Valuable Chemicals Derived from Pyrolysis Liquid Products of *Spirulina platensis* Residue

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Abstract: *With a motto of preserving nature, the use of renewable resources for the fulfillment of human needs has been seen echoing these days. In response, microalgae, a water-living microorganism, is perceived as an interesting alternative due to its easy-to-cultivate nature. One of the microalgae, which possess the potential for being the future source of energy, food, and health, is* Spirulina plantesis. *Aiming to identify valuable chemicals possibly derived from it, catalytic and non-catalytic pyrolysis process of the residue of* S. plantesis *microalgae has been firstly carried out in a fixed-bed reactor over the various temperature of 300, 400, 500, 550 and 600 °C. The resulting vapor was condensed so that the liquid product consisting of the top product (oil phase) and the bottom product (water phase) can be separated. The composition of each product was then analyzed by Gas Chromatography-Mass Spectrometry (GC-MS). In the oil phase yield, the increase of aliphatic and polyaromatic hydrocarbons (PAHs) and the decrease of the oxygenated have been observed along with the increase of pyrolysis temperature, which might be useful for fuel application. Interestingly, their water phase composition also presents some potential chemicals, able to be used as antioxidants, vitamins and food additives.*

Keywords: Spirulina platensis *residue; pyrolysis; oil phase; water phase; chemicals*

■ INTRODUCTION

The excessive exploitation of non-renewable resources, i.e., coal, petroleum, natural gas, etc., to fulfill human needs has some serious drawbacks on the environment [1]. Efforts need to be made to reduce the damages by searching alternative to preserve mother nature. In this regard, renewable resources could be seen as an alternative, able to provide materials for the energy [2], food and health industries [3], with fairly less negative consequences to the environment as compared to the non-renewable one. That makes plants and biomasses a very interesting option to be developed further [4-5]. Microalgae, one of the least developed biomasses, has many advantages over the others such as; i) easy to grow and can grow in extreme environments, ii) able to produce 15 to 300 times more oil than other plantation (based on the land used for biodiesel production) [6-7], iii) very short harvest cycles (1-10 days depending on the process) [6], (iv) contain substances for energy, nutrients and drugs [6-9].

Substances in microalgae are in the form of carbohydrates, proteins, lipids and some other chemicals [10]. Among them, some valuable chemicals such as fatty acids (omega 3, DHA, EPA), pigments (carotenoids, antioxidants), and stable biochemical isotopes, are also found. Some metabolites appear to have pharmacological activity: anti-cholesterol, anti-tumor, immunomodulators, antibacterial and antifungal. Thus, microalgae have great potential as a resource for food supplement, cosmetics and public health care [11], as long as the technology to convert microalgae into those useful products is available.

For that purpose, pyrolysis comes as an option of the technology [12-13]. Pyrolysis, processed at a temperature of 300–600 °C and atmospheric pressure, yields the liquid product (bio-oil and water phase), gas and char [14-15]. Its liquid product is also known as liquid smoke, wood vinegar, bio-oil, pyrolysis liquid, pyrolysis oil, bio-crude oil, biofuel oil, pyroligneous tar, pyroligneous tar, pyroligneous acid, wood liquid, and wood oil [16]. Liquid smoke, famous for its ability as antimicrobial and antioxidants, contain aldehydes, carboxylic acid and phenol, for later used as a food preservative [16-17]. Other than that, bio-oils containing aliphatic, aromatic, phenol, acids, aldehydes, ketones, alcohols, PAHs and nitrogenated compounds are suitable for high calorific value fuel [12]. Bio-oil from microalgae differs from lignocellulosic-derived bio-oil since it contains high nitrogenated and low phenolic compounds that originate from the high amount of protein and likely the absence of lignin, respectively. Microalgae suitable for pyrolysis are the one with low lipid content so that such a high quantity of lipid is to be initially extracted [12]. *Spirulina platensis* is a type of microalgae with lipid (4–9 wt.%), protein (46–63 wt.%) and carbohydrate (8–14 wt.%) content. Such a low quantity of lipid is yet to be removed, hence the lipid-free residue, so-called *S. platensis* residue (SPR), is then available for pyrolysis [12].

As pyrolysis product is highly dependent on processing condition, this paper aims to investigate the influence of temperature on: i) yield percentage, ii) composition of bio-oil and iii) water phase of liquid product of SPR pyrolysis. Prior to that, the experiment started with the identification of SPR component and heating rate validity of the pyrolysis process. SPR is given catalytic and non-catalytic pyrolysis using a fixed-bed reactor whose performance is tested first by setting the heating rate in the range of 20 °C/min. Pyrolysis has been conducted at a temperature of 300, 400, 500, 550 and 600 °C with the amount of catalysts of 5, 10, 25, 45 and 65 wt.% at atmospheric condition, the liquid product in the form of oil phase and water phase are separated and counted, each of which is tested with GC-MS. The composition of the content in the oil phase and the water phase are grouped according to aliphatic, aromatic, phenol, oxygenated, nitrogenated and hydrocarbon aromatic poly. Water phase, the type of compound with the largest component and its usefulness is identified. This opens opportunities for the use of the water phase in the field of food and health.

Table 1. Characteristics of *Spirulina platensis* residue (SPR) [12]

Component	*Spirulina platensis* residue
Moisture (wt.%)	9.99
Ash (wt.%)	8.93
Volatiles (wt.%)	68.31
Fixed carbon (wt.%)	12.77
Proximate analysis (wt.%)	
Lipid	0.09
Carbohydrate	25.59
Protein	49.60
Ultimate analysis (wt.%)	
Carbon	41.36
Hydrogen	6.60
Nitrogen	7.17
Oxygen	35.33
Higher heating value (MJ/kg)	18.21

EXPERIMENTAL SECTION

Materials

The materials used in this study is *S. platensis* residue (SPR), a by-product of *S. platensis* extraction with methanol and hexane. The Spirulina plantesis iwas obtained from Algae Park UGM. The properties of SPR referring to its proximate, ultimate and higher heating value (HHV) analysis were characterized in TekMIRA testing laboratories, Center for Research and Development of Mineral and Coal Technology, Bandung, where the results are presented in Table 1. Components and quantities in SPR materials determine the chemicals produced by liquid products from pyrolysis.

Methods

The reactor used in this study is a fixed-bed reactor, of a tubular vessel with ID x L of 40 x 600 (mm) equipped with a heating coil and temperature controller where the setup is shown in Fig. 1.

The reactor consists of two-stacked cylinders with an internal diameter of 40 mm and 2 mm wall thickness, where the upper part is for the sample and the catalyst was placed at the bottom. A fifty (50) g of SPR microalgae with a size of 60-120 mesh was inserted in a fixed-bed reactor, sealed and heated with a coil heater. Initially, the reactor characteristics are tested by observing pyrolysis time and temperature relationship at the selected heating rate range of 20–40 °C/min. to validate and ensure that the reaction has been taken under a similar range of heating condition, as presented in Fig. 2.

The heating rate was maintained constant within the range of 20–40 °C/min, starting from its initial state at a temperature of about 30 °C to the final pyrolysis temperature of 300–600 °C, for both catalytic and non-catalytic process. Then, the temperature was kept constant for about 1 h to ensure optimum pyrolysis at that temperature. As can be observed from Fig. 2, the slope of temperature vs time is yet within the expected value. This would validate that SPR has been subjected to the same processing condition; hence its liquid product composition with respect to temperature can be compared to one another. The resulting vapor products of combustion of SPR was condensed and then collected at the accumulator. The liquid products, a mixture of the oil phase and the water phase, are separated by decantation, for later being compositionally analyzed using GC-MS.

Apart from that, the volume of each product is measured. The total liquid product (oil phase and water phase) is calculated by equation [12]:

$$Y_{Liq} = \left(W_L / W_M\right) x100\ \% \quad (1)$$

$$Y_{oil} = \left(W_{oil} / W_M\right) x100\ \% \quad (2)$$

$$Y_{water} = \left(W_{water} / W_M\right) x100\ \% = Y_L - Y_{oil} \quad (3)$$

In this case, Y_{Liq}, Y_{water}, and Y_{oil} are the yields of the liquid, water phase, and bio-oil products, respectively. Whereas W_{Liq}, W_M, W_{water}, and W_{oil} *are* the weight of the liquid, sample microalgae (SPR), a water phase and bio-oil products, respectively. Provide sufficient detail to allow the work to be reproduced. Methods already published should be indicated by a reference: only relevant modifications should be described.

■ RESULTS AND DISCUSSION

Effect of Pyrolysis Temperature on Yield of Liquid Product for Non-Catalytic Pyrolysis

The effect of pyrolysis temperature on the oil phase and water phase yield percentage is shown in Fig. 3.

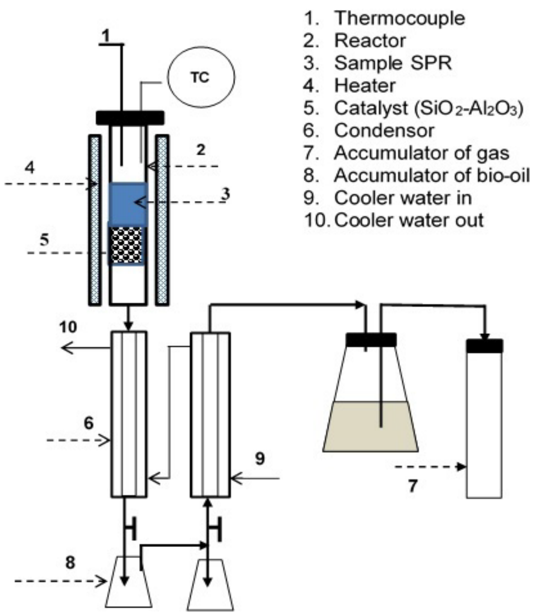

Fig 1. The schematic diagram of the fixed-bed reactor [12]

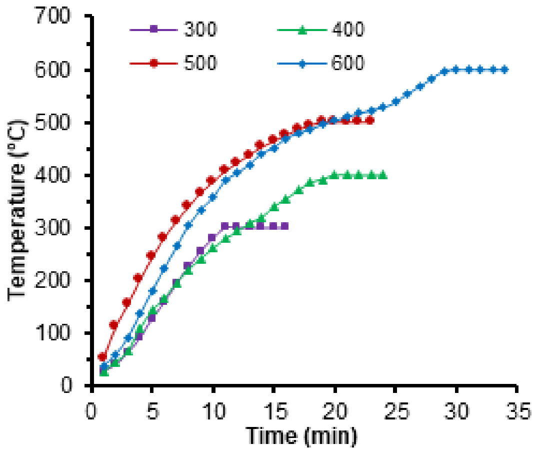

Fig 2. The relationship between time and temperature of the heating

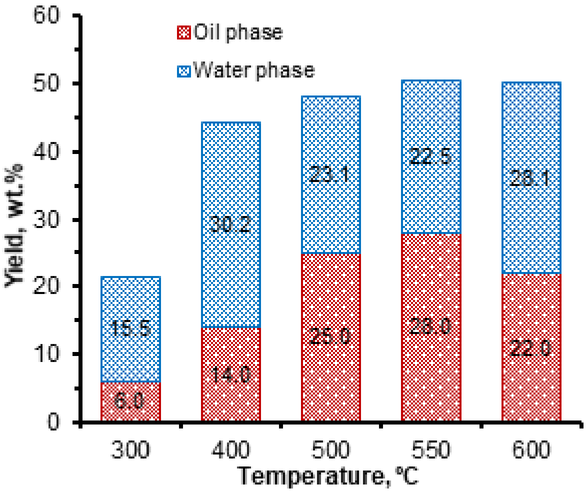

Fig 3. Effect of pyrolysis temperature (°C) on the liquid product (wt.%)

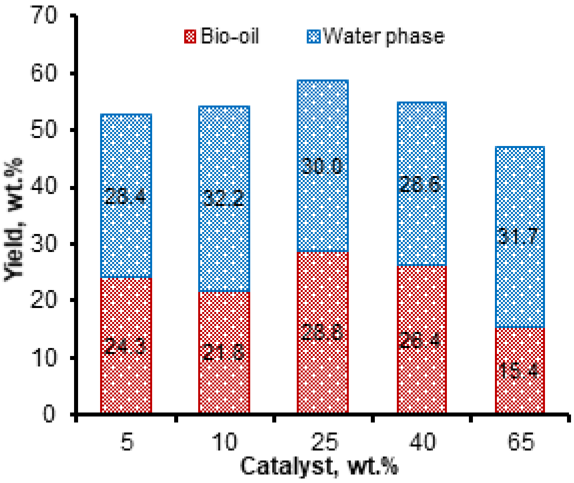

Fig 4. Influence of catalyst weight (wt.%) on liquid product yield (wt.%) at a pyrolysis temperature of 550 °C

Pyrolysis is the decomposition of organic matter by heating without the presence of oxygen that will produce gas (consisted of condensable and non-condensable gas) and a solid residual char. Through condensation, the liquid product can be condensed from the gas stream, while the remaining non-condensable gas will emerge as a gas product, namely CO, CO_2, CH_4, and H_2. Liquid products, containing the mixture of the oil and the water phase, are perceived increasing with the increase of testing temperature. From Fig. 3, it can be seen that the water phase percentage is seen fluctuate with the highest yield collected at 400 °C. Such phenomenon starts with a sudden increase of yield from 15.5 to 30.2 wt.% from 300 to 400 °C, then drops to 22.50 wt.% at 550 °C and bounce back to 28.12 wt.% at 600 °C. The phenomenon of rising and receding of the water phase yield might be explained in term of one or a combination of the following mechanisms, (i) at a temperature of 400 °C, the dehydration reaction optimally increases the yield of the water phase to the maximum [14], (ii) a gasification reaction that involves water as reagents to form of CO_2, H_2, CO_2 and CH_4 over 400–550 °C so that the yield of the water phase drops [18], and (iii) at a temperature of 600 °C, O atom releases from carbohydrate and protein (deoxygenation) joins H in maximum to form H_2O to cause the yield of the water phase increases sharply.

Meanwhile, the oil phase seems to increase with temperature up to 550 °C, which would then be considered as optimum temperature prior to decrease. This decrease seems to be the result of the secondary cracking reaction, for instance, the degradation of the oil phase into gas and char [12]. From Fig. 3, it can be seen that the maximum oil phase is at the temperature between 400 and 600 °C, which is influenced by multiple complex reaction upon pyrolysis such as depolymerization, polymerization, fragmentation, and rearrangement which can produce condensable gases such as hydroxyaldehydes, hydroxyketones, carboxylic acids, compounds ring-containing furan/pyran, anhydrosugars, phenolic compounds and oligocellulose polymer oligomeric fragments that condense by condensation into an oil phase [14].

Influence of Catalyst Weight (%) on Pyrolysis Liquid Product at 550 °C

Fig. 3 shows that the optimum temperature to obtain maximum liquid product consisting of oil and water phase is at 550 °C. This temperature is opted for identifying optimum catalyst weight in order to produce maximum oil phase, as presented in Fig. 4.

As can be observed in Fig. 4, pyrolysis at 550 °C combined with the use of 25 wt.% of Silica-alumina catalyst is able to obtain the maximum yield of liquid products that consist of 28.83 wt.% of the oil phase and

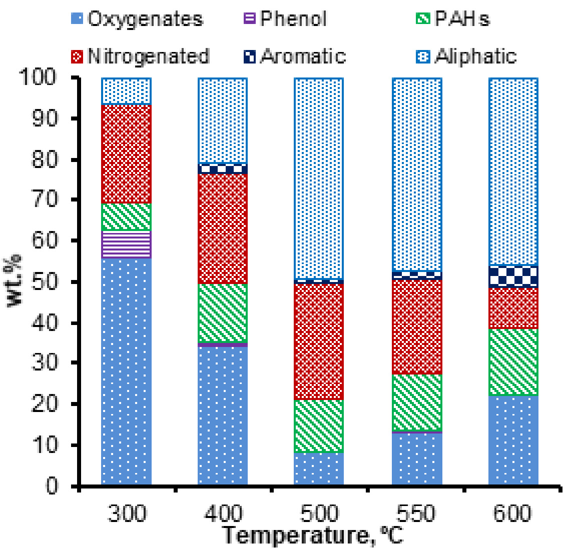

Fig 5. Effect of non-catalytic pyrolysis temperature on oil phase composition

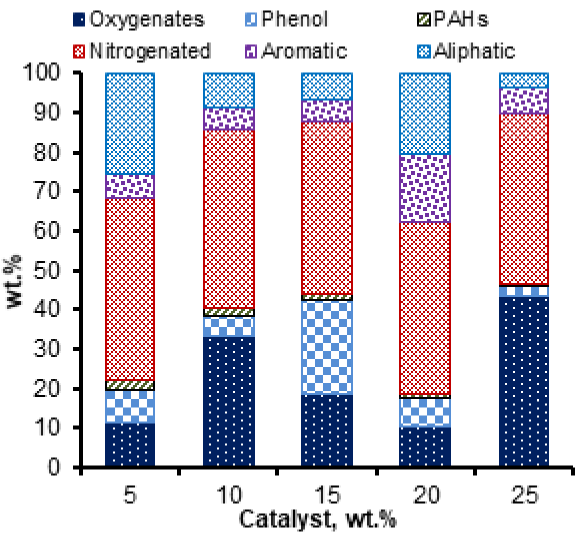

Fig 6. Effect of catalyst weight (%) on oil phase composition at 500 °C

30 wt.% of the water phase. It implies that the use of catalyst activates cracking, decarboxylation, decarbonylation, hydrocracking, hydrodeoxygenation, and hydrogenation process, thus it produces more condensable gas [14], to cause oil and water phase yield increase. However, the use of 65 wt.% catalyst causes the reduction of liquid products with 15.37 and 31.67 wt.%, being oil and water phase respectively. The use excess amount of catalyst may cause more formation of non-condensable gases, and hence its oil phase experience secondary cracking to the gas yield to increase with a lesser quantity of char [15].

Phase Compositions with Respect to the Change in Pyrolysis Temperature and the Amount of Catalyst

Oil phase composition

Characterization of oil phase by grouping based on aliphatic, aromatic, phenol, nitrogenated, oxygenated and polyaromatic hydrocarbon (PAH) compounds at various pyrolysis temperatures from GC-MS test results for non-catalytic pyrolysis is shown in Fig. 5 and for catalytic pyrolysis, at 500 °C is shown in Fig. 6.

From Fig. 5, it can be observed that the increasing pyrolysis temperature would result in the increase of aliphatic and nitrogenated compounds to a certain point prior to decrease. At 500 °C, aliphatic and nitrogenated reach its peak maximum yield of 49.28 and 28.61 wt.%, respectively. Such increase in aliphatic below 500 °C is estimated due to fragmentation reaction of large molecules and complexes into straight-chain compounds. Similarly, nitrogenated also experience severe fragmentation at such temperature. As opposed to that, a peak minimum is observed for oxygenating, having a yield of only 8.2 from its initial percentage of 56.16 wt.% at 300 °C. Such decrease seems to be caused by a dehydration reaction, the breakage of hydroxide bonding. PAH, within the tested temperature, presents an increasing trend with the highest yield obtained at 600 °C which is possibly due to the depolymerization reaction. Meanwhile, aromatics and phenol, found in fairly small quantity, does not seem to be significantly influenced by temperature changing. Simultaneous reactions of dehydration, depolymerization, polymerization, fragmentation and rearrangement in pyrolysis, are thought to be responsible for their yield changes over temperature [14]. Based on this result, the oil phase shows a poor quality for being used as fuel due to fairly high oxygenated and nitrogenated compounds to possibly cause corrosion on the machine. If this oil phase is yet to use, the temperature of 500 or 600 °C might be selected as the pyrolysis temperature considering the fact that oxygenated and nitrogenated are at the lowest point. Alternatively, catalytic pyrolysis might be proposed to improve the reduction of these compounds.

Fig. 6 presents the oil phase compositions based on their functional groups as a function of catalyst weight. The optimum amount of catalyst to produce maximum aliphatic of 25.49 wt.% is 5 wt.%, with a low quantity of oxygenating of 11.51 wt.%. In the use of a catalyst 20%, the aliphatic, oxygenated and aromatic compounds are produced respectively at about 20, 10.5, and 18 wt.%, of which aromatic is at its maximum percentage. The aim of using zeolite is to provide the acid site where the reaction is promoted to occurs. The more catalysts used, the faster the decomposition. Pyrolysis itself is a very complex process where many reactions occurs simultaneously. The use of zeolite catalyst with silica-alumina ratio of 1.67 may promote cracking that produce high enough aliphatic compounds and simultaneously activate deoxygenation that cause sufficiently low oxygenated compounds, particularly in the use of 5 and 20 wt.% of catalyst [14] This might be due to cracking of the complex compound into the simple compound, which are decarboxylation, decarbonylation, hydrocracking, hydrodeoxygenation, and hydrogenation process. These simple compounds include acid, ketones, aldehyde and alcohol with oxygen group. It is to note that bio-oil with good quality should contain a high amount of aliphatic with low oxygenated quantity, so that corrosion (due to high oxygenated level) might be avoided inside vehicle machine [12].

However, the nitrogenate content for all percent catalyst tested is very high due to the high amount of protein the SPR sample (49.6 wt.%). The successful effort to decrease nitrogenate compounds from 5.37 to 1.29 wt.% has been reported by Shakya et al. [19] on catalytic upgrading of bio-oil from Nannochloropsis sp., by using hydrothermal liquefaction technique with the noble catalyst of Ru/C and Pt/C.

Water phase composition

By GC-MS the constituent components of the water phase can be analyzed. The result of water phase composition for catalytic and non-catalytic pyrolysis is presented as one since the grouping of the functional group appears to be fairly similar. The grouping of water phase composition into acid, alcohols, ketones, aldehyde, phenol, nitrogenated, aliphatic, aromatic, oxygen and PAHs could be seen in Fig. 7. As observed, the highest quantity found in the water phase of SPR pyrolysis is polyaromatic hydrocarbons with a percentage between 26.93 and 45.18 wt.%. This is followed by alcohol with 1.58–23.30 wt.%. Carbonyl group, referring to ketones and aldehyde, and nitrogenated are in the range of 10.46–13.02 and 7.47–14.31 wt.%, respectively. Other than that, the remaining grouping appears with low quantity below 10 wt.%. With such component, it seems that the water phase has potential as a food additive such as acid, carbonyl and phenol, and as a food preservative and flavoring agent [20].

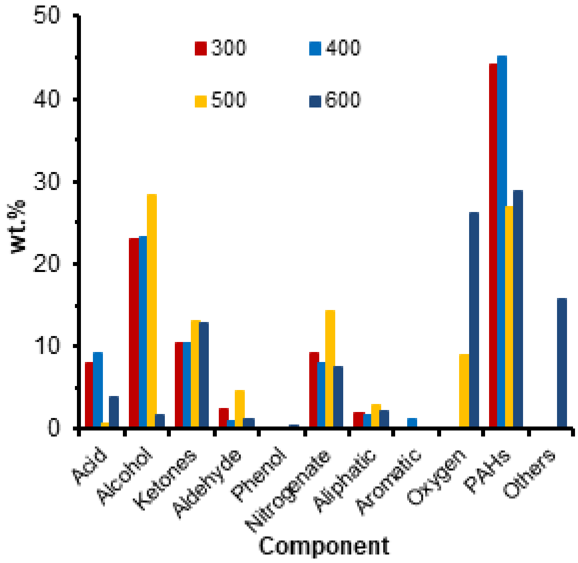

Fig 7. Effect of pyrolysis and non-catalytic pyrolysis temperature on water phase composition

According to Lingback et al. [16], four components, of phenol, acid, carbonyl, and formaldehyde, are to perceive closely for the application of flavor, colors, anti-bacterial and texture resistance. These results show that carbonyls (ketones and aldehyde) appears fairly sufficient with the percentage between 13.47 and 17.69 wt.% to be applied for coloring agent. Unfortunately, acid and phenol are in low quantity for being used as a flavoring agent, shelf (anti-bacterial), and preservative [13], when combined with the carbonyl. Despite, at a temperature of 300 and 400 °C, the acid might be considered quite high for afterward be used in such an application with 8 and 9 wt.%, respectively. Besides, at all

Table 2. Valuable chemicals found in the water phase obtained from catalytic and noncatalytic pyrolysis

No	Component	Formula	Wt. %				Usages
			300 °C	400 °C	500 °C	600 °C	
1	2-Isobutyl-4,4-dimethyl-1,3-dioxane	$C_{10}H_{20}O_2$	22.51	21.30	0.23	-	Food additives Flavoring Agents [3]
2	Methanesulfonic acid, pentyl ester (CAS) N-Pentyl Methanesulfonate	$C_6H_{14}O_3S$	3.61	4.15	-	-	Chemical industry [6]
3	8'-Apo.beta.-caroten-8'-al	$C_{30}H_{40}O$	4.77	4.01	2.82	4.22	Precursors of vitamin A, prevention of cancer, reduce the stroke risk, gives analgesic and anti-inflammatory effects on the body [20-21]
4	trans-Caryophyllene	$C_{15}H_{24}$	39.20	38.48	16.12	10.76	Anti-inflammatory properties, local anesthesia and antifungal [11]
5	4-dimethylaminobut-2-yn-1-ol	$C_6H_{11}NO$	4.99	5.7	0.77	2.13	Chemical industry [12]
6	alpha.-D-Mannopyranoside, methyl 3,6-anhydro- (CAS) Methyl 3,6-Anhydro-.Aapha.-D-Mannopyranoside	$C_7H_{12}O_5$	2.40	-	24.82	-	Pharmaceutical industry [11]
7	Inosine (CAS) Ino	$C_{10}H_{12}N_4O_5$	2.30	1.02	5.11	-	Treat stroke patients to restore nerve function [11]
8	Benzo[g]pteridine-2,4(3H,10H)-dione, 8-hydroxy-7,10-dimethyl- (CAS) 8-Hydroxy-7,10-Dimethyl-Isoalloxazine	$C_{12}H_{10}N_4O_3$	3.30	1.02	3.38	9.52	Potential as an anti-cancer [11]
9	2-Isononenal (CAS) Branched Chain 2-Nonenal	$C_9H_{16}O$	3.40	0.79	4.67	15.95	Food and pharmaceutical industries [11]
10	Methyl tricyclo[6.2.1.0(2,7)]undeca-2(7),4-diene-4-carboxylate	$C_{13}H_{16}O_2$		1.32	0.25	5.06	Chemical industry [6]

pyrolysis temperatures, nitrogenated content is found fairly high which is likely to be used as an additive for protein intake in preserved foods. On the other hand, the higher the pyrolysis temperature, the higher the PAHs content, from 10.53 wt.% at 300 °C to 30.39 wt.% at 600 °C. PAHs content can be removed by using activated charcoal.

From Fig. 7, further investigations on the GC-MS result of the water phase results in the identifications of some valuable chemicals, as presented in Table 2. The influence of temperature, at this stage, is not part of the concern, as would rather be used to present the types of chemicals obtained at a different temperature. As can be observed, the largest component of the water phase is trans-caryophyllene (10.76–38.48 wt.%). Interestingly, this chemical, referring to Suna et al. [20], could be used as an anti-inflammatory, local anesthetic and antifungal properties [18]. In addition, Benzo [g] pteridine-2,4 (3H,10H) -dione, 8-hydroxy-7,10-dimethyl- (CAS) 8-Hydroxy-7,10-Dimethyl-Isoalloxazine, which is in the range of 1.02–9.52 wt.%, might be applicable as an anti-cancer [20]. While, 8'-Apo.beta.-carotene-8'-al might presents several benefits, such as for a precursor of vitamin A, cancer prevention, reducing the risk of stroke, giving analgesic and anti-inflammatory effects to the body [21-23]. Other remaining valuable chemicals and its uses are to be found in Table 2. If desired, it would be very useful to merge information obtained in Fig. 7 and Table 2.

■ CONCLUSION

Catalytic and non-catalytic pyrolysis was done in a fixed-bed reactor at a temperature of 300–600 °C that yields gas, liquid and char products. Of those, liquid products, consisting of the oil phase and the water phase is of interests for further investigation. The yield of the oil phase is found maximum at 550 °C (28 wt.%), while the water phase is at 400 °C (30.2 wt.%) for non-catalytic pyrolysis. Besides, the catalytic pyrolysis at 550 °C produces maximum oil phase yield of 28.83 wt.% at the optimum use of 25 wt.% of the catalyst. As for the water phase, the maximum of 32.22 wt.% appears to be at the use of 10 wt.% of the catalyst.

The oil phase pyrolysis product appears to contain aliphatic, phenol, aromatic, polyaromatic hydrocarbon, oxygenated and nitrogenated. The first four compounds could be useful as fuel, while for the same application, the last two compounds might present adverse effects on the engine concerning corrosion issue. Interestingly, with an increase in temperature, the quality of the oil phase can be improved presenting higher aliphatic and PAHs, but fairly lower oxygenated and nitrogenated. The use of catalysts at 5 and 20 wt.% can produce quite a high amount of aromatic compound and rather reduce significantly the oxygenated compounds at the oil phase.

Based on the GC-MS result, water phase of SPR catalytic and non-catalytic pyrolysis contains many useful chemical compounds for food and pharmaceutical applications. For instance, study suggests that 8'-Apo.beta.-carotene-8'-al is beneficial for the prevention of cancer, reducing the risk of stroke, providing analgesic and anti-inflammatory effects on the body and as a precursor of vitamin A.

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