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Initial Studies of Hydrothermal Liquefaction of Bryophytes into Bio-Oil in Sub and Super-Critical Water Media Without Catalysts

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----------ABSTRACT----------

Bryophyte are the oldest land plant. Bryophyte places this group between algae and Pteridophyte. Bryophyte exist in a wide variety of habitats. They can be found growing in a range of temperatures, cold arctics and in hot deserts, in a range of elevations sea-level to hilly land, and moisture dry deserts to wet rainforests. The usefulness of bryophytes is relatively unknown to most people. Studies of HTL to proceed bryophyte into bio-oil was attempted. Process parameters were attempted such as temperature (300,350 dan 374 ^{o}C). Increase the temperature reaction increased the degradation rate, liquid and gaseous products. Residual solid decreased from 70.82% to 52.65%, liquid product increased from 16.34 to 27.44%, and gaseous product increased from 12.84 to 19.11%. Substrate bryophyte load of
(4, 6 and 8 %), increase the substrate load decreased the degradation rate. Residual solid increased from 53.37% to 64.27%, liquid products decreased from 15.77 % to 9.07%, and gaseous prouct decreased from 30.86 to 26.66%. Reaction time of 2, 3 and 4 hrs. Increase reaction time commontly, increased the degradation rate of solid, reduced the liquid product, and increase the gaseous product.Substrate bryophyte load 8% and temperature 300 oC, the residual solid decreased from 70.8 to 64.3%, liquid product decreased from 16.3 to 9.0%, and gaseous product increased from 12.8 to 26.7%.

KATA KUNCI: *bryophyte, HTL, bio-oil, conversion*

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I. INTRODUCTION

Exploration alternative energy to substitute fossil energy was very attractive, because of the rapid shortage of fossil energy. People has a big worry by the supply of energy in the future. There are three categories of biofuels, The first generation was converted edible feedstocks, for example soya beans, wheat corn, rape seed, sugarcane, molasses and carbohydrate into ethanol. Because those materials compete with human needs, the raw material supply will unsafe. The second generation was used lignocellulosic waste to convert into ethanol, but the cost was significantly increase. The third generation was used algae to convert into fuels.[1]

Bryophyte has almost neglected exploring it's potential as raw materials for energy alternative. Bryophytes are the second largest taxonomic group in the plant kingdom, but their chemical composition are limited.[2] Bryophytes have about 25000 species,[3] and they can be found in any kind of ecosystems. [4]

Bryophyte are the oldest land plant. Bryophyte places this group between Algae and Pteridophyte. Bryophyte exist in a wide variety of habitats. They can be found growing in a range of temperatures, cold arctics and in hot deserts, elevations, sea-level to hilly land, and moisture dry deserts to wet rainforests. The usefulness of bryophytes is relatively unknown to most people.[5]

The fisrt used of bryophytes were for environmental benefits, such as ecological uses, horticultural uses, moss industry, household uses, oxygen supply, bryophyte cleaner the atmosfer, and reduce the noise pollution.[6] Further exploration of bryophyte was to explore it's active content such as phenolic acids, flavonoids, triterpenes and alkaloids, [7,8,9] and it's elements content.[2,10] More specifically bryophytes demonstrate antibacteral, antifungal, antiviral activities, antioxidant, antiplatelet, antithrombin, insecticidal, and neurorotective activities. [11]

Table 1. Elemental composition (%) of bryophyte species .[2]

Species	C	H	N	O	C/H
Aulacomnium palustre	43.51	5.72	0.51	50.25	7.606
Polytrichum commune	43.79	6.06	2.02	48.13	7.226
Polytrichum funiperum	41.99	5.89	1.99	50.14	7.129
Ptilium crista-castrensis	42.25	5.68	1.21	50.87	7.438
Pleurozium schreberi	43.15	5.52	1.12	50.21	7.817
Rhytidiadelphus triquetrus	42.47	5.56	1.12	50.85	7.638
Sphagnum girgensohnii	42.04	5.74	0.85	51.17	7.324
Sphagnum magellanicum	42.21	5.55	0.52	51.72	7.605
Sphagnum capillifolium	40.98	5.58	0.42	53.02	7.344
Sphagnum angustifolium	41.78	5.52	0.43	52.27	7.569
Plagiochila asplenioides	41.97	5.63	0.92	51.48	7.455

Elemental content of bryophyte species was shown in Table 1. The ranges in concentrations of basic elements in the studied bryophytes were C: 40 to 43%, H 5.5 to 6%; N 0.4 to 2%; S 0%; O 48 to 53% and C/N ratio from 7.13 to 7.82. There was high similarity in the basic organic structural molecules of the bryophytes. Research activities to convert bryophyte into bio-oil as an alternatve energy was pioneer by Sirohi,[12], the technology used is stil to extract the lipid from a species of bryophyte. For instance 0.044 g of lipid was extracted from 8 gram of the bryophyte. By extraction of lipid, just lipid content in the bryophyte will converting into bio-fuel.

Hydrothermal liquefaction (HTL) process is used hot compressed water as the reaction medium, and HTL technology is totally environmentally friendly. HTL can proceed any biomass with high water content directly, without drying and extraction process. Not just extracted lipid, all content of bryophyte such protein, lipid and carbohydrate will distructed in the HTL process into bio-oil.

The main objectives of this paper is to study the effect of various operation parameters affected to the converting of the bryophytes into bio-oil, such solid residue, liquid and gaseous products.

2. Experimental

2.1. Materials and chemicals

Harvested bryophytes types liverworts were rinse with water until the contaminant were leaft, and then bryophytes were drying in the oven for several days at temperature 60 ^{o}C. After dried bryophytes were ground and then shiefed in the certain sizes. All solvents are analytical reagent grade provided by Merck.

2.2 Experimental procedures

Liquefaction experiments were carried out in a reactor volume of 60 ml stainless steel cylindrical. 4, 6, and 8% of grounded bryophyte was contained into the reactor, water solvent of 50 ml was added and then the reactor was sealed properly and make sure that there is no leakage. The reactor was mounted into the furnace that the temperature can be set in certain point as the reacting temperature (300, 350 and 374^{o}C) . The reactor leave for several hours as the reacting time (2,3 and 4 hrs). After reacting time was reached the reactor was pull out and poured with tap water to chill and stop the reaction until at ambient temperature, and then the reactor valve was open to leave the gas out, and then the reactor was opened properly to pull out the reaction products. The solid and liquid products are separated by filtering. The solid was rinsed with same solvent and dried at 105 ^{o}C until the weight remained unchanged as solid product. The liquid was dried in vacuum dryer at temperature 50 ^{o}C, until weight remained unchanged as liquid products. The liquid products were analysis by GC-MS.

Yield of bio-oil = Mass of bio-oil / mass of bryophyte x 100% (1)

Yield of solid residue = Mass of carbon / mass of bryophyte x 100% (2)

Conversion rate = 100 wt% - yield of solid residue (3)

2.3 Products analysis

The gas produced was leave out not to be analyzed. The soluble liquid products were analyzed using GC-MS, Agilent technologies 7890B, with DB5 Column (30 m x 0.32 mm x 0.25 µm, detector MSD 5977A, Helium (He) was used for mobile phase or carrier gas with flow rate 1 ml/min. Injector temperature was 250 ^{o}C. The temperature of ion source and MS Quadruple were 230 ^{o}C and 150 ^{o}C, respectively.

II. RESULTS AND DISCUSSIONS

3.1 CONVERSION OF BRYOPHYTE INTO SOLID RESIDUE, LIQUID AND GASEOUS PRODUCTS

The results of experiment were shown in Figures 1 - 10. The effects of temperatures, substrate load and reaction times were examined in water media.

Increase the reaction time (2, 3, and 4 hrs) commonly, conversion of solid and gaseous products were increased, but the liquid products were decreased slightly (Fig. 1- 8). It's meant that increase the reaction time more liquid products were converted into gaseous products. Other words gasification rate increase by increasing reaction time. Increase the reaction time, the degradation of solid also increased, it can be seen that the residual solid was decreased. The bryophyte substrate of 4% and temperature of 300 ^{o}C, the residual solid decreased from 59.7 to 53.4%. Liquid product decreased from 19.2 to 15.8%, and gaseous product increased from 21.2 to 30.7% (Figure 1). From figure 2. Can be shown that residual solid decreased from 66 to 59.4%, liquid product decreased from 14.1 to 11.8%, and gaseous product increased from 20 to 28.9%. From figure 3. Can be shown that residual solid decreased from 70.8 to 64.3%, liquid product decreased from 16.3 to 9.0%, and gaseous product increased from 12.8 to 26.7%. That is a similar result in increasing reaction time and bryophyte load resulted increased the degradation and gaseous products, and liquid products were decreased (Fig. 4-8).

Increase the substrate load of (4,6 and 8%) decreased of the degradation rate and gaseous products, and the liquid product was inceeased. The solid residue increase from 53.37 % to 64.27%, liquid product was increased from 16.89% to 20.43%, and gaseous products were decreased 23.73% to 18.79% (Fig. 9). It's meant that gassification rate was reduced with increasing substrate load.

Temperature is important parameter that has high influent to the reaction rate. Degradation of biomass increases with increasing temperature, indicated the solid residues were decreased. Increase the temperature (300, 350 and 374 ^{o}C) might cause increase the conversion rate, the gaseous products and also liquid products increased slightly (Fig.10). At temperature 300 to 374 ^{o}C, substrate bryophyte 8%, and reaction time is 2 hrs, the residual solid was decreased from 70.8 to 52.7%, it's meant that conversion rate of solid biomass almost 50%, liquid product was increased from 16.3 to 27.4% and gaseous product was increased from 12.8 to 19.1%.

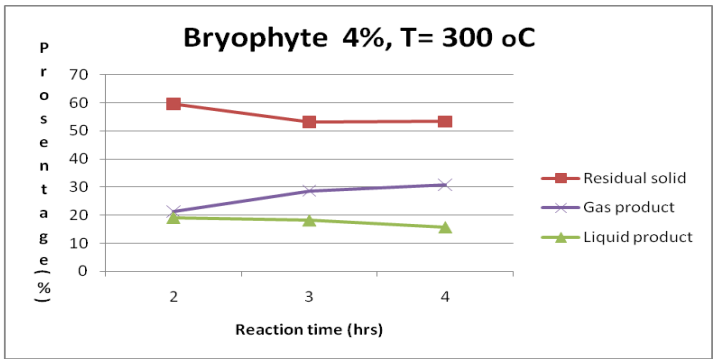

Figure 1. Solid residue, liquid and gaseous product for bryophyte 4% and T = 300 ^{o}C, for increasing reaction time.

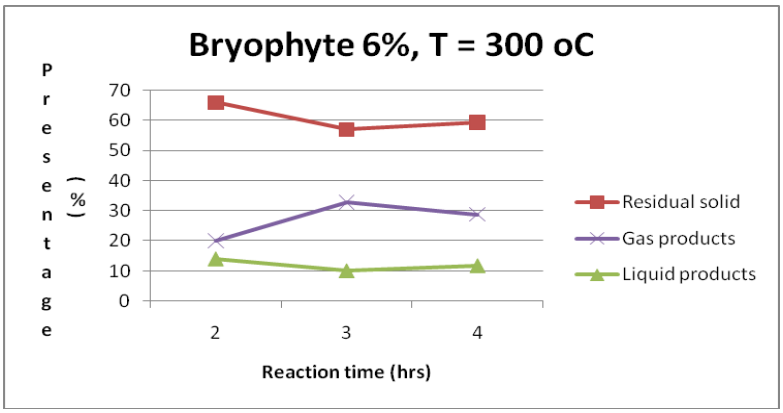

Figure 2. Solid residue, liquid and gaseous product for bryophyte 6% and T = 300 ^{o}C, for increasing reaction time.

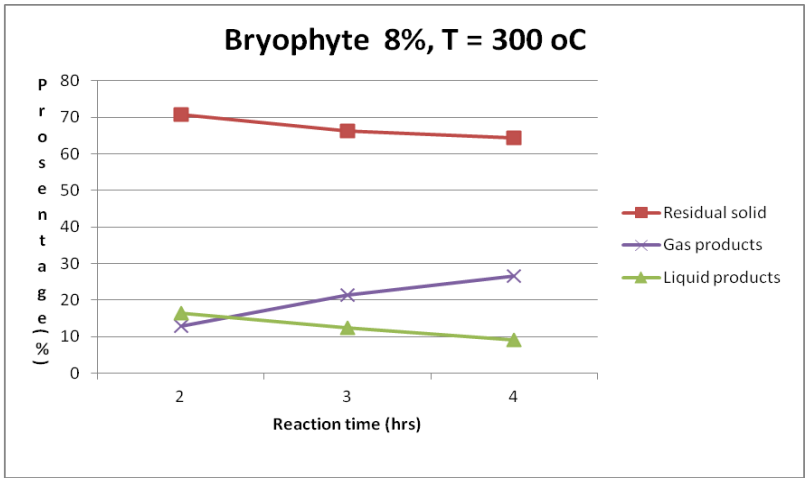

Figure 3. Solid residue, liquid and gaseous product for bryophyte 8% and T = 300 ^{o}C, for increasing reacting time.

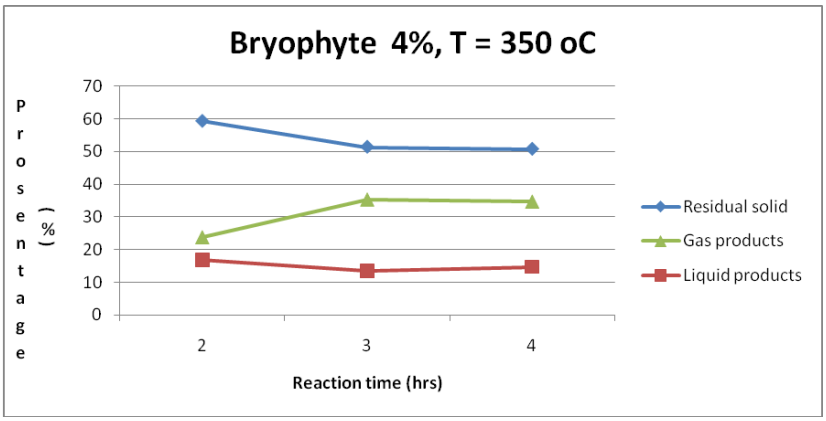

Figure 4. Solid residue, liquid and gaseous product for bryophyte 4% and T = 350 ^{o}C, for increasing reaction time.

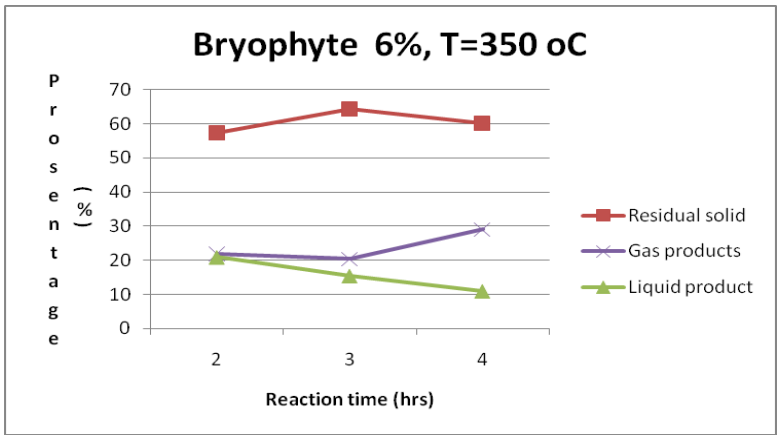

Figure 5. Solid residue, liquid and gaseous product for bryophyte 6% and T = 350 ^{o}C, for increasing reaction time.

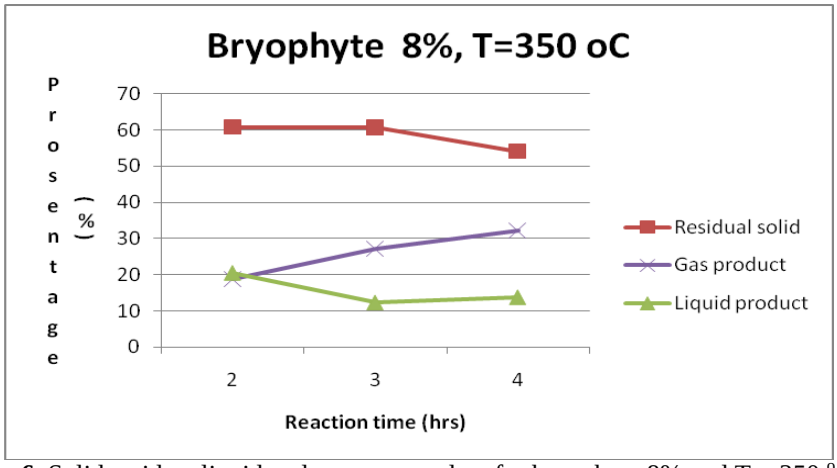

Figure 6. Solid residue, liquid and gaseous product for bryophyte 8% and T = 350 ^{o}C, for increasing reaction time.

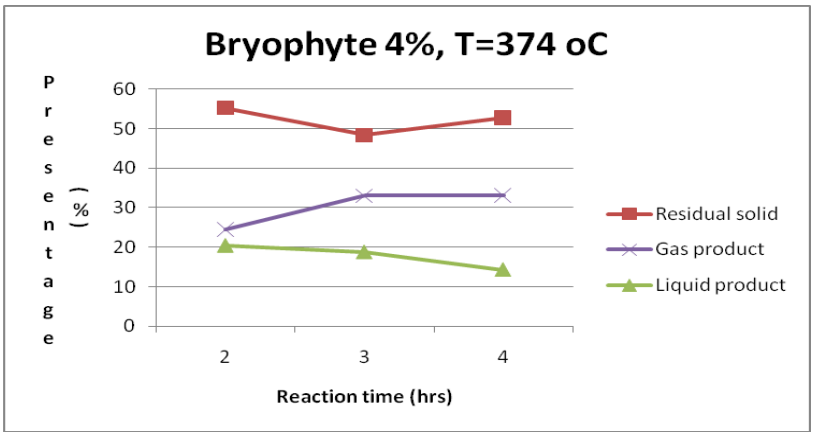

Figure 7. Solid residue, liquid and gaseous product for bryophyte 4% and T = 374 ^{o}C, for increasing reaction time.

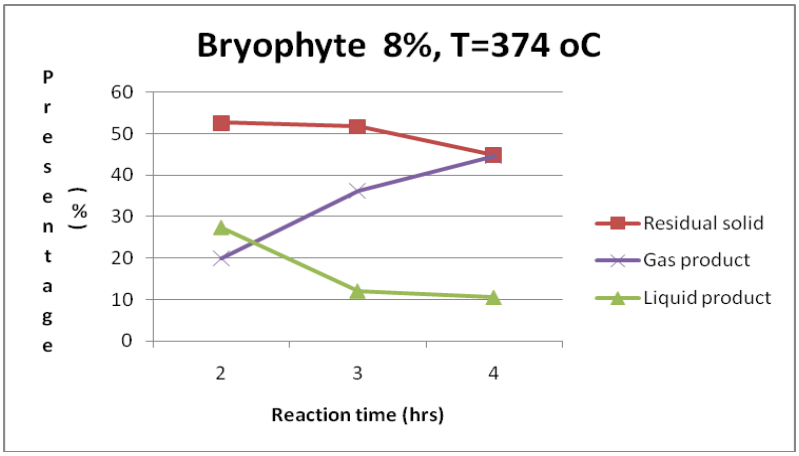

Figure 8. Solid residue, liquid and gaseous product for bryophyte 8% and T = 374 ^{o}C, for increasing the time of reaction.

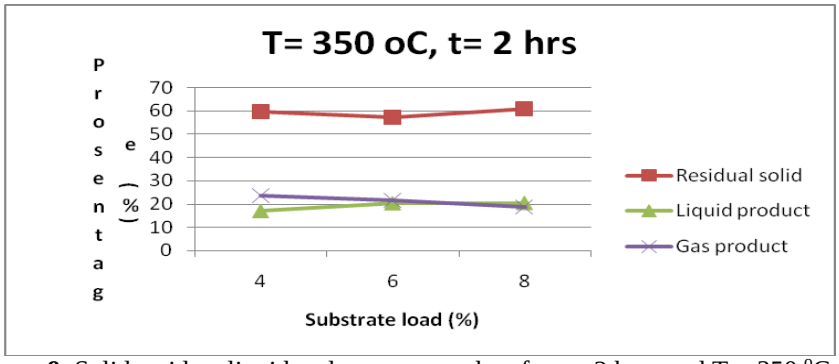

Figure 9. Solid residue, liquid and gaseous product for t = 2 hrs, and T = 350 ^{o}C, for increasing the substrate load (%).

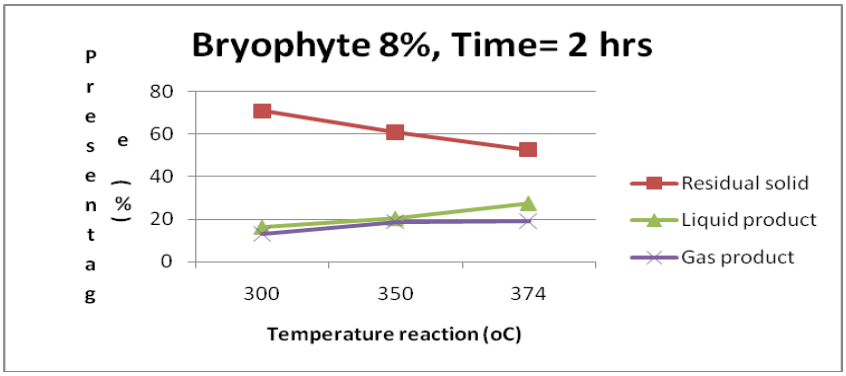

Figure 10. Solid residue, liquid and gaseous product for bryophyte 8% and t = 2 hrs, for increasing the temperature reaction.

The basic reaction mechanisms of biomass liquefaction can be described: (i) depolimerization of the biomass; (ii) decomposition of the biomass monomers by cleavage, dehydration, decarboxylation and deamination; (iii) recombination of the reactive fragments through condensation, cyclization, and polymerization to form new compounds.[13] In the first step cellulose is converted into glucose, hemi-cellulose into xylose, and lignin into polyols. [14]

Before chemical reaction acts, the microcrystalline of cellulose reacts in sub- and supercritical solvents require an extra step and time to break down the cellulose crystallite. In subcritical water, the crystallite is hydrolyzed at the surface region without swelling or dissolving. Therefore, the overall conversion rate of microcrystalline cellulose is slow, and there is no cellulose crystal formed in the residue. In contrast, in near-critical and super-critical water, the crystallite can swell or dissolve around the surface region to form amorphous-like cellulose molecules. These molecules are inactive; therefore, they can be easily hydrolyzed to celluloses and cellooligosaccharides. Some of the hydrolysate can pass from the polymer phase to the water phase by cleavage of their hydrogen-bond networks.[15]

In the first step of reaction hydrolysis, dehydration and hydration were take places, celluose was converted into glucose and then into carboxylic acid in strong alkalines. In weak alkaline glucose converted into carboxylic acid and 5-hydroxymethyl furfurol (5-HMF). In medium alkaline both reaction pathways take places. [16] In acidic pathway 5-HMF further converted into formic acid and levulinic acid by hydration reaction, further dehydration reaction into 1,2,4 benzentriol.[17]

In the whole process, the substances of biomass are first hydrolyzed to small molecul compounds, then further reaction of repolimerization, decomposition and condensation of the intermediates from the different phase may be favored with the increment of reaction temperature and residence time. Carbohydrate is hydrolyzed to produce reduced sugar and non-reduced sugar. Glucose itself reversibly isomerizes into fructose, this is an important reaction since a number studies have confirmed that fructose is more reactive than glucose.[18] Pedersen[19] made overall reaction system for the formation of biocrude from lignocellulosic material macromolecules. Macromolecules were hydrolyzed into monomers. Further reaction involves reaction formation C_{1-4} compounds through retro aldol reaction, and C_{5-6} compounds formation through dehydration reaction. The reactive fragments still continoue reaction into bio-oil through condensation to form ketones and derivatives. Through reaction of dehydration to form oxygenated aromatic derivatives. The last reaction was gasification to form gaseous products.

HTL process with bryophyte as a raw materials have conversion into liquid, gas and residual solid. Increase the temperature increased the liquid products, and increased degradation rate of solid. It was similar to the HTL that microalgae as raw material. [20]

3.2 GC-MS analysis

Liquid products were analysis in gc-ms to know the substance contains in the liquid. The peak area (%) for each component identified was defined by peak quality more than 50%.

Table 2. Typical composition of the liquid product resulted from the GC-MS analysis

K	RT	Area Pct	Library/ID	Ref	Quality
1	7.3933	1.6923	4-Methylvaleric acid, TMS derivative	59754	53
2	9.1325	1.7505	2-Propanamine	284	53
7	11.086	3.1889	5-Hydroxymethylfurfural	12390	70
9	11.6531	4.7033	Ethylene glycol Formate Isobutyrate	34971	56
10	11.8295	1.7754	1-(2,3-Dihydroxyphenyl)ethanone	28888	50
11	11.9682	2.3571	1,2-Hexanediol	9789	59
15	12.6235	0.3986	Propane, 1,1,3,3-tetraethoxy-	90643	50
24	14.1107	0.5917	Hexanoic acid, 2-ethoxycarbonyl-3-hexanoyloxypropyl ester	223055	59
28	15.0937	1.6642	4(5H)-Benzofuranone, 6,7-dihydro-3,6-dimethyl-, (R)-	37747	78
30	15.4592	3.7646	7-Octen-4-one, 2,6-dimethyl-	29894	50
32	15.8121	2.4836	Glutaric acid, 2-chloro-6-fluorobenzyl pentadecyl ester	293518	53
35	17.022	1.8493	2-Butenamide, N-(1-naphthyl)-3-methyl-	96945	50
37	17.3119	1.1243	Benzoic acid, 2,4-dihydroxy-3,6-dimethyl-, ethyl ester	80619	55
38	17.753	0.6911	Tetradecanoic acid	100044	97
39	19.8703	3.5372	n-Hexadecanoic acid	129145	99
40	20.1602	2.2625	Hexadecanoic acid, ethyl ester	159424	99
41	20.9668	0.3704	2-Thiopheneacetic acid, 4-chlorobenzyl ester	138836	72
42	21.1936	0.2239	8-Octadecenoic acid, methyl ester, (E)-	172346	99
43	21.5339	0.5597	Oleic Acid	156901	99
44	21.7355	0.5833	Octadecanoic acid	159386	99
45	22.0254	0.5563	Octadecanoic acid, ethyl ester	190057	99
46	23.563	0.3032	Octadecanoic acid, 10-oxo-, methyl ester	189908	55
47	24.8737	0.2626	Phthalic acid, hexyl isoporpyl ester	167650	92
49	26.7389	0.1684	13-Docosenamide, (Z)-	216037	99

GC-MS analysis results of the bio-oil obtained from liquefaction of bryophyte based on peak areas are listed in Table 2. Based on table 2 bio-oil resulted from bryophyte mainly consist of compound organic acid about 13.2%, ketones about 11.3% , amine about 7.9% , and ester about 7.1%

III. CONCLUSION

Hydrothermal liquefaction process can convert the bryophyte to residual solid, liquid and gaseous products. Liquid product is called bio-crude or bio-oil as a fuel raw material. Increase the reaction time of (2,3 and 4 hrs) commonly, conversion of solid and gaseous products were increased, but the liquid products were decreased slightly. Increase the substrate load of (4,6 and 8%) decreased of the degradation rate and gaseous products, and the liquid product was inceeased. Increase the temperature (300, 350 and 374 ^{o}C) might cause solid increase the conversion rate, the gaseous products and also liquid products increased slightly. The optimum operation parameter of hydrothermal liquefaction was come from substrate bryophyte 8%, temperature of 374 ^{o}C, and reaction time of 4 hours, resulted solid residue of 52.7%, liquid product of 27,1%, and gaseous product of 19.9%.

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