CHARS FROM HYDROTHERMAL AND HYDROTHERMAL TANDEM PYROLYSIS CARBONIZATIONS OF POLYVINYL CHLORIDE: DECHLORINATION ABILITY AND ITS SURFACE CHARACTERIZATION

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Abstract: The hydrothermal carbonization method has been applied in polyvinyl chloride (PVC) conversion. The polymer was transformed to char safely without the formation of harmful emissions. PVC's chlorine content was removed through a nucleophilic reaction by reactive subcritical water and captured by alkali ions as stable salt. The PVC bulk was dechlorinated and carbonized by subcritical water inside the hydrothermal reactor at 200 °C for 120 minutes. The solid chars obtained then were characterized by Fourier Transform Infra-Red, Scanning Electron Microscope, Energy Dispersive X-ray, and Transmission Electron Microscope. As a comparison, the chars were also pyrolyzed further to obtain the thermal char characteristics. The char products obtained by hydrothermal (hydrochar) and hydrothermal-pyrolysis (hydro-pyrochar) yielded 94.96% and 48.08%, respectively. The infrared spectra showed that both hydrochar and hydro-pyrochar consist of aliphatic carbon and hydrophilic functional groups of C=O and OH. The morphological images observed by Scanning Electron Microscope on the magnification of 3000x showed the smooth granular particle for hydrochar and the irregular rough particle for hydro-pyrochar. The chlorine contents from surface analysis by energy dispersive X-ray in hydrochar were decreased down to 23.24 mass percentage from 56.80 mass percentage in PVC, while in hydro-pyrochar, there is no chlorine content observed in the particle surfaces. The particle images investigated by Transmission Electron Microscope revealed that the particle shape of hydrochar was granular while the hydro-pyrochar was cylindrical. The particle sizes of hydrochar and hydro-pyrochar were calculated in the range of 36-180 nm and 8-40 nm, respectively.

Keywords: polyvinylchloride; hydrothermal carbonization; surface characterization; hydrochar; hydro-pyrochar.

Abstrak: Metode karbonisasi hidrotermal telah berhasil diaplikasikan dalam konversi polivinil klorida (PVC). Polimer diubah menjadi arang dengan cara yang aman tanpa menghasilkan emisi berbahaya. Klorin dalam PVC dikeluarkan melalui reaksi nukleofilik oleh air subkritis yang reaktif dan ditangkap oleh ion alkali menjadi garam yang stabil. Serbuk PVC dideklorinasi dan dikarbonisasi oleh air subkritis didalam reaktor hidrotermal pada 200 °C selama 120 menit. Arang padat yang diperoleh selanjutnya dikarakterisasi dengan *Fourier Transform Infra Red*, *Scanning Electron*

Microscope, *Energy Dispersive X-Ray* dan *Transmission Electron Microscope*. Sebagian arang selanjutnya juga dipirolisis untuk mendapatkan arang dengan karakteristik arang pemanasan kering sebagai pembanding. Rendemen arang yang dihasilkan secara hidrotermal (hidrochar) sebesar 94,96% dan secara hidrotermal-pirolisis (hydro-pyrochar) sebesar 48,08%. Spektra infra merah menunjukan bahwa kedua jenis arang tersebut mengandung karbon alifatik dan gugus fungsi hidrofilik C=O dan OH. Morfologi permukaan yang teramati dengan *Scanning Electron Microscope* pada pembesaran 3000x menunjukkan bahwa hidrochar merupakan partikel bulat yang lembut dan hidro-pirochar merupakan partikel kasar tidak beraturan. Analisis dispersi energi X-Ray menunjukkan bahwa persentase klorin pada hidrochar turun menjadi 23,24% (b/b) dari persentase awal klorin pada PVC sebesar 56,80% (b/b), sedangkan pada hidro-pirochar, tidak ada klorin yang terdeteksi pada permukaan partikel. Analisis *Transmission Electron Microscope* menunjukkan bahwa partikel hidrochar berbentuk bulat, sedangkan partikel hidro-pirochar berbentuk silinder. Ukuran partikel hidrochar berada pada rentang 36-180 nm sedangkan ukuran partikel hidro-pirochar berada pada rentang 8-40 nm.

Kata Kunci: polivinil klorida; karbonisasi hidrotermal; karakterisasi permukaan; hidrochar; hidro-pirochar.

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Introduction

A conversion method for carbon-based material still has several problems (Gong et al., 2019). The uses of incineration and pyrolysis in biomass and plastic conversions are considered practical from technical and economic perspectives, but they produce harmful emissions such as Polycyclic Aromatic Hydrocarbon (PAH) and Carbon Monoxide (CO) (Conesa et al., 2020). In case of halogenated polymer such as Polyvinyl Chloride (PVC), the hazardous level of the emission increases by the present of Polychlorinated Dibenzodioxins (PCCDs), Polychlorinated Dibenzofurans (PCDFs) (McKay, 2002), Chlorophenol, Chlorobenzene (Font et al., 2010) and inorganic chlorine (Sadat-Shojai & Bakhshandeh, 2011). These reports are worthy of attention remembering the fact that the cheap material (Bidoki & Wittlinger, 2010) is related to the massive application of PVC in many sectors such as roof material, hydrant, electrical cable protectors, and electronic devices (Lieberzeit et al., 2022). Open dumping or burial isn't wise because higher chlorine content reaches 58 mass percentage (Li et al., 2023). It will potentially pollute the environment over a long period (Yamahara et al., 2024).

Another method, which is allegedly relatively safe, hydrothermal method, has been introduced to carbonize carbon-based materials. This method not only makes use of thermal but also pressure as sources and forces in carbonization reaction (González-Arias et al., 2022). The hydrothermal carbonization method

has been applied to several biomass subjects such as corn stalk (Tu et al., 2016), stark, rice (Cui et al., 2006), beer industry waste (El Korhani et al., 2013), pinewood (Liu et al., 2010), poultry litter, swine solids (Sun et al., 2011), chicken feather (Kuncaka et al., 2021) and carbohydrate (Titirici et al., 2007). The hydrothermal methods produce higher yield and lower carbon dioxide during the process compared to thermal methods (Titirici et al., 2007). This condition is also supported by the isolated reactor system and the ability to dilution by subcritical water during the process (Ischia & Fiori, 2021). It considers that the said method is greener and safer than other conversion ones (Yu et al., 2024).

The application of hydrothermal conversion on PVC showed good results. The polymer can convert to hydrochars (chars from hydrothermal conversion) perfectly (Zhang et al., 2022). The chlorine contents are released into subcritical or supercritical water through a nucleophilic reaction mechanism as hydrochloric acid. Even though further procedures are needed to deal with the acid solution, the result is the absence of hazardous by-products. There are no chlorinated organic contents of PCCDs and PCDFs detected in the solution. It makes the hydrothermal technique a proper solution to be studied in handling material with high-risk emissions like plastic or rubber (Poerschmann et al., 2015).

The characteristic of chars by thermal conversion is identical with high surface area and aromatic carbon. However, the hydrochars by hydrothermal conversion converted from biomass mostly reported low surface area but high oxygen-functional groups in the surface. This hydrophilic functional group from biomass can endure during the hydrothermal process. But in thermal one, it is otherwise (Tu et al., 2016). The oxygen-functional groups play an important role in material development and application as same as the surface area (Leng et al., 2021). It is possible to modify the surface in functional group sites for some purpose or even for direct applications such as sensors, catalysts, or adsorbents (Kong et al., 2024). In the PVC case, it is more interesting because PVC doesn't have the oxygen-functional group from the start. Does the char product have the same functional group characteristics as biomass hydrothermal products? If it is related to the predicted nucleophilic substitution mechanism in the carbonization process, it becomes interesting to study this potential.

Carbonization using the hydrothermal or pyrolysis method has been widely used to carbonize several carbon-containing materials including biomass and plastics. However, in the PVC case, this method is not very suitable because of the chlorine content. The combination of both methods in a one-way process is proposed in this research to minimize the emission and increase the dechlorination safely. The purpose of the research is to study the dechlorination ability between hydrothermal and hydrothermal tandem pyrolysis carbonization procedures. The surface characteristics of both products were also studied.

Materials and Methods

Materials

The materials used in this research were polyvinyl chloride, sodium bicarbonate, sulfuric acid, sodium hydroxide from Sigma-Aldrich, and double distilled water from Merck. The tools used were a hydrothermal reactor, pH meter, and analytical balance.

Methods

Carbonization of PVC

One gram of PVC and 1 gram of sodium carbonate were dispersed into an autoclave containing 50 mL of distilled water. Two molars of sulfuric acid and two molars of sodium hydroxide were used to adjust pH 6. The autoclave was sealed and put into a hydrothermal reactor. The reactor was run at 200 °C for 3 h. Char's slurry was filtered and washed using 50 mL of double distilled water. Chars were dried at 100 for 24 h. This product was labeled as hydrochars.

The procedure was repeated in the same way as hydrochars. The hydrochar powder was then pyrolyzed at 250 for 2 h. Char obtained was washed with 50 mL of double distilled water. Chars were dried at 100 for 24 h. This product was labeled as hydro-pyrochars.

Characterization

The functional groups on the surface of the product were identified by Perkin Elmer Fourier Transform Infra-Red at 4,000-400 cm^{-1} infra-red wavelength. The surface morphology was analyzed using a JEOL JSM-6510 LA Scanning Electron Microscope equipped with Energy Dispersive X-Ray. The particle images were observed using the JEOL JEM-1400 Transmission Electron Microscope.

Result and Discussion

Dechlorination in direct thermal carbonization of PVC mostly occurs through the free radical mechanism. The polyene formed then undergoes polymerization, while the chlorine was separated as HCl gas. As the direct thermal principle, the pyrolysis of PVC is an unsafe technique because of HCl gas formation. This research is started by hydrothermal carbonization of PVC in subcritical water conditions. In this technique, the thermal and the pressure force water to change into nucleophilic which substitutes chlor. The polyol formed the polymerization including the oxygen functional group, while mostly chlorine was separated as HCl aqueous. This acid substance was further captured by sodium ion from sodium carbonate to form safer sodium chloride. The remind chlorine in the carbon bond was then removed from the product through the second procedure of pyrolysis. The schematic illustration of both procedures is presented in Figure 1.

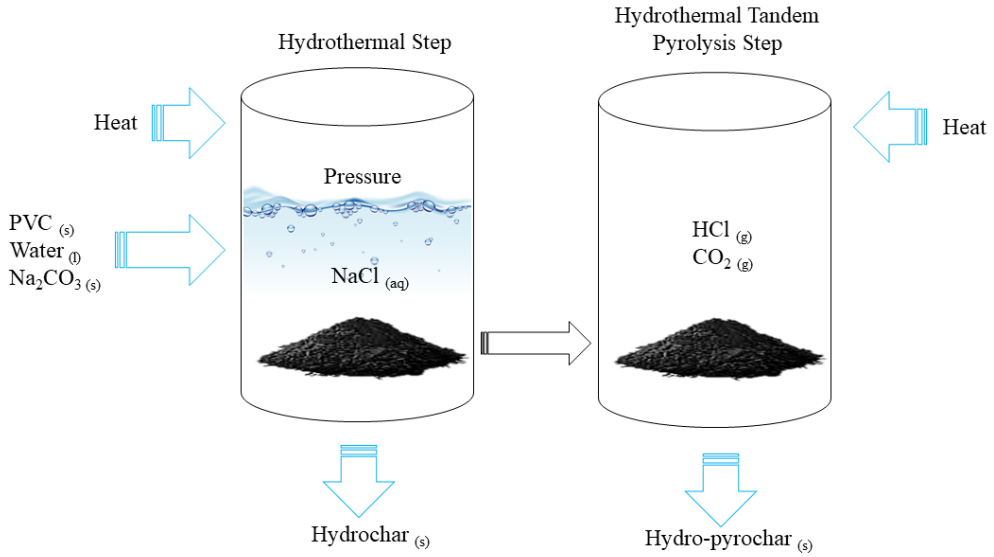

Figure 1. Schematic illustration of PVC conversion into hydrochar and hydro-pyrochar

Infra-red spectra of PVC, hydrochar, and hydro-pyrochar are shown in Fig 2. The spectra of PVC show the presence of typical absorption of alkanes that includes C-H, -CH_2-, and –CH_3 at wavenumbers of 2908 cm^{-1}, 1427 cm^{-1}, and 1327 cm^{-1}, respectively. The identity of C-Cl absorption was detected in a fingerprint area of 612 cm^{-1}. The unusual broad spectra are detected at 3448 cm^{-1} which is often connected to the hydroxyl functional group. Although it doesn't contribute to a part of the PVC structure, it firmly appears in PVC spectra which originated from H_2O. The PVC contains hydrophilic groups from Cl which can absorb and interact with water molecules (Muslem et al., 2019).

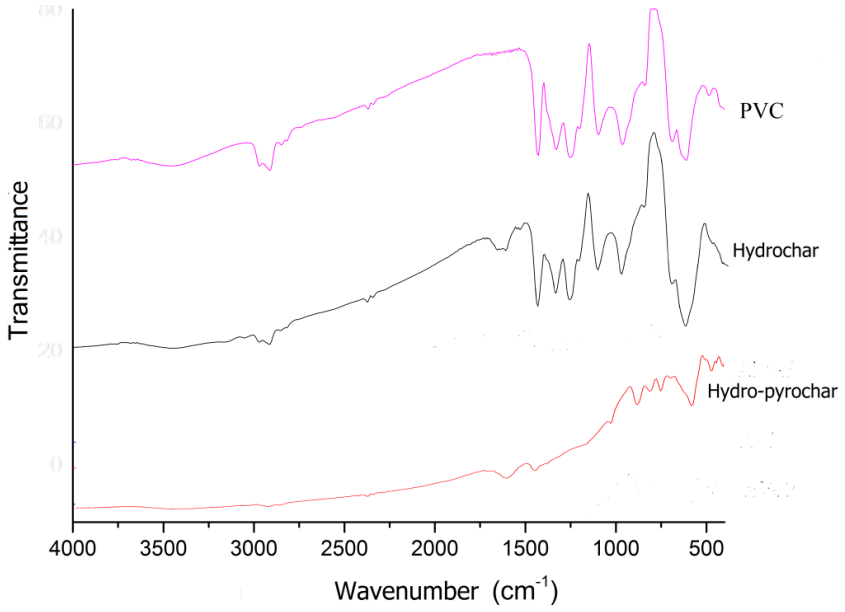

Figure 2. FTIR spectra of PVC, hydrochar, and hydro-pyrochar

The presence of new spectra which don't previously exist in PVC at 1635-1651 cm^{-1} in both hydrochars and hydro-pyrochars products shows the formation of C=O during the carbonization process (Kruse & Zevaco, 2018). The intensity of spectra in hydrochar is the same but higher than in hydro-pyrochar which indicates the high polarity in hydrochar surface. The decrease of spectra in hydro-pyrochar product also occurs for other spectra including the identic spectra of aliphatic alkane. All these findings indicate that the feature changes in the hydro-pyrochar surface happened during the pyrolysis process. A similar finding was also reported by (Liu et al., 2010) that the percentage of oxygen contained functional group rose by 95% in hydrochar from pinewood, but it decreased by 56% after the hydrochar continuously pyrolyzed.

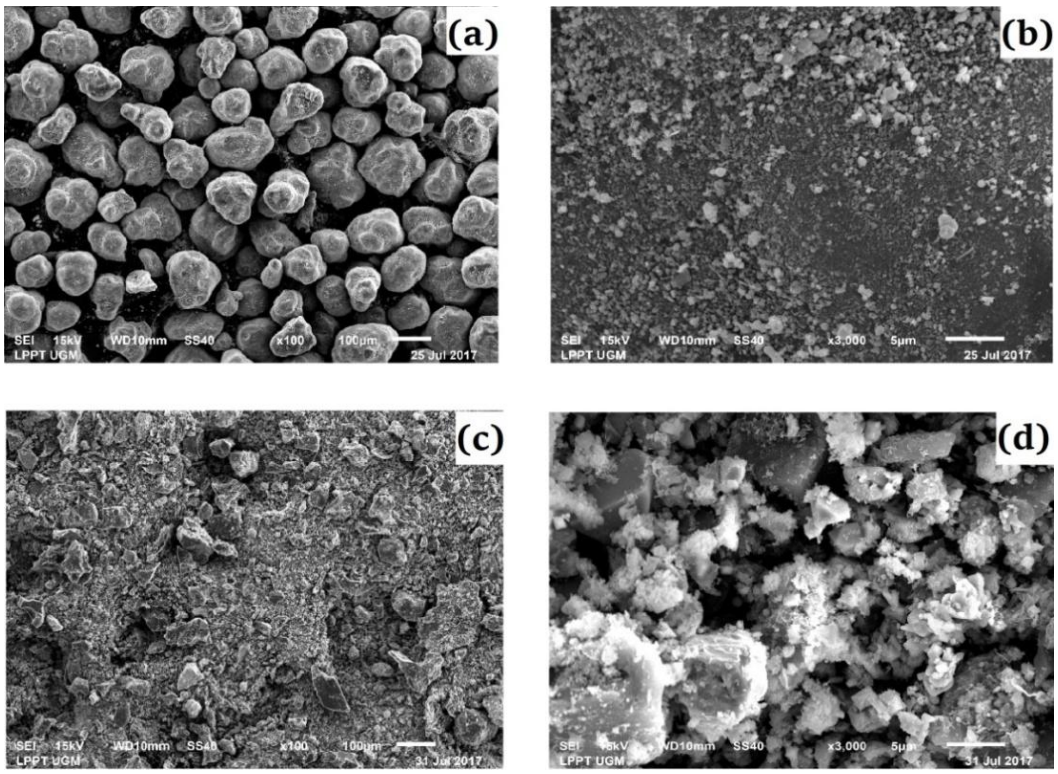

Figure 3. The SEM images of a) hydrochar with 100x magnification, b) hydrochar with 3000x magnification, c) hydro-pyrochar with 100x magnification and hydro-pyrochar with 3000x magnification.

Table 1. The element content of hydrochar and hydro-pyrochar surfaces was analyzed by EDX.

Element	Hydrochar		Hydro-Pyrochar	
	Mass (%)	Atom (%)	Mass (%)	Atom (%)
C	23,85	33,38	60,22	66,85
O	52,91	55,61	39,78	33,15
Cl	23,24	11,01	0	0

The Scanning Electron Microscope (SEM) images show that the morphology of hydrochar surfaces is completely different from hydro-pyrochar ones. The hydrochar surfaces which are visible in SEM image with 100 times magnification consist of homogenous granular particles dispersed with each other (Fig. 3a). Meanwhile the hydro-pyrochar one showed the heterogeneous finer particles which are agglomerated with each other (Fig. 3c). In 3000 times magnification, the SEM image of hydro-pyrochar surface shows the presence of pores which is relatively evenly distributed in the surface (Fig. 3d). Meanwhile hydrochar one provides the relatively rough exterior without the appearance of obvious pores (Fig. 3b). The variation of surface morphology of different char product showed there is the influence of carbonization method used in char preparation. The presence of pores in hydro-pyrochar is caused by thermal decomposition in the char surface during the pyrolysis process (Tu et al., 2016).

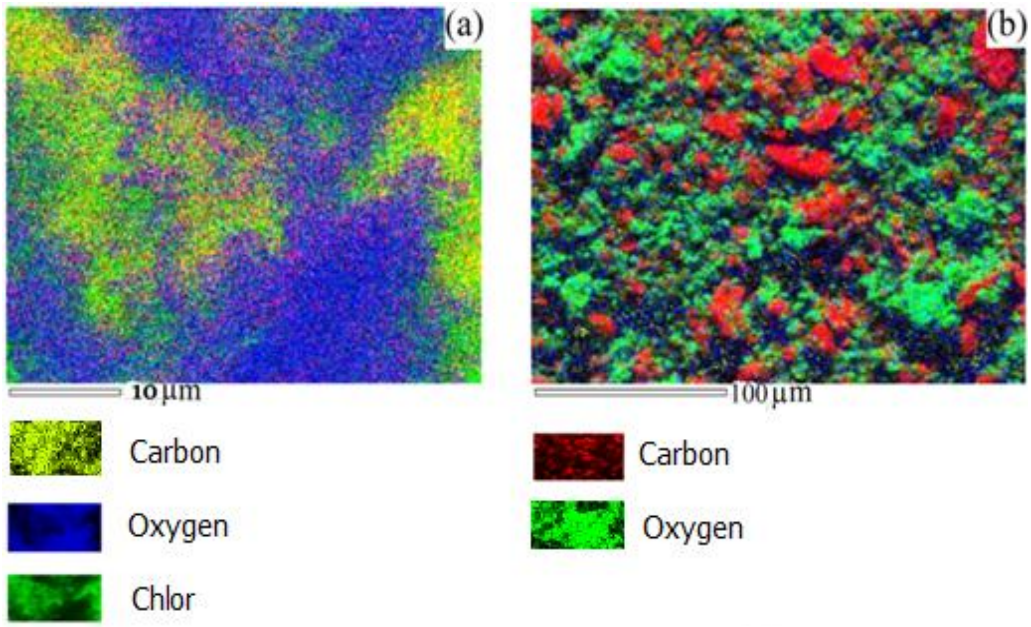

Figure 4. The mapping EDX of a) hydrochar surface and b) hydro to-pyrochar surface

EDX analysis (Table 1) showed that chlor element amounting to 23.24% by mass or 11.01% by atom is still detected in hydrochar. However, in hydro-pyrochar, the chlor content has all been eliminated from the char. If it is compared with the initial chlor content in PVC which reached 56.80% by mass (Poerschmann et al., 2015), 60.92% of chlorine has been removed during the hydrothermal process. The composition of carbon and oxygen content between hydrochar and hydro-pyrochar is amount significantly different. Hydrochar contains higher oxygen elements than hydro-pyrochar. After the hydrothermal process, the percentage of oxygen contained functional group rose by 53% in hydrochar from PVC, but it decreased by 25% after the hydrochar was

continuously pyrolyzed (Table 1). The decrease of oxygen and the total loss of chlor contents in hydro-pyrochar indicate the release of CO_2 (Chia et al., 2020) and HCl gases during the pyrolysis process. Losing a lot of carbon and oxygen through CO_2 release is correlated with the yield of less hydrothermal-pyrolysis product compared to hydrothermal one. Although the less oxygen content, the carbon content in hydro-pyrochar is higher than in hydrochar. This indicated that the decomposition during the pyrolysis process is dominated by carbonyl and hydroxyl groups on the hydro-pyrochar surface (Niu et al., 2021). This finding is also by SEM images (Fig. 3) and FTIR spectra (Fig. 2) where the increase of the pore is detected on SEM images and also the decrease of the carbonyl and hydroxyl peaks is observed on FTIR spectra.

The dominant element on the char surface can be observed by mapping EDX images. The existence of chlor in hydrochar is illustrated by green and it is dispersed on the char surface (Fig. 4a), while in hydro-pyrochar, the chlor content is undetected (Fig. 4b). The chlor content on the hydrochar surface is predicted to be bound to carbon sp^3 of char (Mochizuki et al., 2021). This is to the infra-red information that the carbon type of hydrochar is single-bound aliphatic.

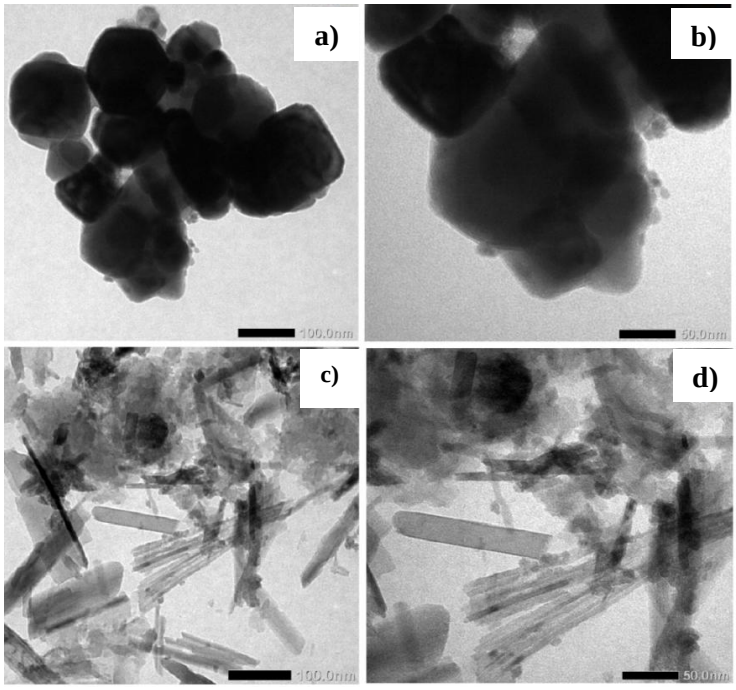

Figure 5. The TEM images of a-b) hydrochar and c-d) hydro-pyrochar

TEM investigations show more detailed morphology of both hydrochar and hydro-pyrochar. The particle shapes of those two chars with distinct carbonization processes are completely different. The hydrochar particles are mostly spherical (Fig. 5a and 5b) but the hydro-pyrochar ones are mainly cylindrical (Fig. 5c and 5d). Based on these particle shapes, the hydrochar is a granular carbon type (Dong et al., 2021), while the hydro-pyrochar is a cylindrical one (Oberlin, 2021).

The calculations of both hydrochar and hydro-pyrochar particle sizes show the nanometer level. The diameters of spherical hydrochar particles are in the range of 36-180 nm (Fig. 6a), while the breadth of cylindrical hydro-pyrochar ones is in the range of 8-40 nm (Fig. 6b). The different particle size of both chars is related to different carbonization processes and temperatures. The hydrochar particles were split into smaller sizes when it was further pyrolyzed at a higher temperature than hydrothermal ones. Additionally, high temperatures cause solid decomposition which also affects the reduction in particle sizes (Pan et al., 2021).

Based on all characterization data, both products show a potential amorphous carbon material with different surface characteristics. The hydrochar provides more hydrophilic functional groups which are allowed to modify and have good ability in ionic matter adsorption. The hydro-pyrochar provides a higher surface area which is fit as a basic material for making composite and has the ability in non-polar matter adsorption. These kinds of materials are suitable for application as a soil amendment, starting material of artificial humus, and adsorbent.

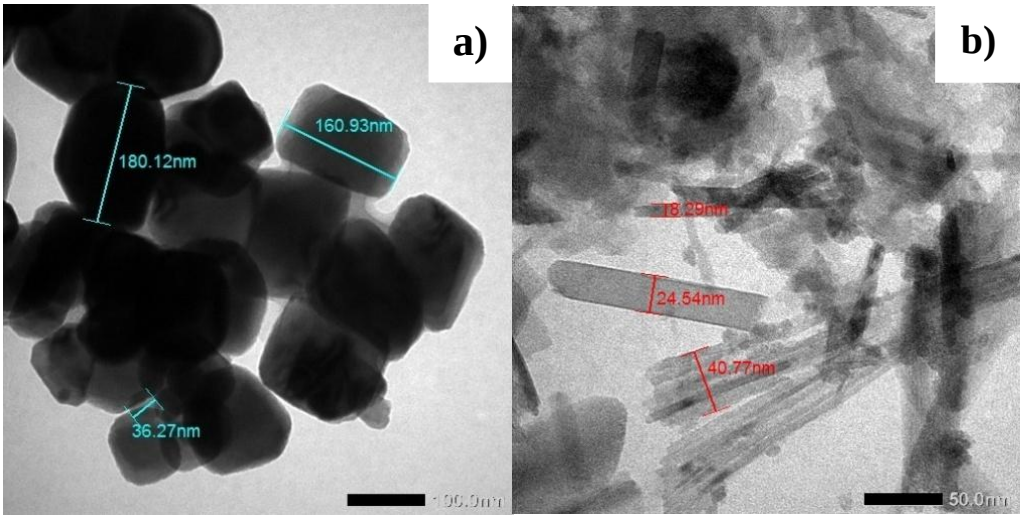

Figure 6. The particle size calculation of a) hydrochar and b) hydro-pyrochar

Conclusion

Hydrochar and hydro-pyrochar have been synthesized from PVC using both hydrothermal and hydrothermal-pyrolysis methods. Both chars have the same aliphatic carbon types. The hydrochar exhibited a greater abundance of oxygenated functional groups compared to hydro-pyrochar. Additionally, the hydro-pyrochar had higher porosity compared to hydrochar. Hydrochar contained more uniform surfaces, but In contrast, hydro-pyrochar had more heterogeneous surfaces. The chlorine content in hydrothermal products can be caused to dismount from 56.58% in PVC starting material to 23.24% in hydrochar. Furthermore, in hydrothermal-pyrolysis products, there is no chlorine content detected. The particle shape of hydrochar is spherical with particle size in the

range of 36-180 nm, while the hydro-pyrochar is cylindrical with smaller particle size in the range of 8-40 nm. These results showed that hydrothermal assisted the greener process when it was further pyrolyzed. The surface characteristics of both chars from carbon type, surface morphology, particle shape, and particle size showed the high applicated potential material in adsorption, sensor, or catalyst-based material.

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Conflict of Interest

The authors declare that there are no conflicts of interests

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