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Comparative analysis of humic substances of soil organic matter and liquid products from rice husks pyrolysis

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ABSTRACT

Agriculture has an important role in maintaining food availability. One of the most popular plant nutrition additives in agriculture is inorganic fertilizer, however, it can degrade soil health. This problem can be solved by naturally composting formed soil organic matter (SOM), of which humic substances are one of the main components. However, this process takes a very long time. Humic substances can be obtained faster through the rice husk pyrolysis process. This paper aims to study the characteristics of the humic substance from rice husk pyrolysis and understand its correlation with humic substances from SOM. Rice husk pyrolysis was performed in a fixed bed reactor at a temperature of 400, 500, and 600 °C, weight of 10 g, and retention time of 45 min. The results show that the minimum pyrolysis temperature to obtain sufficient liquid product is 365 °C. The liquid product from the pyrolysis process consists of two phases, water phase and tar phase. Based on its chemical properties, namely colour, solubility, organic species (functional group), acidity, hydrophilicity, carbon number, molecular weight, and carbon content, a liquid product from pyrolysis has similarities with humic substances derived from SOM, where the water phase (liquid smoke) has similarities to fulvic acid, while tar has similarities to humin. The results also suggest that pyrolysis can be a faster alternative method for producing humic substances.

Keywords: agriculture, humic substances, rice husk, pyrolysis, soil organic matter, humin, liquid smoke.

INTRODUCTION

Agriculture has an important role in maintaining food availability. One of the most popular plant nutrition additives in agriculture is inorganic fertilizer. Despite increasing crop output, their usage degrades soil health in several direct and indirect ways, making the agro-ecosystem unsustainable. This problem can be solved by naturally formed SOM, of which humic substances (HSs) are one of the main components. Adding humic substances to agricultural soil improves the physiology of plants, absorption of nutrients, heavy metal confinement, resistance against drought and other disruptions [Tiwari et al., 2023], and disease suppression function [Guo et al., 2019].

HSs are yellow to black in appearance, acidic, and polydisperse (having different compositions and molecular weights). There are three primary forms of HSs: fulvic acid (FA), humic acid (HA), and humin (HM). The elemental composition of HSs reveals that C, H, O, N, and S are the main constituents [Rupiasih, 2005]. Research on the characterization of aquatic and soil HSs revealed that FA had more phenolic and carboxylic groups and HA had more aromatic [Tiwari et al., 2023].

The weak acid behavior and overall acidity of HSs can be attributed to carboxylic and phenolic groups [Jindo et al., 2016]. The solubility of nutrient elements can be influenced by the complex forms that these acidic functional groups can form with metal cations, such as Ca^{2+}, Mg^{2+}, and Al^{3+}, which are crucial nutrient ions for plants [Tahir et al., 2011]. The ability of acidic functional groups to ionize and protonate depending on the pH of the surrounding environment gives them a strong buffering capacity over a broad pH range [Campitelli and Ceppi, 2008]. Carboxylic and phenolic groups have hydrophilic properties due to OH/OOH deprotonation. The presence of a hydrophilic group in the soil will increase the water-holding capacity of the soil [Piccolo et al., 1996]. Besides that, phenolic groups have antioxidant effects because of their free radical scavenging capacity and can exert toxic effects directly on pathogens. Meanwhile, carboxylic groups have antioxidant and anti-inflammatory properties [Cao et al., 2014].

Meanwhile, HM is the most recalcitrant HSs and has been shown to account for approximately 50% of the organic carbon (OC) in soils. HM is composed mostly of aliphatic hydrocarbon and wax derivates and some carbohydrate and peptide-derived materials [Hayes et al., 2017]. The increased weight of the molecule and polymerization degree of HM compared to HA and FA suggests that HM has greater stability and longer-lasting effects [Qin and Leskovar, 2020]. Consequently, a higher HM content in soil is essential for boosting HS storage and, ultimately, carbon sequestration [Wei et al., 2020]. Soil microbes live on the remaining C-containing material in soil HM. Beneficial soil microorganisms (yeast, algae, fungi, bacteria, mycorrhizae, nematodes, and tiny animals) could enhance soil nutrient content [Buckau et al., 2000].

Humic substances are formed during natural long-term degradation and alteration of remaining biomass [Guo et al., 2019]. Several studies have shown that humic substances can be synthesized faster using the pyrolysis process. Liquid products from the pyrolysis process have been shown to produce active compounds that can enhance the quality of soil, neutralize soil acid, control pests on plants, and accelerate the roots' growth, stems, tubers, and leaves [Elsadek and Yousef, 2019]. Khatoon et al. (2020) reported that plant-derived smoke has a role in changes in mineral-nutrient status, enhancing germination and post-germination [Khatoon et al., 2020]. Amiroh et al. studied the effect of liquid smoke concentration on the growth and production of several rice varieties. They reported that the highest results were found in the Inpari 42 variety with the application of liquid smoke at a concentration of 2% [Amiroh et al., 2022]. Istiqomah and Kusumawati (2019) studied the effect of the application of rice husk liquid smoke on rice growth and production. They reported that the effective and efficient concentration of liquid smoke in increasing rice growth and production was 2% [Istiqomah and Kusumawati, 2020]. They also studied the effect of administering liquid smoke from rice husks to control brown planthopper pests in rice plants. The results of the study showed that administering liquid smoke with a concentration of 1–3% can suppress the brown planthopper population and increase crop yields [Istiqomah and Kusumawati, 2019]. These findings indicate a relationship between liquid smoke from pyrolysis and humic substances when viewed from the effects.

Several studies have been conducted related to the characterization of liquid smoke from different sources [Adi Saputra et al., 2021; Komarayati and Wibowo, 2015]. However, these studies have several shortcomings, namely a) the characterization and application are only limited to liquid smoke (water phase) not include tar products; b) the characterization is only limited to observations of the chemical components contained therein, while their relationship with humic substances extracted from SOM has not been studied. Hence, this paper aims to study the characteristics of liquid products from rice husk pyrolysis and to understand its correlation with humic substances extracted from SOM. Understanding the characteristics of liquid products as humic-like substances produced from the pyrolysis process can be the basis for further development such as the isolation of active components and application in agricultural land. Therefore, this study adds something substantial and valuable to the novelty of the relevant literature.

MATERIALS AND METHODS

Materials

In this study, a sample of rice husk (RH) provided by a local paddy farmer in Tamanan, Banguntapan, Bantul, Yogyakarta was used. RH sample preparation is done by washing the sample with clean water to remove impurities. After that, drying is carried out under sunlight until a constant sample weight is obtained. The pyrolysis process, proximate, ultimate, and composition analysis of the sample are carried out after the drying. Proximate analysis was performed to identify the content of moisture, volatile matter, fixed carbon, and ash. Composition analysis was conducted to obtain lignocellulose content. Meanwhile, ultimate analysis was performed to identify the potential content of C, H, O, N, and S in rice husks. The results of the proximate, ultimate, and composition analysis are presented in Table 1.

Pyrolysis experiment

A fixed bed reactor with a height of 600 mm, inner diameter of 400 mm, and outer diameter of 440 mm was used to conduct the investigation. The reactor had an electric heater made of nickel wire that was spirally coiled around the reactor's exterior. The heating temperature was measured using a K-type thermocouple, and a 0.5 kva TGDC regulator was used to control the heating rate [Jamilatun et al., 2022]. The experiment setup can be seen in Figure 1.

Pyrolysis was conducted by inserting 10 g samples into the reactor. The sample was heated to the temperature of 400, 500, or 600 °C at a heating rate of 10 °C/minute. Once the temperature reached the required level, the heating was continued isothermally at a reaction time of 45 min. The liquid product (water phase and tar) was accumulated in a cylinder glass, then weighed and analysed.

Table 1. Physicochemical properties of rice husk

Proximate analysis	Value (wt.%)	Ultimate analysis	Value (wt.%)
Moisture content	5.43	C	33.89
Fixed carbon	19.57	H	5.87
Volatile matter	66.50	N	0.38
Ash	8.50	S	0.79
Composition analysis	Value (wt.%)	O	59.06
Cellulose	33.80	O/C	1.74
Hemicellulose	28.34	H/C	0.17
Lignin	19.40		

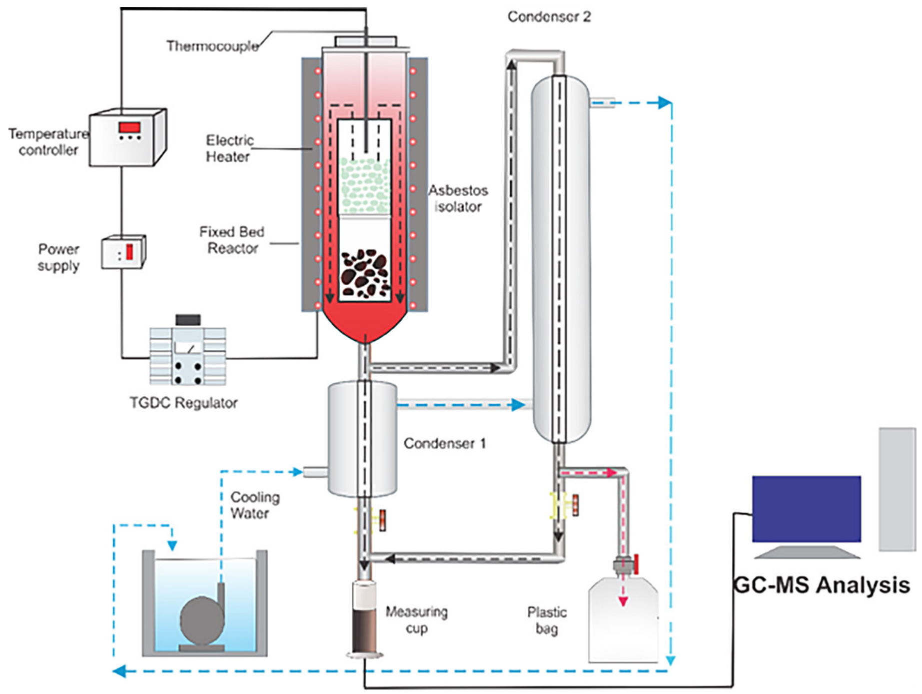

Figure 1. Experimental setup of rice husk pyrolysis

Liquid product analysis

Liquid product of RH pyrolysis was analyzed using gas chromatography-mass spectrometry (GC-MS), Fourier-transform infrared spectroscopy (FT-IR), and ^{13}C-NMR. GC-MS analysis was carried out using Shimadzu QP2010-SE, Chemstation software was used in acquiring and processing the data. The component identification was done by comparing their mass spectra to spectral data in the instrument database. FT-IR analysis was carried out using FTIR spectrometer Alpha II, Bruker Opus software was used in processing and evaluation the spectra. ^{13}C-NMR analysis was conducted using NMR spectrometer, Jeol Delta NMR software was used in data processing. The ^{13}C-NMR was used for determining functional groups using characteristic of ^{13}C chemical shift.

GC-MS/ ^{13}C-NMR analysis

Identifying the relationship between liquid product and humic substances from SOM was carried out by comparing the GC-MS data from liquid product (water phase and tar) with VACP ^{13}C-NMR spectra of the humic acid isolated from the IHSS Mollisol soil standard [Hayes et al., 2017] and DPMAS ^{13}C-NMR spectra of organic soil at the Muck Crops Research Station [Gamage et al., 2024]. Data for the analysis were taken from GC-MS data of liquid products at pyrolysis temperatures of 400, 500, and 600 °C, and retention time of 45 min. The ^{13}C-NMR is used for determining functional groups using characteristic shift values. For comparison, the GC-MS data which is still in the form of component concentration (% area) is changed into the proportion of functional groups. The data source in the form of ^{13}C-NMR spectra obtained from National Center for Biotechnology Information [PubChem, 2024] is used to identify the presence of functional groups in each component. The proportion of each functional group is calculated by Equation 1:

$$x_{fg,i} = \frac{Mr_{fg}}{Mr_i} c_i \quad (1)$$

The total proportion of functional groups in liquid product is calculated by Equation 2:

$$X_{fg} = \sum_{i=1}^{n} x_{fg,i} \quad (2)$$

where: fg – the functional group, c_i – the component concentration, i = the specific component, n = the number of components.

RESULT AND DISCUSSION

Rice husk thermal decomposition characteristic

Figure 2 presents the thermal decomposition of rice husk using thermogravimetry analysis (TGA) at heating rates of 10, 20, and 30 °C/min. The figure shows that the initial weight loss was detected at a temperature of 250 °C. Significant weight loss of 82.5% occurs in the temperature range of 250–360 °C. Weight loss tends to

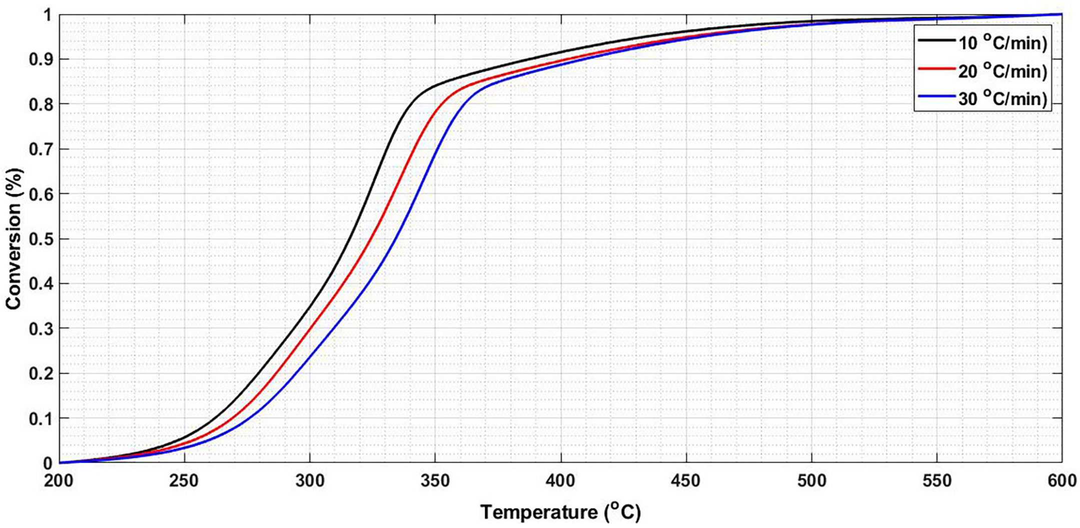

Figure 2. Thermogravimetry analysis (TGA) curve of rice husk decomposition

decrease in the temperature range of 360–600 °C. The significant weight loss occurs in the temperature range of 250–360 °C due to the simultaneous decomposition of cellulose, hemicellulose, and lignin [Jamilatun et al., 2023]. Literature shows that the temperature decomposition of hemicellulose occurs between 250 and 350 °C, cellulose at the range of 325 to 400 °C, and lignin at the range of 300–550 °C [Yogalakshmi et al., 2022]. This finding shows that to obtain a sufficient conversion, rice husk pyrolysis must be carried out at a minimum temperature of 360 °C. These results are similar to the study conducted by Vieira [Vieira et al., 2020].

^{13}C-NMR characteristic

The spectra of ^{13}C-NMR are attributed to their appropriate functional groups according to the literature [Gamage et al., 2024]. The alkyl carbon (aliphatic) functional group is related to the chemical shift at 1–54 ppm. The methoxy or hydroxy functional group is responsible for the chemical shift at 54–70 ppm. Carbohydrate or anomeric functional group is responsible for chemical shift at 70–103 ppm. The chemical shift at 103–163 is associated with aromatic (phenolic) functional group. The chemical shift at 163–180 is associated with carbonyl (carboxylic, ester, amide) functional group. While, the aldehyde or ketone group is related to the chemical shift at 180–220 ppm.

Figure 3 shows ^{13}C-NMR spectra of rice husk pyrolysis product. Based on the ^{13}C-NMR spectra (Figure 3a), water phase (liquid smoke) contains alkyl, methoxy-hydroxy, carbohydrate, aromatic (phenolic), and carbonyl (carboxylic, ester, amide) functional groups. ^{13}C-NMR spectra (Figure 3b) shows that the tar product contains alkyl, methoxy-hydroxy, carbohydrate, aromatic (phenolic), and carbonyl (carboxylic, ester, amide) functional groups. Methoxy-hydroxy of water phase product has more non-equivalent carbons which is possibly attributed to the high content of alcohol or phenolic functional group. While, alkyl of tar product has more non-equivalent carbons which is possibly attributed to the high content of alkyl (aliphatic) group.

FT-IR characteristic

The peaks of FT-IR are attributed to their appropriate functional groups according to the literature [Fan et al., 2021; Yang et al., 2007]. The OH- stretch of phenolic and hydroxyl C groups is

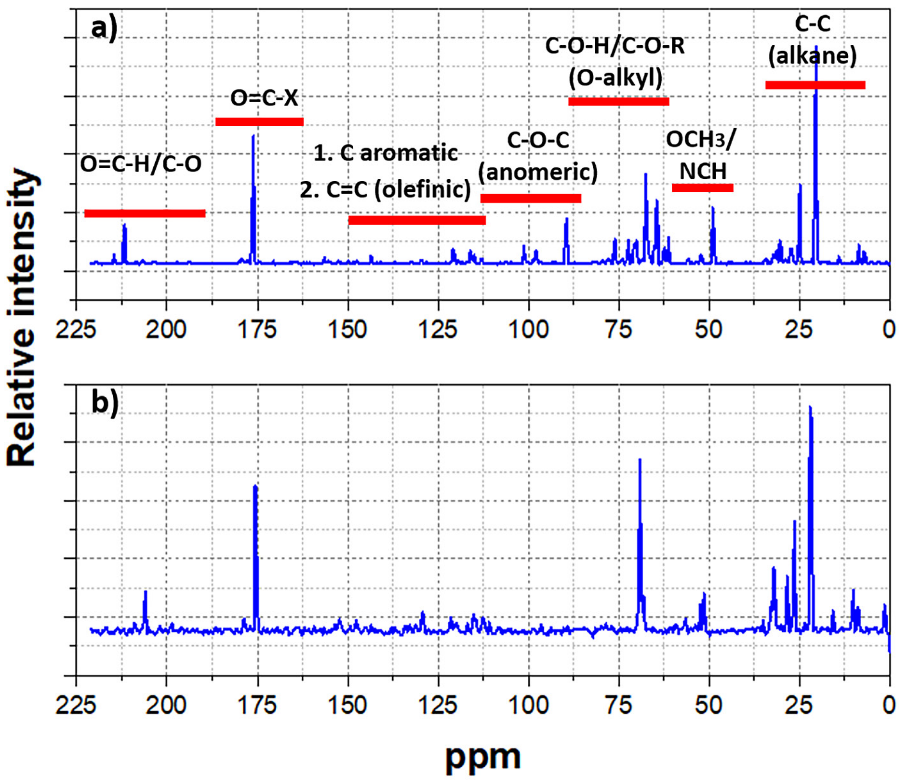

Figure 3. ^{13}C-NMR spectra of rice husk pyrolysis product: (a) water phase (liquid smoke) product at 400 °C, (b) tar product at 400 °C

related to the absorption peak at 3400 cm^{-1}. The symmetric and asymmetric stretching of aliphatic CH-bonds in CH_3 and CH_2 groups, respectively, are responsible for the peaks at around 2920 cm^{-1} and 2850 cm^{-1}, respectively. Carboxyl, ketone, and aldehyde groups are responsible for C-O stretching, which is the cause of the absorption peak at 1720 cm^{-1}. The peak at 1620 cm^{-1} is associated with aromatic structure C-C vibrations, while the peak at 1510 cm^{-1} is associated with C-O stretching of ketone and carbonyl. The peak at 1460 cm^{-1} is associated with O-CH_3 stretching of methoxy group and the defomation vibration of methyl of an aliphatic hydrocarbon. The peak at 1060 cm^{-1} is associated with C-O stretching and C-O deformation of an ethanol. The peak at 750 cm^{-1} is correlated to out of plane bending vibration of aromatic C-H.

The FT-IR spectra of the water phase (liquid smoke) at a pyrolysis temperature of 400 °C (Figure 4) depict strong absorbance at peak of 1060, 1250, 1620, 1720, and 3375 cm^{-1}. For tar products at a pyrolysis temperature of 400 °C, intense absorbance is located at peak of 750, 1060, 1250, 1470, 1720, 2920, and 3375 cm^{-1}. These indicated that the water phase contains aromatic ether, alcohol, aromatic, ketone/carboxylic, and phenolic groups, respectively. While tar product consists of aromatic, alcohol, methoxy, ketone/carboxylic, aliphatic, and phenolic groups, respectively.

Pyrolysis product characteristic

Pyrolysis is a thermal decomposition process in the absence of or with limited oxygen [Terry et al., 2021]. Pyrolysis is a more effective method for converting biomass compared to other conversion processes such as combustion, gasification, fermentation, anaerobic digestion, hydrolysis, and extraction. Pyrolysis can be carried out at a wide temperature range, at atmospheric pressure, and produces three valuable products, namely bio-oil, syngas, and bio-char [Jamilatun et al., 2022]. Figure 5 shows the distribution of pyrolysis products at temperatures ranging from 400, 500, and 600 °C. The increase in temperature causes an increase in the yield of the water phase (liquid smoke) from 35.06 to 46.16% and gas from 1.37 to 1.85%. While the decrease in tar yield from 7.32 to 3.53% and char 56.25 to 48.46% occurs along with increasing temperature. The decrease in tar yield due to the secondary tar decomposition promotes the formation of non-condensable gas [Jamilatun et al., 2022] which affects the increase in gas yield.

GC-MS analysis method was used to determine the liquid product composition. Using the available instrument database, the primary peaks that represented components in a significant fraction of the liquid product were identified. Figure 6a shows that water phase (liquid smoke)

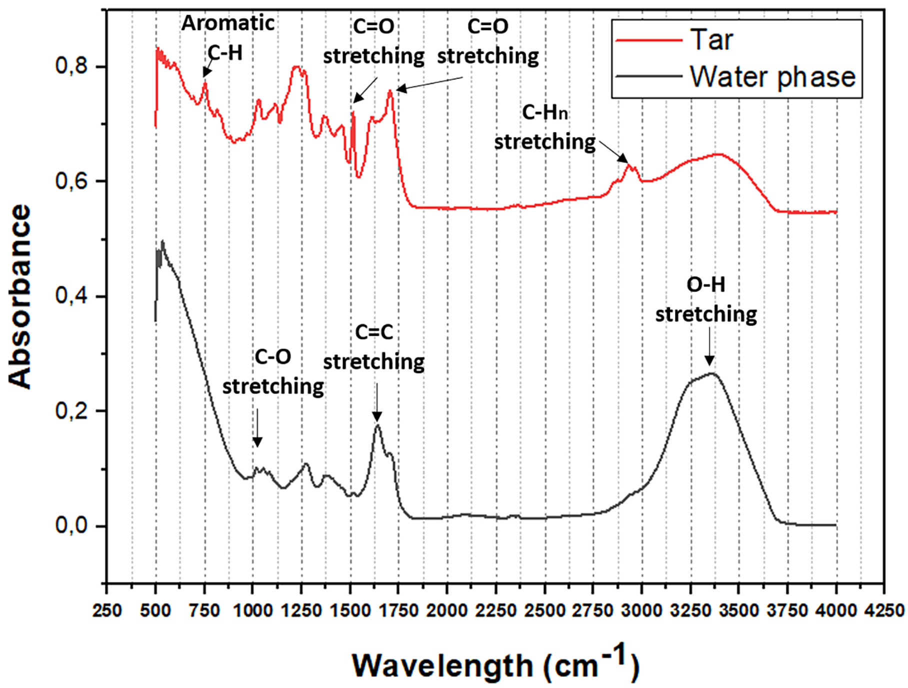

Figure 4. FT-IR spectra of water phase (liquid smoke) and tar product of rice husk pyrolysis

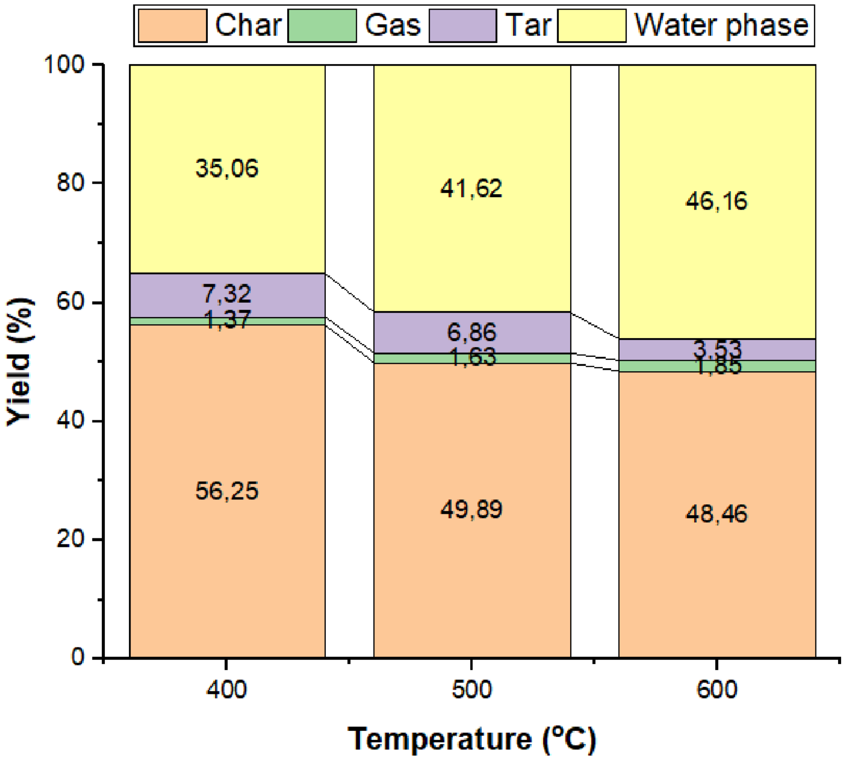

Figure 5. The yield of pyrolysis product at different pyrolysis temperatures

composition at a pyrolysis temperature of 400 °C consisted of phenolic and ketones which appear at a retention time of 5–15 min), carboxylic acid and ester at a retention time of 25–30 min. Figure 6b shows that tar composition at a pyrolysis temperature of 400 °C has a more complex tar composition with the main components being phenolic compounds at a retention time of 6–10 min, alcohol at a retention time of 17–20 min, and ester at retention time 14–18 min. Tar composition at a pyrolysis temperature of 500 °C (Figure 6c) was dominated by alcohol, carboxylic acid, and ester. While tar composition at a pyrolysis temperature of 600 °C (Figure 6d) was dominated by carboxylic acid and ester, which appear at the retention time range of 14–20 min. GC-MS spectra show that the components in the water phase mostly appear at the beginning of the retention time (5–15 min). While the components in tar appear at a longer retention time (14–22 min). In GC-MS, the order of components peaks based on the volatility of the component. The lowest one will appear in the first order. High molecular weight components appear at the end of the sequence [Nugraha and Nandiyanto, 2021]. High molecular weight typically has higher boiling temperatures (lower volatility) in their compounds because they contain more electrons and nucleons, which produce Van der Waals attractive forces [Patel et al., 2020]. Based on the spectra of GC-MS, it can be concluded that the tar from pyrolysis possibly contains components with a higher molecular weight than the water phase (liquid smoke) product.

Figure 7 shows that water phase (liquid smoke) composition at a pyrolysis temperature of 400 °C consists of carboxylic acid, ketone, alcohol, phenolic, and aldehydes, with phenolic as the most dominant product. While, pyrolysis at a temperature of 400 °C produces complex tar compounds consisting of aliphatic hydrocarbons, aldehydes, ketones, carboxylic acids, esters, alcohols, phenolics, and aromatics. Heating at a temperature of 500 °C causes an increase in the amount of carboxylic acids, alcohols, esters, and aromatics in the tar product, but decreases the amount of aldehydes, ketones, and phenolics. The degradation of both cellulose and hemicellulose causes this rising of carboxylic acid through the depolymerization of oligosaccharides into xylose, which then decomposes further to form acids, furfural, and furan. Likewise, it occurs due to the dehydration of hydroxyl aldehydes, which become aldehydes such as furan, which are then further hydrated to become acids [Yang et al., 2020]. This could also occur due to the breaking of the branch

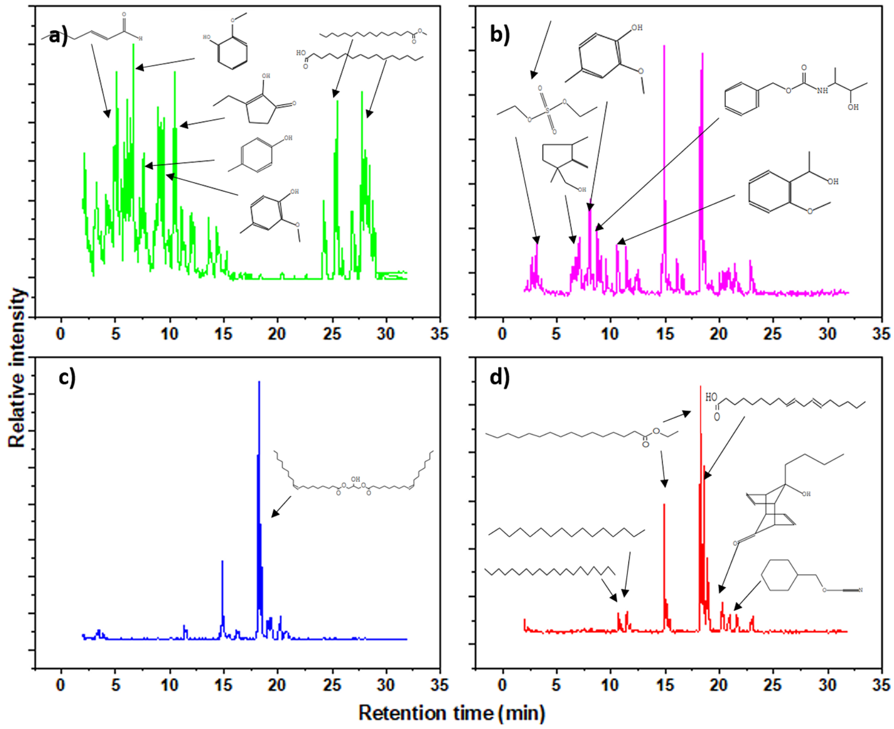

Figure 6. GC-MS spectra of pyrolysis product (a) water phase (liquid smoke) at 400 °C, (b) tar 400 °C, (c) tar 500 °C, (d) tar 600 °C

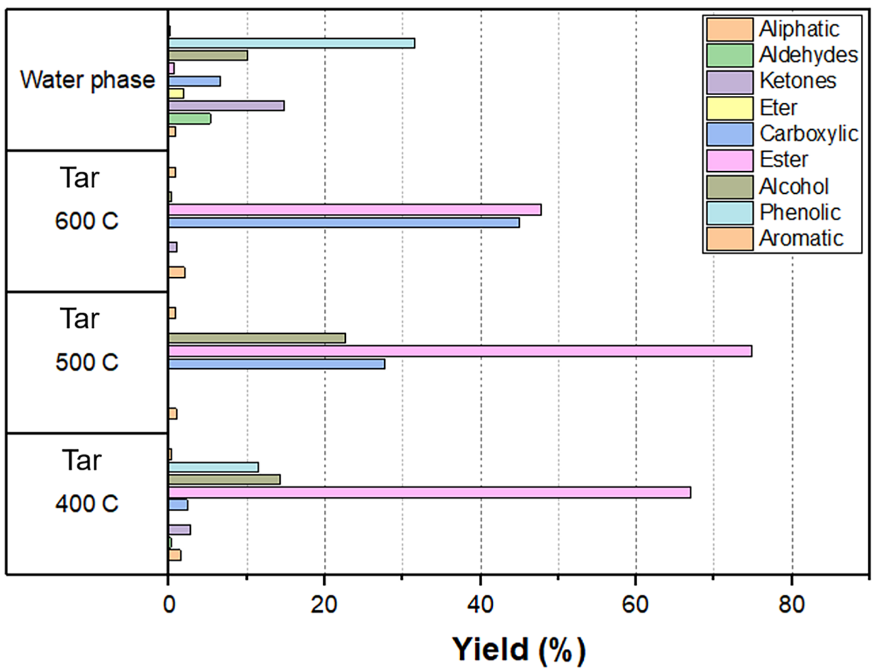

Figure 7. Functional group distribution of pyrolysis product

chain of ferulic acid ester in xylan to carboxylic acids [Kan et al., 2016; Nastasiienko et al., 2021; Stefanidis et al., 2014]. The increase in the amount of alcohol is due to the increasingly intensive decomposition of cellulose and hemicellulose [Kan et al., 2016]. Meanwhile, the increase in the number of aromatic compounds is due to the occurrence of hydrodeoxygenation, demethylation, and demethoxylation reactions that change phenolic compounds into aromatic compounds [Nastasiienko et al., 2021]. The decline in ketone content is probably due to the decarbonylation of ketones into aliphatic hydrocarbons. Pyrolysis at a temperature of 600 °C causes an increase in the number of aliphatic hydrocarbons and carboxylic acids but decreases alcohol and ester compounds. The decrease in alcohol content is due to the hydrodeoxygenation of alcohol into aliphatic hydrocarbons. The decrease in ester content is due to the demethylation of ester into carboxylic acid [Stefanidis et al., 2014].

Liquid product of pyrolysis and humic substances correlation

The similarity between liquid products of pyrolysis and humic substances can be determined based on several parameters, namely color, solubility, organic species (functional group), acidity, hydrophilicity, carbon number, molecular weight, and carbon content.

Color and solubility characteristic

Figure 8 shows the color and solubility of liquid products from rice husk pyrolysis. As a pigmented polymer, humic acid has different color characteristics between humic acid, fulvic acid, and humin. Fulvic acid is yellow-brown, humic acid is dark brown, and humin is black [Stevenson, 1995]. The name "humin" has been used in recent years to refer to the black precipitates produced in second-generation bio-refining processes when lignocellulose biomass is hydrolyzed. Figure 8a shows that rice husk pyrolysis produces a liquid with two phases, water phase (liquid smoke) and tar. The water phase (liquid smoke) is a reddish brown color on top of the liquid and tar is a black color liquid at the bottom of the liquid [Pitoyo et al., 2024]. Hence, based on the color, the water phase has similarities with fulvic or humic acid due to its brown color, while tar has similarities with humin due to its black color.

Figures 8b, c, d, and e show the solubility of liquid products from pyrolysis in water and acid media (pH 1-2), respectively. Solubility is a common classification used to distinguish the three components in humic substances. Humic acid is soluble in the entire pH range except below 2, fulvic acid is soluble in all pH ranges, and humin is insoluble in all pH ranges [Rupiasih, 2005]. Figure 8b shows the solubility of tar in water media, it can be seen that tar is insoluble in water media. The solubility of tar in media with pH 1-2 is shown in Figure 8c, it can be seen that tar is insoluble in media with pH 1-2. Figure 8d shows the solubility of the water phase (liquid smoke) in water media, it can be seen that the water phase is soluble in water media. Figure 8e shows the solubility of the water phase at pH 1-2, it can be seen from the figure that the water phase remains soluble in media with pH 1-2. Hence, based on its solubility properties, the water phase (liquid smoke) has similarities with fulvic acid, while tar has similarities with humin.

Carbon species characteristic

Figure 9 shows the relationship between liquid products of pyrolysis with the humic substances model. The humic substances model is represented by humin isolated from Muck Crops soil

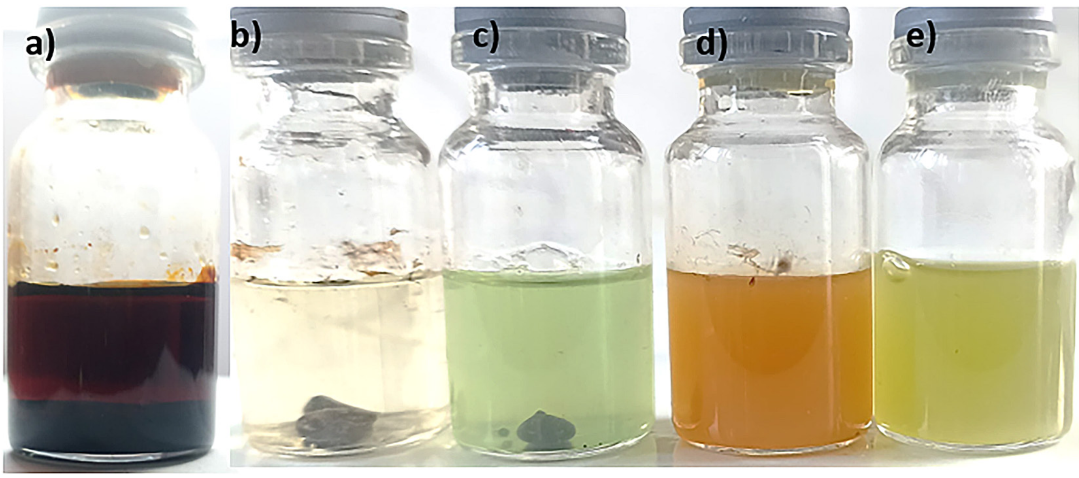

Figure 8. Liquid product of rice husk pyrolysis characteristic: (a) liquid product, (b) solubility tar product in aqueous medium, (c) solubility tar product in pH 1–2 medium, (d) solubility water phase (liquid smoke) product in aqueous medium, (e) solubility water ph

(Figure 9e), fulvic acid isolated from cow manure (Figure 9f), and humic acid extracted from IHSS Mollisol standard soil (Figure 9g). Based on the ^{13}C-NMR spectra, Muck Crops soil (representative of humin) contains alkyl (aliphatic), methoxy-hydroxy, O-alkyl, carbohydrate, aromatic, phenolic, and carbonyl (carboxylic, ester, amide) functional groups, with alkyl functional groups as the highest [Hayes et al., 2017]. The ^{13}C-NMR spectra of fulvic acid contain a more diverse functional group, with alkyl, aromatic (phenolic), and carbonyl groups as the dominant functional group [Jindo et al., 2016]. While the ^{13}C-NMR spectra of humic acid extracted from IHSS Mollisol standard soil are dominated by aromatic and carbonyl (carboxyl, ester, amide) functional groups, with aromatic as the most dominant [Gamage et al., 2024].

Related to the liquid product of pyrolysis, the water phase (liquid smoke) product (Figure 9a) contains carbonyl, phenolic, aromatic, and hydroxyl groups, with phenolic as the dominant group followed by alkyl, hydroxyl, and carboxylic. Tar pyrolysis products at a temperature of 400 °C (Figure 9b) consist of alkyl and considered amounts of O-alkyl, carbonyl, phenolic, and carbohydrate, with alkyl being the dominant group. While tar pyrolysis products at temperatures of 500 °C (Figure 9c) and 600 °C (Figure 9d) are dominated by alkyl and carbonyl groups.

Based on the distribution of carbon species (functional group), water phase (liquid smoke) product has similarities with fulvic acid, indicated by the variety of content which includes phenolic, carboxyl, lesser aromatic, and alkyl groups. Meanwhile, tar pyrolysis products at temperatures of 400, 500, and 600 °C have alkyl (aliphatic) as the most dominant functional group, hence, tar pyrolysis products have similarities with humin.

Water phase (liquid smoke) and tar pyrolysis products at a temperature of 400 °C consist of a considered amount of carboxylic (carbonyl) and phenolic groups. Carboxylic and phenolic groups are responsible for their total acidity and weak acid behavior [Jindo et al., 2016]. The solubility of nutrient elements can be influenced by the complex forms that these acidic functional groups can form with metal cations, such as $Ca^{2+,}$ Mg^{2+}, and Al^{3+}, which are crucial nutrient ions for plants [Tahir et al., 2011]. The ability of acidic functional groups to ionize and protonate depending on the pH of the surrounding environment gives them a strong buffering capacity over a broad pH range [Campitelli and Ceppi, 2008]. Carboxylic and phenolic groups have hydrophilic properties due to the existence of OH/OOH deprotonation. The presence of a hydrophilic group in the soil will increase the water-holding capacity of the soil [Piccolo et al., 1996]. Besides that, phenolic groups have antioxidant effects because of their free radical scavenging capacity and can exert toxic effects directly on pathogens. Meanwhile, carboxylic groups have antioxidant and anti-inflammatory properties [Cao et al., 2014]. The presence of aliphatic, carbonyl, and O-alkyl

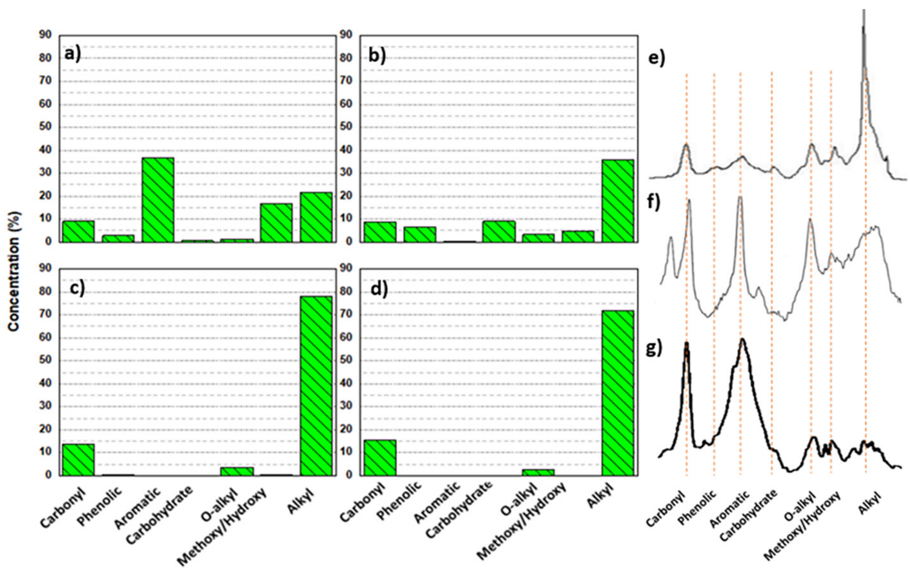

Figure 9. Carbon species distribution of (a) water phase (liquid smoke) at 400 °C, (b) tar at 400 °C, (c) tar at 500 °C, (d) tar at 600 °C, (e) humin of Muck Crops soil, (f) fulvic acid cow manure, (g) humic acid of IHSS Mollisol standard soil

groups in tar supports the opinion that carboxyl-rich alicyclic structures (CRAM) and carboxyl-containing aliphatic molecules (CCAM) are significant components of humin [Gamage et al., 2024]. Aliphatic groups are nonpolar, so they have hydrophobic properties. The hydrophobic nature of these aliphatic components makes humin more resistant to microbial degradation. Aliphatic groups could provide favorable organic-organic interactions as well as metal ions-organic interactions, which would be the scenario for organic-rich soils [Olivelli et al., 2020]. The presence of aliphatic groups can give the products a higher hydrophobic protection, therefore making them more stable in terms of their existence (lifespan) in the soil solutions, having slowly beneficial effects [Zherebker et al., 2016]. Enriching soil macro-aggregates with aliphatic alkyl-C and hydrophobic-C is thought to be important for the long-term stabilization of soil C and improving soil aggregation [Zhang et al., 2019].

Acidity and hydrophilicity characteristic

Figure 10 shows the Van-Krevelen diagram of liquid products from pyrolysis. From an energy perspective, this diagram is used to compare the heating value of various fuel sources. From an agricultural perspective, this diagram can be used to compare the acidity level, hydrophilicity level, aromatization degree, and complexity of the molecular structure. The higher the O/C relative to H/C, the higher the acidity level and hydrophilicity level. The higher the H/C relative to O/C, the lower the aromatization degree, the higher the aliphatic content, and the simpler the molecular structure [Ndzelu et al., 2021]. Water phase (liquid smoke) product at a pyrolysis temperature of 400 °C has the highest O/C relative to H/C value compared to the tar products at pyrolysis temperatures of 400, 500, and 600 °C. The water phase contains components with O/C values ranging between 0.1–0.5, therefore it has higher acidity levels and hydrophilicity levels. Tar at a temperature of 400 °C has components with O/C values ranging between 0.1–0.35 and the H/C value distributed between 0.08–0.18. Tar at a temperature of 500 °C has components with O/C values ranging between 0.00–0.20 and the H/C value distributed between 0.15–0.18. While tar at a temperature of 600 °C has components with O/C values ranging between 0.00–0.20 and the H/C value distributed between 0.10–0.20. Hence, tar products from pyrolysis at a temperature of 600 °C have a low aromatization level, high aliphatic content, and high hydrophobicity level.

Carbon number and molecular weight characteristic

Figure 11 shows the carbon distribution of liquid products based on retention time and molecular weight. Information on the carbon content and molecular weight of humic substances is important for understanding their role in agricultural land improvement. The increased weight of the molecule and polymerization degree suggest greater stability and longer-lasting effects [Qin and Leskovar, 2020]. Soil microbes live on the remaining C-containing material that is present in soil. Beneficial soil microorganisms (yeast, algae, fungi, bacteria, mycorrhizae, nematodes, and

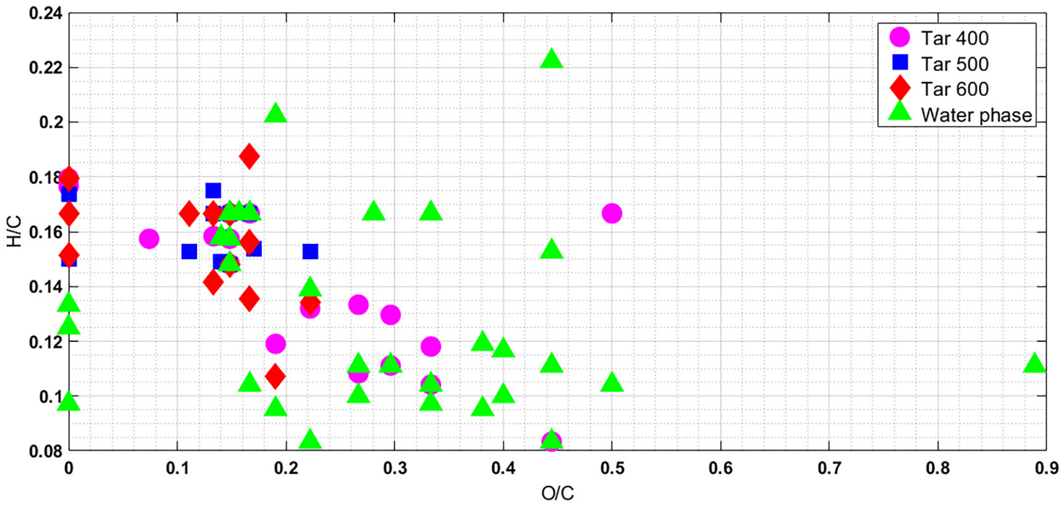

Figure 10. Van-Krevelen diagram of rice husk pyrolysis product

tiny animals) could enhance soil nutrient content [Buckau et al., 2000]. The carbon content and molecular weight of humic substances generally increase in the order of fulvic acid < humic acid < humin [Ni Nyoman and Pandit B., 2008].

Figure 11a shows that the majority of components in the water phase (liquid smoke) at a pyrolysis temperature of 400 °C appear at the beginning of the GC-MS spectra at a retention time of 2–15 min. These components are distributed with the number of carbon atoms between 6–18 with an average number of carbon atoms of 8.35. Based on the number of molecules, the components in the water phase are distributed between molecular weights of 60–160 with an average molecular weight of 144.30. Figure 11b shows that the components in tar 400 °C are evenly distributed, appearing at a retention time of 5–20 min. Based on the number of carbon atoms, these components are distributed between 4–22 with an average number of carbon atoms of 14.76. Meanwhile, based on the number of molecules, the components in tar 400 °C are distributed between molecular weights of 100–300 with an average molecular weight of 235.36. The components in tar 500 °C (Figure 11c) appear at a retention time of 11–20 min. Based on the number of carbon atoms, these components are distributed between 8-26 with an average number of carbon atoms of 22.58. Meanwhile, based on the number of molecules, the components in tar 500 °C are distributed between molecular weights of 200–350 with an average molecular weight of 358.62. While the majority of components in tar 600 °C (Figure 11d) appear at a retention time of 16–20 min. Based on the number of carbon atoms, these components are distributed between 8–22 with an average number of carbon atoms of 17.41. Meanwhile, based on the number of molecules, the components in tar 500 °C are distributed between molecular weights of 120–320 with an average molecular weight of 272.26.

Based on the amount of carbon and its molecular weight, the water phase (liquid smoke) product of pyrolysis has a compatibility with fulvic acid or humic acid which is characterized by its low carbon content and molecular weight. While tar product of pyrolysis has a compatibility with

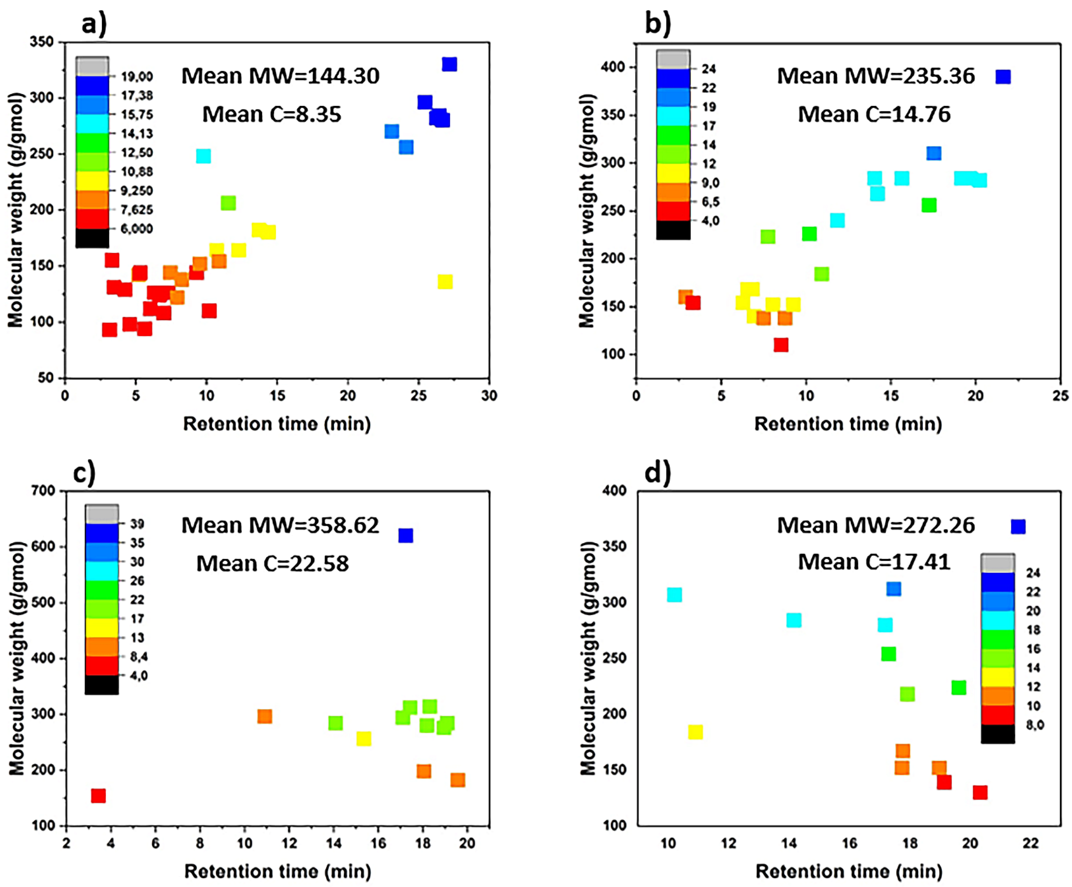

Figure 11. Carbon distribution of rice husk pyrolysis product in (a) water phase (liquid smoke) at 400 °C, (b) tar at 400 °C, (c) tar at 500 °C, (d) tar at 600 °C

humin because it has a high carbon content and large molecular weight.

Carbon content characteristic

Figure 12 shows the carbon, hydrogen, and oxygen content in the liquid product of rice husk pyrolysis. In humic substances, carbon, hydrogen, and oxygen have varying contents in the range of C (45–60), H (4–7), and O (25–45) [Buckau et al., 2002; Davies et al., 2003]. The carbon content in humic substances usually increases in the order of fulvic acid < humic acid < humin [Rupiasih, 2005], while oxygen has the opposite order. So the high oxygen content and low carbon content in humic substances indicate a similarity to fulvic or humic acid, while the low oxygen content and high carbon content indicate a similarity to humin. In the liquid product of pyrolysis, the water phase (liquid smoke) has the highest oxygen content at a concentration of 22–24% and the lowest carbon at a concentration of 68–71%, this indicates the similarity of the water phase to humic or fulvic acid. Conversely, tar has a high carbon content at a concentration of 75–77% and low oxygen content at a concentration of 11–14%, so it has a similarity to humin.

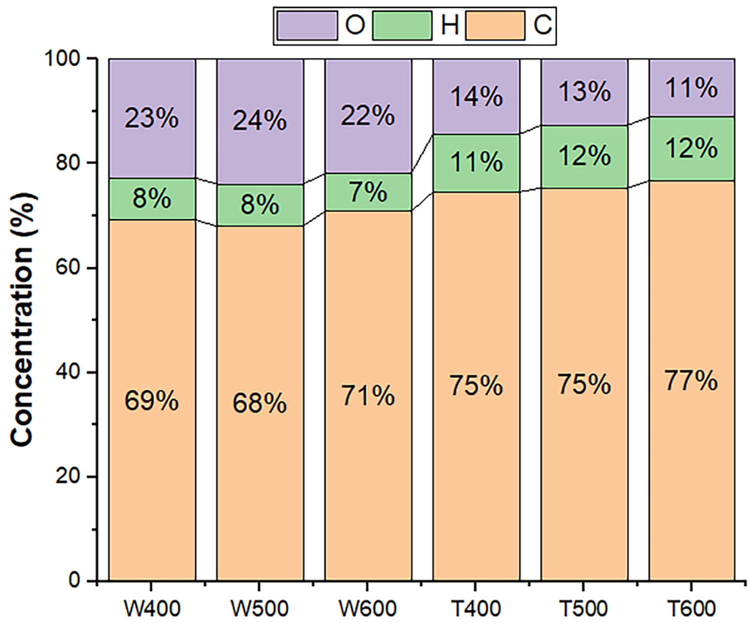

Figure 12. Carbon, hydrogen, and oxygen content in the liquid product of pyrolysis

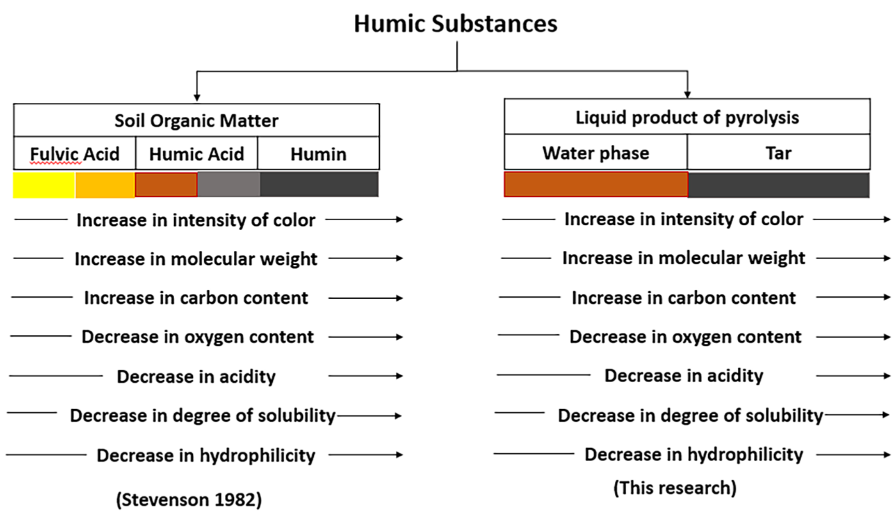

Figure 13. Comparison of chemical properties between soil organic matter (SOM) and liquid product from pyrolysis

Figure 13 presents the chemical properties relationship between the humic substances derived from soil organic matter [Stevenson, 1995] and liquid product from the rice husk pyrolysis process. Figure 12 shows the similarity of chemical properties among the two. Based on the aforementioned explanation, water phase (liquid smoke) products have similarities with fulvic acid, while tar product has similarities with humin.

CONCLUSIONS

The study shows that the minimum of rice husk pyrolysis temperature for sufficient liquid product is 365 °C. Based on its chemical properties, namely color, solubility, organic species (functional group), acidity, hydrophilicity, carbon number, molecular weight, and carbon content, a liquid product from pyrolysis has similarities with humic substances derived from SOM, where the water phase (liquid smoke) has similarities to fulvic acid, while tar has similarities to humin. Water phase (liquid smoke) product dominated by phenolic group, while tar product dominated by alkyl (aliphatic) group.

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