



Hydrothermal Liquefaction of Mentha-Waste: Effects of Operating and Reaction Parameters on Product Yields

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ABSTRACT

The production of essential oils leads to the production of huge amounts of residual aromatic biomass after extraction. Hydrothermal Liquefaction of Mentha-waste was performed at different temperatures (220-300°C) using solvents such as water (H₂O), acetone (C₃H₆O), methanol (CH₃OH) and ethanol (C₂H₅OH) at reaction times ranging from 15-60 min. There was a significant increase in bio-oil yield with the use of organic solvents as compared to water. It increased from 9.84 wt.% (water as a solvent) to 20.17-31 wt.% using C₃H₆O, CH₃OH and C₂H₅OH as solvents. The highest bio-oil yield (31 wt.%) was when C₂H₅OH was used as a solvent. Maximum bio-oil yield at 220°C was obtained with water at a residence time of 45 min. At temperatures 240°C, 260°C and 280°C, maximum bio-oil was obtained at optimum reaction time of 30 min. The highest bio-oil yield i.e. 9.84 wt.%, was attained at 300°C with reaction time of 15 min. The bio-oil yield(s) increased discernibly with increasing temperature and decreasing reaction time. The organic solvent reactions were specifically performed at the reaction temperature and residence time which yielded the highest bio-oil (9.84 wt.%) under H₂O as a solvent i.e., 300°C and 15 min respectively. NMR and GC-MS analysis results show that use of organic solvents has a considerable effect on the decomposition of mentha-waste.

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1. Introduction

The field of biomass derived energy has garnered a lot of attention and research efforts globally. Many environmental and economic factors have led to a recent upsurge in the utilization of renewable and sustainable sources of energy. The perturbed climate pattern worldwide, exorbitant coal and oil prices and their limited availability are the contributing factors in this regard. The fossil fuels have much higher consumption rates than their regeneration rates whereas the biomass feedstocks have faster growth rates. The different ratifications in the form of Kyoto Protocol and the Paris Climate Agreement often referred to as the Paris Climate Accords [Rogelj et al., 2016] have highlighted the growing global greenhouse emissions of human made CO₂. In the recent COP26 as well, the developed and developing countries have committed to adopt environment friendly policies. The European Union has made the highly ambitious commitment to become carbon neutral by 2050 [Potrè et al., 2021]. Biomass being a sustainable and carbon neutral source of energy has renewed the interest of many countries to opt for abundant and cleaner sources of energy and to the subsequent fulfilment of several Sustainable Development Goals or SDGs [Blair et al., 2021].

Mentha, which is also known as mint or pudina (commonly in India) is in great demand worldwide due to its medicinal and aromatherapeutic properties [Kumar et al., 2011]. It is widely cultivated in tropical to temperate regions of America, Europe, China, Brazil, India, etc [Chauhan

et al., 2009]. The oils obtained from the plant are of immense economic value and are widely used in industries manufacturing food items (herbal teas), perfumes, essential oils and pharmaceuticals [Dorman et al., 2003]. Presently, India is the largest producer of mentha and accounts for about 75% of the world's mint production followed by China, Brazil and USA [Shrigod et al., 2017]. Mentha cultivation in India is mostly confined to Himachal Pradesh, Uttar Pradesh, Uttarakhand and Punjab [Chauhan et al., 2009].

There are different thermochemical conversion routes which have been studied with respect to biomass feedstocks such as pyrolysis, gasification and liquefaction [Biswas et al., 2017a]. Hydrothermal liquefaction is one of the promising methods for conversion of biomass to valuable products [Nazari et al., 2015]. It is considered highly economical from the viewpoint of energy savings as the biomass feedstock have to be pre-treated or dried intensively [Singh et al., 2015c]. HTL process reactions can be conducted with or without the use of potential catalysts and feedstocks with very high moisture content can also be processed which otherwise cannot be used for pyrolysis [Baloch et al., 2018]. The water present in the feedstock itself acts as a solvent [Biswas et al., 2021b]. The HTL process reactions generate four different phases: organic fraction of bio-oil, aqueous phase bio-oil, bio-residue and gases [Madsen et al., 2017]. The HTL process employs elevated temperatures and pressures to convert the biomass into bio-oil, however, the operating temperature is generally lower than that required during pyrolysis [Yu et

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al., 2011]. This process is sometimes also considered similar to the geological formation of fossil fuels. However, fossils fuels such as crude oil and coal are formed over a time spanning millions of years, whereas in the case of HTL, bio-oil is obtained in a time window of just a few hours [Tekin et al., 2014].

The earlier literature studies on mentha-waste biomass predominantly focussed on its use as a potential biosorbent to remove cations such as Pb(II), Cr(VI), etc. from wastewater streams [Hanif et al., 2009; Riaz et al., 2013]. The mentha plant waste, which is a by-product of mentha oil distillation, possesses various surface active functional groups which play a pivotal role in adsorption of cations from wastewater streams containing municipal wastes and industrial wastes (primarily textile dyes) [Rawat and Singh, 2019a]. The most commonly used adsorbent in factories for dye removal is carbon. However, due to increased costs of activated carbon, the search for a low-cost, maximum efficiency and highly versatile adsorbent is still ongoing [Riaz et al., 2013]. Rawat et al. [2020b] and Rais and Kumar [2008] have investigated the use of mentha-waste as a biosorbent for removal of potentially hazardous dyes such as Alizarin Red S, Patent Blue VF and Methylene Blue dyes in wastewater. To the best of our knowledge, this is the first comprehensive report on the hydrothermal liquefaction of mentha residual biomass, left after the extraction of essential oil.

The primary objective of this report is to study the influence of different solvents, temperatures and reaction times on the product yield. Literature suggests that there is a sharp increase in bio-oil yields when organic solvents are used as compared to when water is used as a solvent [Biswas et al., 2021b; Singh et al., 2015b; Akhtar and Amin, 2011]. The advantage of using organic solvents over water is associated with the possible alkylation and esterification reactions between liquefied biomass intermediates and organic solvents and stabilization of reaction intermediates [He et al., 2016]. It is also seen that there is an increase in bio-oil yields when temperature is raised till a certain optimum value [Akhtar and Amin, 2011]. Eboibi et al. [2014] conducted the HTL of halophytic microalga *Tetraselmis* sp. at different temperatures (310, 330, 350 and 370°C) and maximum bio-crude yield of 65 wt.% was obtained at 350°C. In another study, Jadhav et al. [2021] conducted HTL of locally sourced Malaysian oil palm fronds or OPF at temperatures ranging from 160-260°C. The bio-oil yield percentage increased from 27.3% at 160°C to 41.9% at 260°C. The reaction or residence time is another important operating factor which has been discussed in several earlier studies on HTL [Jadhav et al., 2021; Xu and Savage, 2015; Carpio et al., 2021]. Like reaction temperature, no particular trend has been observed with respect to residence time since in some cases the yields have increased and in some they decreased. There are cases where the changes in bio-oil yields are also negligible as discussed by Jadhav et al. [2021]. A study on the HTL of *Azolla filiculoides* [Biswas et al., 2021b] discussed the effect of different solvents (water, methanol and ethanol), reaction temperatures (260-300°C) and reaction times (15-60 min) on the product yields. Maximum bio-oil yield of 28.8 wt.% was obtained at 280°C using ethanol as a solvent at a reaction time of 60 min. Therefore, it is observed that there is an intricate interplay of different parameters and by manipulating these, the desired optimum product yields can be obtained.

The objective of this study is to propose mentha residual biomass (waste after extraction of essential oil) as a potential biomass feedstock for production of bio-oil/functional hydrocarbons and shed light on the effect of operating and reaction parameters such as solvent, temperature and reaction time on the desired product yields.

2. Materials and methods

2.1 Materials

The biomass feedstock mentha-waste was obtained from Central Institute of Medicinal and Aromatic Plants (also known as CSIR-CIMAP), Lucknow, Uttar Pradesh. The feed sample that was used for HTL was dried and ground to obtain feed in powder form. Distilled water was prepared in the laboratory. Organic solvents acetone, methanol and ethanol were purchased from Merck Company (ACS grade), India.

2.2 Apparatus and Experimental Procedure

Hydrothermal liquefaction reactions were carried out in a high-pressure autoclave Parr reactor made of hastelloy (nickel-molybdenum-chromium superalloy with an addition of tungsten designed to have excellent corrosion resistance in a wide range of severe environments) along with Parr 4848 controller. In a typical HTL experiment, initially the weight of the empty parr reactor was taken and it was then loaded with mentha-waste biomass and solvent in a 1:6 by weight ratio. The weight of the reactor containing the solvent and biomass was then recorded. After

fixing the reactor in the experimental setup, it was purged with nitrogen gas to remove air and also to check for any undesirable leakages. The gas supply is turned off and the controller program is set at the desired reaction temperature. The reactants are blended with the help of a stirrer (280 rpm). The HTL reactions for mentha-waste were performed at temperatures 220, 240, 260, 280 and 300°C with reaction times of 15, 30, 45 and 60 min. The organic solvent (acetone, ethanol and methanol) reactions were carried out at 300°C and 15 min residence time. After the reaction is complete, the reactor is cooled and the product gases are vented out. The next steps involved the extraction of bio-oil from the bio-char using diethyl ether which is subsequently followed by vacuum filtration. After separating the bio-oil into its aqueous and organic fractions, anhydrous sodium sulphate is used for dehydrating the organic fraction. The bio-oil obtained was filtered and evaporated to remove ether. This fraction of bio-oil was labelled as bio-oil 1. The solid product was extracted using a Soxhlet extraction apparatus. The extraction is done using acetone as solvent and solid products were extracted until the acetone in the thimble became colourless. The extracted bio-oil is filtered for removal of any char particles and the acetone is removed in a rotary evaporator. This fraction of bio-oil was weighed and labelled as bio-oil 2. The total bio-oil was the combination of the ether-soluble and the acetone-soluble fraction. In case of HTL using organic solvents, the extraction was carried out with the solvent which had been used in the reaction and no Soxhlet was carried out, hence only bio-oil 1 yield was obtained in this case. For calculating various product yields, the six equations given below were used [Biswas et al., 2021b].

$$\text{Conversion (\%)} = (W1 - W2)/W1 \times 100 \quad (1)$$

$$\text{Bio-oil 1 yield (wt.\%)} = (W_{\text{ether soluble}}/W1) \times 100 \quad (2)$$

$$\text{Bio-oil 2 yield (wt.\%)} = (W_{\text{acetone soluble}}/W1) \times 100 \quad (3)$$

$$\text{Solid residue yield (wt.\%)} = (W_{\text{solid}}/W1) \times 100 \quad (4)$$

$$\text{Gas yield (wt.\%)} = \frac{(W_{\text{vessel}} + \text{feed} + \text{water before HTL} - W_{\text{vessel}} + \text{feed} + \text{water after HTL})}{(\text{Amount of feed taken (g)} + \text{Amount of water added (g)})} \times 100 \quad (5)$$

$$\text{Other yield (wt.\%)} = 100 - (\text{bio-oil 1} + \text{bio-oil 2} + \text{bio-residue} + \text{gas}) \quad (6)$$

W1 is the weight of mentha-waste biomass and W2 is the weight of bio-residue. Wether soluble is the weight of ether-soluble bio-oil (bio-oil 1); Wacetone soluble is the weight of bio-oil (bio-oil 2) obtained after soxhlet extraction.

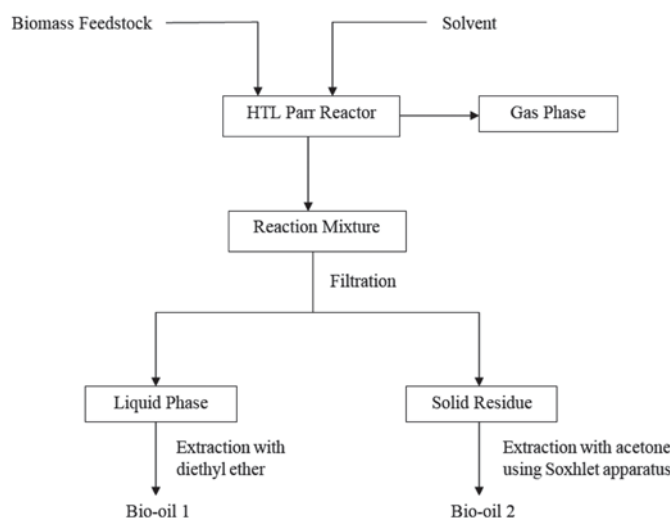


Figure 1: Hydrothermal Liquefaction: product recovery and separation procedure

2.3 Characterization Techniques

Thermogravimetric analysis (TGA) and derivative thermogravimetric analysis of mentha-waste was performed in a Shimadzu DTG-60 instrument. Around 5 mg of the biomass feedstock sample was carefully placed in a sample pan supported by a precision balance and then heated in a temperature range of 25-900°C in a nitrogen environment and a heating rate of 10°C/min is maintained. The gross calorific value (or

GCV) was calculated using Parr 6300 Bomb Calorimeter. The moisture content of mentha-waste was calculated using HR-83 Mettler Toledo Halogen Moisture Analyzer. For analysing the types of protons present in the bio-oils, Bruker Avance 500 Plus instrument was used with CDCl_3 as a solvent. The various functional group compounds present in the organic fraction of the bio-oil were analysed with the help of gas chromatography-mass spectroscopy (GC/MS Agilent Technologies 7890B). GC/MS begins with a gas chromatograph, where the sample is effectively volatilized. The carrier gas used was Helium at a flow rate of 1 ml min^{-1} . An HP (25 m x 0.32 mm x 0.17 micrometres) column was used for separation. The principle used is that the difference in the chemical properties between different molecules will separate the molecules as the sample travels the length of the column. An isothermal oven program was set at 50°C for 2 min, the column was heated from 50°C to 280°C with a heating rate of 5°C/min where it was held for 5 min. Using a computer library of mass spectra for different compounds, various unknown compounds and analytes were identified as well as quantified. The proximate analysis, i.e., volatile matter, ash and fixed carbon percentage was measured by placing the sample in a muffle furnace similar to ASTM D3175 method.

3. Results and Discussions

3.1 Raw material characterization

The proximate analysis of the mentha-waste feedstock is summarised in Table 1 and it shows that the biomass contains 8.45 wt.% of moisture, 73.26 wt.% of volatile matter, 1.67 wt.% of fixed carbon and 16.62 wt.% of ash.

Table 1: Proximate Analysis of Mentha-Waste (wt.% dry basis)

	Proximate Analysis
Moisture	8.45
Ash Content	16.62
Volatile Matter	73.26
Fixed Carbon	1.67

Thermogravimetric analysis or TGA of mentha-waste was performed to investigate the change in the mass of the biomass sample as a result of thermal decomposition over time as the temperature increases (Fig. 2). The biomass showed a two-step decomposition with some minor peaks between $700\text{--}900^\circ\text{C}$. From the TGA curve, it can be perceived that the first small peak ($60\text{--}180^\circ\text{C}$) occurs due to the moisture content [Kim et al., 2013] present in mentha-waste (8.45 wt.%). The second weight loss peak which is the strongest peak is observed between $180\text{--}560^\circ\text{C}$. Major fraction of cellulose and hemicellulose, with a small fraction of lignin decomposes in this region. During this stage, the bulk of volatiles are released which results in a major loss of weight [Damartzis et al., 2011]. The very small peaks between $700\text{--}900^\circ\text{C}$ occurred due to the slow decomposition of the lignin component of the biomass [Skreiberg et al., 2011]. The different functional groups present in the mentha-waste biomass were characterized with the help of FT-IR. Fig 3 shows the typical FT-IR

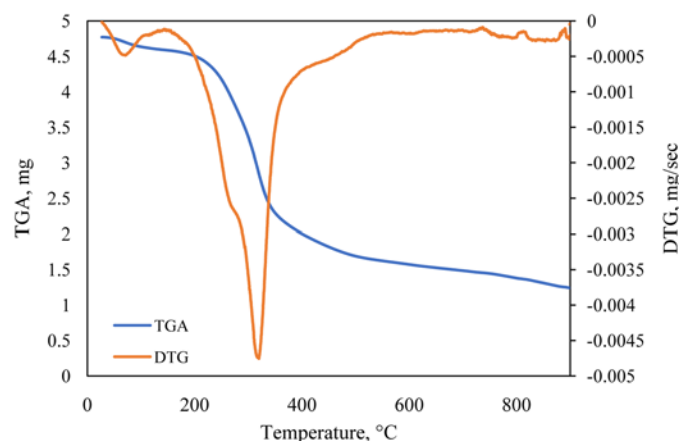


Figure 2: TGA/DTG of mentha-waste

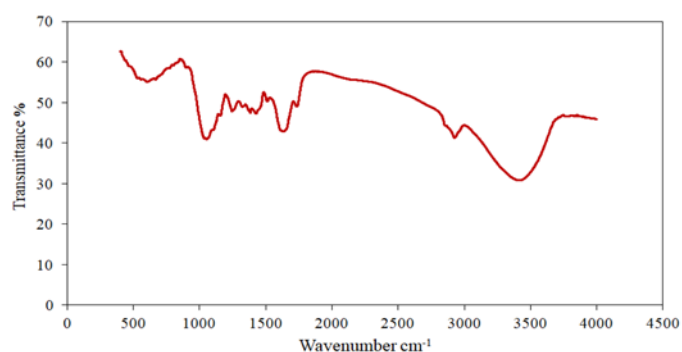


Figure 3: FT-IR of mentha-waste

spectrum of the biomass feedstock in which the broad band of CH, CH_2 stretching is observed around 2900cm^{-1} . The vibrations corresponding to 3413cm^{-1} are due to the presence of O-H groups of water and carbohydrates and the N-H group in proteins. The presence of amides containing C=O group corresponds to wave number 1636cm^{-1} due to the presence of proteins. The peak at 1054cm^{-1} corresponds to C-O, C-C bond stretching which evidently suggests the presence of a considerable amount of polysaccharide carbohydrates as also observed by Biswas et al. [2021b].

3.2 Product Yields from HTL

The material balance of hydrothermal liquefaction of mentha-waste biomass using different solvents (water, ethanol, methanol and acetone) at different reaction temperatures is shown in Table 2. HTL is a thermochemical conversion route of processing biomass into liquid as the main product as well as solid residue (bio-char), aqueous phase and

Table 2: Product distribution of mentha-waste from hydrothermal treatment at varying reaction conditions and operating parameters

Sample with temperature $^\circ\text{C}$ and optimum reaction time	Bio-oil wt. %		Total bio-oil (wt. %)	Gas (wt. %)	Bio-residue (wt. %)	Conversion (wt. %)	Other yield (wt. %)
	Bio-oil 1	Bio-oil 2					
MW220-45	5.67	1.17	6.84	6.18	46.67	53.33	40.31
MW240-30	3.0	4.17	7.17	7.62	40.83	59.17	44.38
MW260-30	2.83	5.40	8.23	7.86	32.67	67.33	51.24
MW280-30	4.50	3.83	8.33	7.84	26.67	73.33	57.16
MW300-15	6.67	3.17	9.84	10.47	25	75	54.68
MWACET300-15	-	-	20.17	11.67	35	65	33.16
MWETH300-15	-	-	31	9.26	21.67	78.33	38.07
MWMETH300-15	-	-	24	13.33	23.33	76.67	39.34

Where, MW = Mentha-Waste; ACET = acetone as a solvent; ETH = ethanol as a solvent; METH = methanol as a solvent; 220, 240, 260, 280 and 300 are temperatures and 15, 30 and 45 are reaction times.

gases as by-products [Barreiro et al., 2013]. Maximum bio-oil yields obtained at different temperatures and reaction times were: 6.84 wt.% (220°C; 45 min); 7.17 wt.% (240°C; 30 min); 8.23 wt.% (260°C; 30 min); 8.33 wt.% (280°C; 30 min); 9.84 wt.% (300°C; 15 min). The bio-oil yields reported are the total bio-oil yields which are calculated by adding bio-oil 1 wt.% and bio-oil 2 wt.%. This holds true when the solvent used is water. In case of organic solvents, the bio-oil yields are directly obtained by evaporating the solvent used in the reaction. It was observed that the bio-oil yields increased with increase in temperature up to 300°C and there was a subsequent decrease in the amount of bio-char observed. As seen in table 2, higher temperature favoured further breakdown into simpler compounds which led to higher gas yields and the corresponding bio-residue yields reduced with temperature. An in-depth compilation of earlier literature studies has been reported by [Akhtar and Amin, 2011] and similar observations about the effect of temperature on bio-oil and bio-char yields have been reported. As the maximum bio-oil yield using water as a solvent was obtained at 300°C and 15 min reaction time, the organic solvent (acetone, ethanol and methanol) HTL reactions were conducted at this temperature and reaction time. The highest bio-oil yield obtained was almost threefold (31 wt.% using ethanol) of that obtained using water as observed in Table 2. The bio-oil yields obtained using acetone and methanol were 20.17 wt.% and 24 wt.% respectively. Similar findings about the considerable increase in bio-oil yields using organic solvents have also been reported in many of the earlier studies on hydrothermal liquefaction [Biswas et al., 2017a; Mazaheri et al., 2010; Hao et al., 2021]. In our study, with the increasing temperature, the holding or residence time followed a decreasing trend to obtain higher bio-oil yields (reduced from 45 min (220°C) to 15 min (300°C)). An optimum reaction time of 30 min was conducive to obtain higher bio-oil yields for the temperatures 240°C, 260°C. As clearly observed in Table 2, the conversion was highest in case of ethanol as a solvent. Hence, this study clearly elucidates the importance of using organic solvents as potential solvents for future studies on hydrothermal liquefaction as they have a considerably higher efficiency as solvents when compared to water.

3.3 Bio-oil Characterization

3.3.1 ¹H Nuclear Magnetic Resonance (NMR) of bio-oil

The ¹H NMR spectra are representative of the features in the bio-oils produced at the investigated reaction conditions [Xu and Savage, 2015]. The resonance peaks obtained in the spectra are indicative of the functional group compounds present in the obtained bio-oil (Fig 4a and 4b). The figure 4a corresponds to reactions where water was used as a solvent and the figure 4b provides a lucid explanation of the peaks obtained representative to different functional group classes corresponding to the organic solvent (acetone, ethanol and methanol) reactions. The figure 4a provides the spectral distribution of bio-oils obtained using water as a solvent at different reaction temperatures and optimum reactions or holding times. A considerable percentage of protons (greater than 50%) resonate in the region from 0.5-3.0 ppm as observed from the graphical information provided in fig 4a. The proton percentages in the region 0.5-1.5 ppm are about 50% for bio-oils obtained at 220 and 240°C with residence times of 15 min and 30 min respectively. For the bio-oils obtained at temperatures 260, 280 and 300°C the proton percentages are 30-40% range. The region from 0.5-1.5 ppm is representative of protons on aliphatic carbon atoms which are at least two bonds away from C=C or heteroatom. For the region 1.5-3.0 ppm, the proton percentages are due to protons on aliphatic carbon atoms that may be bonded to a C=C double bond or heteroatom. The proton percentages are close to 40% for bio-oils obtained at 280 and 300°C with a reaction time of 30 min and 15 min respectively. For bio-oils obtained from reactions conditions corresponding to 220, 240 and 260°C with reaction times of 15, and 30 min (for 240 and 260°C) the proton percentages are 32%, 27% and 34% respectively. These results align with the findings reported by Xu and Savage[2015]. The next region 3.0-4.5 ppm corresponds to methoxyl protons or methylene group that join two aromatic rings [Singh et al., 2015a]. There is almost negligible resonance reported in the region 4.5-6.0 ppm. This region corresponds to aromatic ethers i.e., lignin derived methoxy phenols. The resonance spectrum between the regions 6.0-8.5 ppm is representative of the aromatic region. The proton percentages range between 5 to 12% for this area. In the case of organic solvents (fig 4b), similar observations were seen. The major proton percentages lie in the region spanning 0.5-3.0 ppm with the highest peaks of 57%, 47% and 52% for acetone, ethanol and methanol respectively. The aliphatic region is much greater in fig 4b than fig 4a, this corresponds to larger number of protons on aliphatic carbons. The region between 3.0-4.5 ppm shows proton percentages in the range of 5-11%.

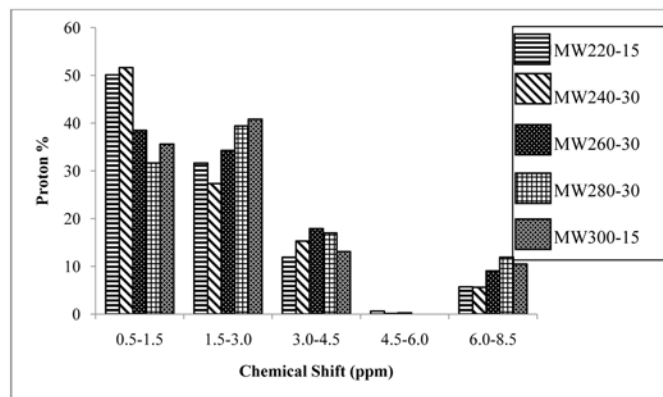


Figure 4a: ¹H NMR spectral distribution of functional groups present in bio-oil from liquefaction in water at a: 220°C, 45 min; b: 240°C, 30 min; c: 260°C, 30 min; 280°C, 30 min; 300°C, 15 min

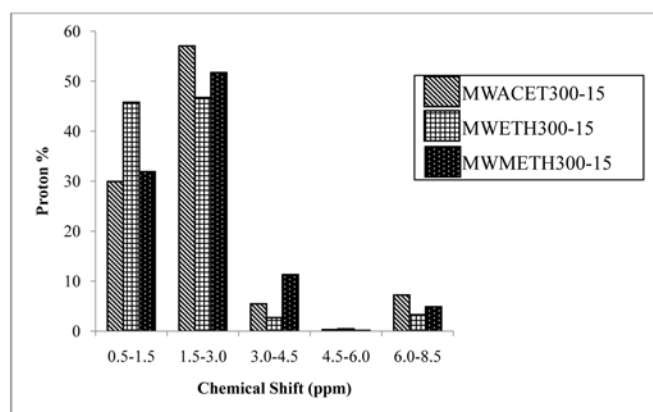


Figure 4b: ¹H NMR spectral distribution of functional groups present in bio-oil from liquefaction in organic solvents (acetone, ethanol and methanol) at 300°C and 15 min.

This is also consistent with very low percentages of alcohols or ethers present in the bio-oils. The minute peaks observed in 4.5-6.0 ppm are representative of almost negligible amount of aromatic ether present in the bio-oils. The aromatic region corresponding to the spectrum 6.5-8.0 ppm ranges from ~5-7% and the highest peak area is observed in case of acetone. This is indicative of the greater amount of aromatics present in bio-oils obtained using acetone as a solvent.

3.3.2 Gas Chromatography Mass Spectroscopy (GC/MS) of bio-oil

Gas Chromatography Mass Spectroscopy or GC-MS was performed to identify the major types of compounds present in the bio-oils obtained at various reaction conditions as presented in table 3.1 and 3.2. The bio-oil is mainly composed of phenol and its derivatives, ketones, alcohol, esters, alkanes, aromatics. Phenol and its various derivatives were formed because of hydrolysis of organic bonds present in lignocellulosic structure of biomass [Jadhav et al., 2021]. The GC-MS results further cement the findings of NMR and provide more information about the various classes of compounds present in the bio-oils. As seen in table 3.1, the major compounds present in bio-oil obtained at 220°C with a 15 min holding time are Phenol, 2,6-dimethoxy (8.04%); Ethanone, 1-(4-hydroxy-3,5 dimethoxyphenyl)- (5.95%); 2(1H)Pyrimidinone,4-amino-1,N-dimethyl- (6.56%); Butylated Hydroxytoluene (6.53%) and 3-Pyridinol (23.47%).

For bio-oil obtained at 240°C with 30 min holding time, some of the major compounds are Phenol, 2,6-dimethoxy- (19.09%); 2-Pentanone, 4-hydroxy-4-methyl- (15.10%); Butylated Hydroxytoluene (8.76%) and 3-Pyridinol (19.18%). The area % for Phenol, 2,6-dimethoxy- are 16.21%, 14.76% and 13.97% for bio-oils obtained at 260°C with 30 min holding time, 280°C with 30 min holding time and 300°C with 15 min holding time respectively. Similarly, 3-Pyridinol was found in high amounts (12.42%, 10.86% and 8.13%) for the bio-oils obtained at the above-mentioned three reaction conditions respectively. Other major compounds

obtained were Phenol, 2-methoxy- (5.82%) for reaction conditions 280°C and 30 min holding time; 1,2-Benzenediol, 3-methoxy- (8.97%) for 300°C and 15 min; Butylated hydroxytoluene (6.07%) for bio-oil obtained at 280°C and 30 min reaction time and 4-Acetylanisole with area percentages 6.18% and 5.75% for bio-oils at 280°C with 30 min holding time and 300°C with 15 min reaction time respectively. A few compounds (Phenol, 2,6-dimethoxy-; Phenol, 4-ethyl-2-methoxy-; 2-Pentanone, 4-hydroxy-4-methyl-; Butylated Hydroxytoluene and 3-Pyridinol) were common among all the bio-oils obtained at various reaction conditions as seen in table 3.1. In case of organic solvent (acetone, ethanol and methanol) reactions, the highest area percentages of compounds observed were for compounds Phenol, 3,4-dimethyl- (13.1% for acetone); Hexadecanoic acid, ethyl ester (7.09% for ethanol); Hexadecanoic acid, methyl ester (13.08% for methanol); p-Cresol (8.33% for acetone) and 1H-Pyrazole, 4,5-dihydro-5,5-dimethyl-4-isopropylidene- (11.47% for acetone). None of the compounds were found to be common among all three solvents as observed in table 3.2.

4. Conclusions

Table 3.1: GC-MS analysis of HTL-produced bio-oil compounds from mentha-waste at optimum reaction conditions using water as a solvent (MW= mentha-waste; 220, 240, 260, 280 and 300 are temperatures and 15, 30 and 45 are reaction times)

Compounds identified in the Bio-oil	Area %				
	MW220-45	MW240-30	MW260-30	MW280-30	MW300-15
Phenol	-	1.13	1.22	2.13	1.80
Phenol, 2,6-dimethoxy-	8.04	19.09	16.21	14.76	13.97
Phenol, 2-methoxy	-	4.12	3.79	5.82	4.34
Phenol, 4-ethyl-2-methoxy-	1.01	1.43	1.17	1.48	1.63
Imidazole-2-hydrazide-1-carboxylic acid, methyl ester	-	5.10	-	-	-
Fumaric acid, di(pent-4-en-2-yl) ester	-	-	1.68	-	-
Hexadecanoic acid, ethyl ester	3.33	-	-	-	-
Fumaric acid, 3,4-dimethoxyphenyl nonyl ester	-	-	-	0.57	-
1H-Imidazole-4-carboxylic acid, methyl ester	0.89	-	-	-	-
Phthalic acid, butyl 2-ethylbutyl ester	-	-	-	-	0.35
Oxalic acid, 2-isopropoxyphenyl heptyl ester	-	-	1.00	-	-
Linoleic acid ethyl ester	2.03	-	-	-	-
Ethanone, 1-(4-hydroxy-3,5 dimethoxyphenyl)-	5.95	1.97	1.01	0.54	-
Ethanone, 1-(2-hydroxy-5-methoxyphenyl)-	2.31	-	-	-	-
2-Pentanone, 4-hydroxy-4-methyl-	3.70	15.10	5.30	3.75	5.23
2-Pentanone, 1-(2,4,6-trihydroxyphenyl)	-	4.33	-	1.49	0.64
2-Cyclopenten-1-one, 2,3-dimethyl-	-	0.67	0.65	0.92	1.03
2-Acetonilycyclopentanone	-	-	0.71	0.74	0.58
1-(4-methylthiophenyl)-2-propanone	-	1.50	1.32	-	-
1,2-Benzenediol, 3-methoxy-	-	-	2.29	5.21	8.97
1,4-Benzenediol, 2-methyl-	0.86	-	1.24	1.45	2.48
2(1H)Pyrimidinone,4-amino-1,N-dimethyl-	6.56	-	-	-	-
Bicyclo[2.2.1]heptane, 1,3,3-trimethyl-	4.64	-	2.46	-	-
Butylated Hydroxytoluene	6.53	8.76	4.62	6.07	3.20
Acetophenone, 4'-hydroxy-	-	-	-	2.07	4.90
4-Acetylanisole	1.80	-	3.07	6.18	5.75
3-Pyridinol	23.47	19.18	12.42	10.86	8.13
Hydroquinone	0.81	-	-	1.00	1.67

Hydrothermal liquefaction is one of the suitable processes for the valorisation of residual mentha biomass. The optimal reaction conditions as obtained from this study are: 300°C and 15 min residence time. The findings from this study have shown that organic solvent ethanol is a suitable solvent for obtaining maximum bio-oil yields. Phenol and its derivatives, esters and aromatics are observed to be the major compounds present in the bio-oil. The bio-oil may thus be a valuable source of functional chemicals.

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References

Table 3.2: GC-MS analysis of HTL-produced bio-oil compounds from mentha-waste at optimum reaction conditions using actone, ethanol and methanol as a solvent (MW= mentha-waste; ACET= acetone; ETH= ethanol; METH= methanol; 300 is temperature and 15 is reaction time)

Compounds identified in the Bio-oil	Area %		
	MWACET300-15	MWETH300-15	MWMETH300-15
Phenol, 2,3,5-trimethyl-	2.48	-	5.46
Phenol, 2,4-dimethyl-	-	1.13	2.99
Phenol, 2-methoxy-4-propyl-	-	3.15	2.74
Phenol, 3,4-dimethyl-	13.1	-	-
Phenol, 3-methyl-5-(1-methylethyl)-, methylcarbamate	-	-	3.72
3-Methyl-4-isopropylphenol	-	-	3.54
1(2H)-Naphthalenone, 3,4-dihydro-3,3,6,8-tetramethyl-	2.90	-	-
2-Pentanone, 4-hydroxy-4-methyl-	4.99	-	4.77
Ethanone, 1-(1-cyclohexen-1-yl)-	-	0.54	1.50
8-Octadecenoic acid, methyl ester, (E)-	-	-	1.91
Benzoic acid, 4-formyl-, methyl ester	2.48	-	-
Hexadecanoic acid, ethyl ester	-	7.09	-
Hexadecanoic acid, methyl ester	2.31	-	13.08
Octadecanoic acid, ethyl ester	-	2.89	-
Pyridine, 5-ethyl-2-methyl-	4.52	-	-
p-Cresol	8.33	-	-
Naphthalene, 1,2,3,4-tetrahydro-2,2,5,7-tetramethyl-	-	0.31	0.97
Benzene, 1-ethyl-4-methoxy-	-	1.09	1.03
Benzene, 1-methoxy-4-(1-methyl-2-propenyl)-	1.19	-	-
Benzyl Alcohol	-	2.89	-
2-Pentanol, 2,4-dimethyl-	-	3.88	-
4-Propyl-1,1'-diphenyl	-	0.92	3.07
Thymol	2.36	-	-
Levomenthol	-	2.20	0.69
1,4-Benzenediamine, N,N,N',N'-tetramethyl-	-	-	3.13
1H-Pyrazole, 4,5-dihydro-5,5-dimethyl-4-isopropylidene-	11.47	-	-
Methyl Stearate	-	-	4.90

- [1]. Akhtar J, Amin NAS, 2011, A review on process conditions for optimum bio-oil yield in hydrothermal liquefaction of biomass, Renewable and Sustainable Energy Reviews, 15(3), 1615-1624.
- [2]. Baloch HA, Nizamuddin S, Siddiqui MTH, Riaz S, Jatoi AS, Dumbre DK, Mubarak NM, Srinivasan MP, Griffin GJ, 2018, Recent advances in production and upgrading of bio-oil from biomass: A critical overview, Journal of Environmental Chemical Engineering, 6(4), 5101-5118.
- [3]. Barreiro DL, Prins W, Ronsse F, Brilman W, 2013, Hydrothermal liquefaction (HTL) of microalgae for biofuel production: state of the art review and future prospects, Biomass and Bioenergy, 53, 113-127.
- [4]. Biswas B, Kumar AA, Bisht Y, Singh R, Kumar J, Bhaskar T, 2017a, Effects of temperature and solvent on hydrothermal liquefaction of *Sargassum tenerrimum* algae, Bioresource technology, 242, 344-350.
- [5]. Biswas B, Kumar AA, Bisht Y, Krishna BB, Kumar J, Bhaskar T, 2021b, Role of temperatures and solvents on hydrothermal liquefaction of *Azolla filiculoides*, Energy, 217, 119330.
- [6]. Blair MJ, Gagnon B, Klain A, Kulišić B, 2021, Contribution of biomass supply chains for bioenergy to sustainable development goals, Land, 10(2), 181.
- [7]. Carpio RB, Zhang Y, Kuo CT, Chen WT, Schideman LC, de Leon R, 2021, Effects of reaction temperature and reaction time on the hydrothermal liquefaction of demineralized wastewater algal biomass, Bioresource Technology Reports, 14, 100679.
- [8]. Chauhan RS, Kaul MK, Shahi AK, Kumar A, Ram G, Tawa A, 2009, Chemical composition of essential oils in *Mentha spicata* L. accession [IIIM (J) 26] from North-West Himalayan region, India, Industrial Crops and Products, 29(2-3), 654-656.
- [9]. Damartzis T, Vamvuka D, Sfakiotakis S, Zabaniotou A, 2011, Thermal degradation studies and kinetic modeling of cardoon (*Cynara cardunculus*) pyrolysis using thermogravimetric analysis (TGA), Bioresource Technology, 102(10), 6230-6238.
- [10]. Dorman HJD, Ko'ar M, Kahlos K, Holm Y, Hiltunen R, 2003, Antioxidant properties and composition of aqueous extracts from *Mentha* species, hybrids, varieties, and cultivars, Journal of Agricultural and Food Chemistry, 51(16), 4563-4569.
- [11]. Eboibi BE, Lewis DM, Ashman PJ, Chinnsamy S, 2014, Effect of operating conditions on yield and quality of biocrude during hydrothermal liquefaction of halophytic microalga *Tetraselmis* sp, Bioresource Technology, 170, 20-29.
- [12]. Hanif A, Bhatti HN, Hanif MA, 2009, Removal and recovery of Cu (II) and Zn (II) using immobilized *Mentha arvensis* distillation waste biomass, Ecological Engineering, 35(10), 1427-1434.
- [13]. Hao B, Xu D, Jiang G, Sabri TA, Jing Z, Guo Y, 2021, Chemical reactions in the hydrothermal liquefaction of biomass and in the catalytic hydrogenation upgrading of biocrude, Green Chemistry, 23(4), 1562-1583.
- [14]. He Y, Liang X, Jazrawi C, Montoya A, Yuen A, Cole AJ, Neveux N, Paul NA, de Nys R, Maschmeyer T, Haynes BS, 2016, Continuous hydrothermal liquefaction of macroalgae in the presence of organic co-solvents, Algal Research, 17, 185-195.
- [15]. Jadhav A, Ahmed I, Baloch AG, Jadhav H, Nizamuddin S, Siddiqui MTH, Baloch HA, Qureshi SS, Mubarak NM, 2021, Utilization of oil palm fronds for bio-oil and bio-char production using hydrothermal liquefaction technology, Biomass

- Conversion and Biorefinery, 11(5), 1465-1473.
- [16]. Kim SS, Ly HV, Kim J, Choi JH, Woo HC, 2013, Thermogravimetric characteristics and pyrolysis kinetics of *Alga Sagarssum* sp. biomass, *Bioresource Technology*, 139, 242-248.
- [17]. Kumar P, Mishra S, Malik A, Satya S, 2011, Insecticidal properties of *Mentha* species: A review, *Industrial Crops and Products*, 34(1), 802-817.
- [18]. Madsen RB, Bernberg RZK, Biller P, Becker J, Iversen BB, Glasius M, 2017, Hydrothermal co-liquefaction of biomasses—quantitative analysis of bio-crude and aqueous phase composition, *Sustainable Energy & Fuels*, 1(4), 789-805.
- [19]. Mazaheri H, Lee KT, Bhatia S, Mohamed AR, 2010, Sub/supercritical liquefaction of oil palm fruit press fiber for the production of bio-oil: Effect of solvents, *Bioresource Technology*, 101(19), 7641-7647.
- [20]. Nazari L, Yuan Z, Souzanchi S, Ray MB, Xu CC, 2015, Hydrothermal liquefaction of woody biomass in hot-compressed water: Catalyst screening and comprehensive characterization of bio-crude oils, *Fuel*, 162, 74-83.
- [21]. Potrè S, Èuèèk L, Martin M, Kravanja Z, 2021, Sustainable renewable energy supply networks optimization—The gradual transition to a renewable energy system within the European Union by 2050, *Renewable and Sustainable Energy Reviews*, 146, 111186.
- [22]. Rais A, Kumar R, 2008, Comparative adsorption study for the removal of Alizarin Red S and patent Blue VF by using mentha waste, *Current World Environment*, 3(2), 261.
- [23]. Rawat AP, Singh DP, 2019a, Synergistic action of adsorption and reductive properties of ash derived from distilled *Mentha piperita* plant waste in removal of Cr (VI) from aqueous solution, *Ecotoxicology and Environmental Safety*, 176, 27-33.
- [24]. Rawat AP, Kumar V, Singh DP, 2020b, A combined effect of adsorption and reduction potential of biochar derived from *Mentha* plant waste on removal of methylene blue dye from aqueous solution, *Separation Science and Technology*, 55(5), 907-921.
- [25]. Riaz B, Ansari TM, Hanif MA, Riaz S, Khan MA, Muhammad R, Jilani MI, 2013, Utilization of Extensively Available Environmental Waste *Mentha spicata* for Uptake of Pb (II) from Aqueous Solutions, *Asian Journal of Chemistry*, 25(8), 4551-4555.
- [26]. Rogelj J, den Elzen M, Höhne N, Fransen T, Fekete H, Winkler H, Schaeffer R, Sha F, Riahi K, Meinshausen M, 2016, Paris Agreement climate proposals need a boost to keep warming well below 2°C, *Nature*, 534(7609), 631-639.
- [27]. Shrigod NM, Swami Hulle NR, Prasad RV, 2017, Supercritical fluid extraction of essential oil from mint leaves (*mentha spicata*): process optimization and its quality evaluation, *Journal of Food Process Engineering*, 40(3), 12488.
- [28]. Singh R, Prakash A, Balagurumurthy B, Singh R, Saran S, Bhaskar T, 2015a, Hydrothermal liquefaction of agricultural and forest biomass residue: comparative study, *Journal of Material Cycles and Waste Management*, 17(3), 442-452.
- [29]. Singh R, Balagurumurthy B, Prakash A, Bhaskar T, 2015b, Catalytic hydrothermal liquefaction of water hyacinth, *Bioresource Technology*, 178, 157-165.
- [30]. Singh R, Chaudhary K, Biswas B, Balagurumurthy B, Bhaskar T, 2015c, Hydrothermal liquefaction of rice straw: Effect of reaction environment, *The Journal of Supercritical Fluids*, 104, 70-75.
- [31]. Skreiberg A, Skreiberg Ø, Sandquist J, Sørum L, 2011, TGA and macro-TGA characterisation of biomass fuels and fuel mixtures, *Fuel*, 90(6), 2182-2197.
- [32]. Tekin K, Karagöz S, Bekta° S, 2014, A review of hydrothermal biomass processing, *Renewable and Sustainable Energy Reviews*, 40, 673-687.
- [33]. Xu D, Savage PE, 2015, Effect of reaction time and algae loading on water-soluble and insoluble biocrude fractions from hydrothermal liquefaction of algae, *Algal Research*, 12, 60-67.
- [34]. Yu G, Zhang Y, Schideman L, Funk TL, Wang Z, 2011, Hydrothermal Liquefaction of Low Lipid Content Microalgae into Bio-Crude Oil, *Transactions of the ASABE*, 54(1), 239-246.