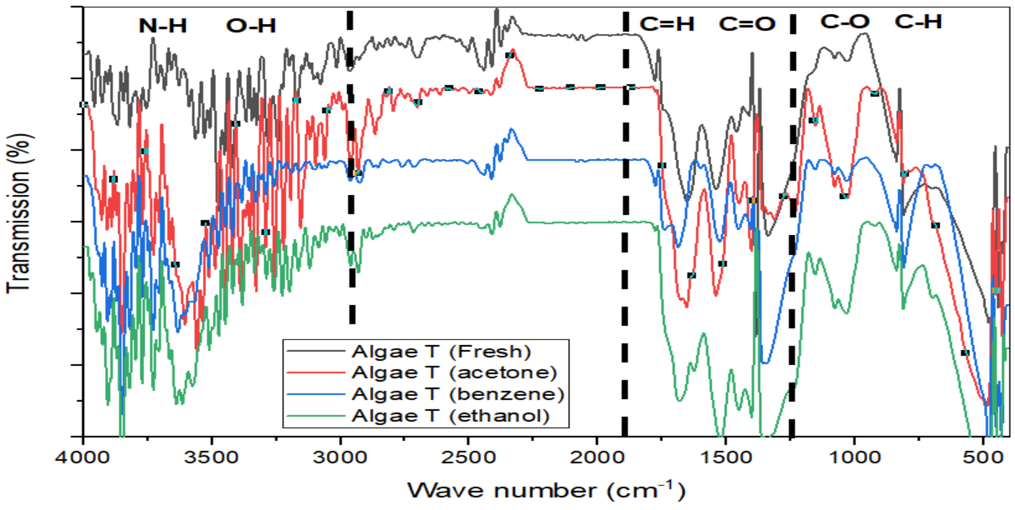


Figure 6FTIR analysis of torrefied algae powder soaked with solvents.

3.5 GC-MS Analysis

GC-MS analysis indicated the presence of nitrogenous and oxygenated compounds in the oil fractions such as amides and fatty acids, as well as a variety of hydrocarbons. Many of the compounds were branched or unsaturated as indicated by the C: H ratios and GC-MS results. The area % for the various types of compounds identified for each oil fraction using GC-MS is summarized in **Table 6** and various nitrogenous species detected in the bio-oil fractions are shown in **Figure 7**. Nitrogenous compounds identified include amines, amides, pyridines, pyrroles, pyrazoles, pyrazines, nitriles, imidazoles and indoles, although the majority of these compounds were amides. The formation of different nitrogeneous compounds by the decomposition of algae feedstock was shown in **Table 7.** Each of these compounds may be the result of primary or secondary reactions that occurred during pyrolysis or in the condensed oil phase. Similar results were obtained by Arif Hakimi Saadon et al., 2022. It was concluded from the report that the amount of nitrogenous compounds formed seems high.

Table 6 Product distributions for select oil fractions based on GC-MS analysis

Compounds (class of compounds)	C2 (area %)	C3 (area %)	C4 (area %)	Filter (area %)
Alkanes	0.0	2.0	0.0	2.6
Alkenes	1.5	8.9	0.0	9.4
Fatty Oxygenates	21.0	12.1	0.0	32.3
Aromatics	0.0	0.0	0.0	1.8
N-containing Compounds	18.7	70.4	86.2	21.7
Unidentified	56.0	6.7	1.0	29.1
Yield of oil fraction (% of total oil recovered)	3.1	28.5	11.4	33.8

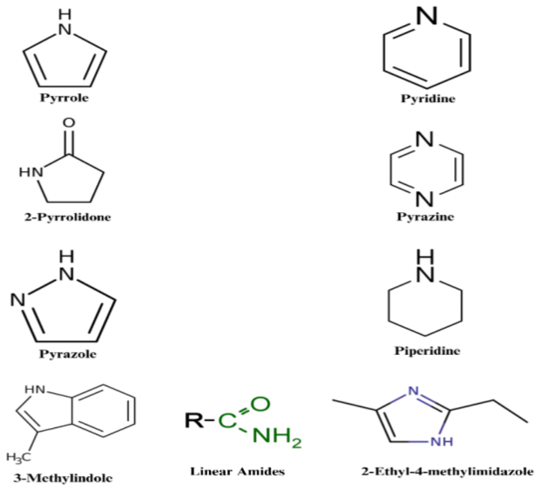


Figure. 7 Nitrogenous species detected in bio-oil fractions via GC-MS.

Table 7 Formation of different nitrogenous compounds by the decomposition of algae feedstock (Harman-Ware et al., 2013).

Compounds	**Formation**
Amides	They varied in chain length ranging from acetamide to stearamide and also included cyclic amides such as 2-pyrrolidone (with these mentioned compounds being dominant).
Cyclic amides	They may be formed from protein and amino acid intramolecular cyclization
Linear amides	They may be formed from primary protein decomposition or from amines in amino acids that reacted with carboxylic acids to produce amides and water.
Pyrroles	The presence of pyrroles can be attributed to the decomposition of glutamine amino acids present in proteins [32], as well as decomposed chlorophyll that was present in the algae feedstock

Pyrazines, pyridines, piperidines and pyrazoles	They are also likely formed from protein decomposition and/or intramolecular cyclization.
Pyrazines and other nitrogenous species	They may form from subsequent reactions of Amadori compounds generated by Maillard reactions.
Imidazoles	They may be formed from the decomposition of histidine amino acids present in proteins.
Indoles	They may be produced from decomposed tryptophan amino acids.

Conclusion

Catalytic microwave pyrolysis using a graphite susceptor and KOH catalyst effectively converted polystyrene into a high yield of condensable oil. Heating rates of 30–50 °C/min enabled fast pyrolysis, achieving up to 95 wt.% oil yield. Increasing catalyst mass from 5 to 7.5 g improved oil yield from 80% to 95%. However, specific microwave power decreased from 90 to 9 W/g with higher polystyrene loading, while specific energy consumption (27–73 kJ/g) declined with increasing heating rate. Overall, KOH significantly influenced heating rate, pyrolysis duration, product yield, and energy efficiency.

For algae, fresh biomass with solvent soaking produced 56.11 wt.% oil yield and 86.48% conversion, while torrefied algae with solvent pretreatment enhanced oil yield to 59.24 wt.% and improved the pyrolysis index (PI). Energy consumption decreased from 688 to 513 kJ, and higher heating value increased to 36.4 MJ/kg. Ethanol proved most effective for fresh algae, whereas benzene performed best for torrefied algae. GC-MS analysis revealed significant nitrogenous compounds, and FTIR confirmed functional groups such as C–H, =C–H, and C=O. Torrefaction combined with solvent pretreatment improved bio-oil stability and quality by forming stronger chemical structures.

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