Physical and chemical characteristics of carbonized corncob through hydrothermal and pyrolysis conversion

Nongnoot Srilek\textsuperscript{1,*} and Pruk Aggarangsi\textsuperscript{1,2}

\textsuperscript{1}Department of Mechanical Engineering, Faculty of Engineering, Chiang Mai University, Chiang Mai Thailand 50200
\textsuperscript{2}Energy Research and Department Institute-Nakornping, Chiang Mai University, Chiang Mai Thailand 50100

* Corresponding Author: k_nongnoot@hotmail.com

Abstract
Thailand and south-east Asia have been struggled with agriculture biomass residues management for decades where open burning causes severe air pollution affecting millions of people every year. Thermal carbonization is one of the most cost-effective and environmentally friendly techniques which converted the low value residues such as straw, corn stovers and corncob into a more valuable material such as solid biofuel, chemical adsorbent feed stocks. This study aims to explore crucial characteristics of carbonized corncob including fibre composition, BET surface area and FT-IR spectrums. The characteristics can be used to identify the potential of the material for further surface enhancement or surface activation to produce the bio-based activated carbon. The carbonization process in this work includes mild temperature hydrothermal technique and high-temperature pyrolysis process. The hydrothermal carbonization temperature is set at 250°C in a pressurized reactor where a pyrolysis is operated at 480°C and 380°C at atmospheric pressure. The BET surface area of “hydrocharred” corncob derived from hydrothermal is 11.53 compared with 16.13 m\textsuperscript{2} g\textsuperscript{-1} of the raw materials. The pyrolized biochar at 480°C and 380°C yields surface area of 7.66 and 6.12 m\textsuperscript{2} g\textsuperscript{-1}. The oxygenated functional groups on char surface and BET surface area are also compared to provide baseline for carbon activation.

Keywords: Hydrothermal carbonization, Hydrochar, Corncob, Bio-based activated carbon, Pyrolysis, Biochar

1. Introduction
A pollution is a major problem in Thailand. It has a huge effect on a living quality, long term health care and tourism economy, and has been recognized as the national agenda. The open burning of agricultural wastes, especially rice and corn residues, is a leading cause of pollution in a particular place, especially in the northern part of Thailand. Corn or maize are the annul crops mainly producing the animal feeds. Corn faming and harvesting take 3-4 months for each period. The first period or rainy season are cultivated during March to June and August to October. The second period or summer are cultivated during November to February. The conversion of low-value residue biomass has been a tremendous challenge for researchers around the world to effective management. It also converts biomass residues
such as corn, an immense amount, to higher value materials. Corn residues are lignocellulose materials which major constituents including cellulose, hemicellulose, lignin and extracted material. These fibres are main compositions and contents can be largely different according to the type and age of the plant, atmosphere and geographic. A cellulose, \((\text{C}_n\text{H}_{2n+2}\text{O}_n)\), is a linear homopolymer that is composed of glucose monomer \((\text{C}_6\text{H}_{12}\text{O}_6)\). Hemicellulose, \((\text{C}_3\text{H}_{10}\text{O}_5)\), is a copolymer that includes various monomer units. The lower degree polymerization of hemicellulose has an effect on a smaller crystalline structure. As such, it is easier to decompose than cellulose. Lignin, on the other hand, is the polyphenol polymer with a three-dimensional mesh of aromatic unit including many hydroxyl and polar groups. Thus, it is insoluble in any solvent [1], which leads to various difficulties limiting options of conversions. The chemical constituents of cellulose are 43.2 % C, 5.7 % H and 51.1 % O and 66.0 % C, 6.0 % H and 26.9 % O of lignin composition [2]. Hemicellulose, cellulose and lignin constituents in lignocellulose material can be decomposed at 180-290, 240-350 and 280-500°C respectively [3].

Pyrolysis process is a non-combustion thermochemical conversion that generally can be classified into slow, fast and flash process (see Table 1). The temperature ranges of pyrolysis depend on the expected products. Solid carbonized products as residues from pyrolysis are often called biochar or char derived from the biological feedstock. Solid carbonized products as residues from pyrolysis are often called biochar or char derived from biological feedstock. Biochar consists of carbon that is molar hydrogen/molar carbon (H/C) ratio of biochar. It was found that it is related to the degree of charring. We can also see that it contains a maximum H/C of the molar ratio of 0.7 and carbon content of at least 10% are fundamental specification [4].

Table 1. Reaction temperature, heating rate and the holding time for thermochemical conversion.

| Thermochemical conversion | Temperature (°C) | Heating rate (°C/min) | Holding time | Ref. |
|---------------------------|------------------|-----------------------|--------------|------|
| Slow pyrolysis            | 400 – 600        | 10 – 30°/minute       | minutes - days | [5],[6] |
| Fast pyrolysis            | 400 – 600        | > 100°/minute         | ~ 1 second   | [5],[6] |
| Hydrothermal carbonization| 180 – 250        | 5 – 10°/minute        | 1 – 12 hours | [5] |

Similar to pyrolysis, a hydrothermal conversion technique is also called a non-combustion thermochemical conversion. This technique is similar to the pyrolysis, however, there is a difference in terms of the process. Its process is conducted under a pressure and typically has a high humidity content. The hydrothermal conversion can be divided into three types: carbonization, liquefaction and gasification [7] (see Figure 1). The HTC is the thermochemical conversion of biomass and its products are aimed for carbon-rich solid material. An HTC reaction process can normally be conducted in a pressurized vessel reactor with a liquid medium which can be vaporized into steam. Thus, it can lead to a decrease in the reaction pressure and it usually consists of the external heating. For example, a condition is placed where the hydrothermal temperature is 180-240°C and the pressure is at 1 - 3 MPa (10 - 30 bars). If the generated pressure is contained and controlled, water still maintains in liquid form. It is the sub-critical water according to water-steam thermodynamic properties [8]. The hydrothermal products is often called hydrochar or hydrothermal char which underlined for wet process. The four major fibre constituent including cellulose, hemicellulose, lignin and extracted material were extracted at different condition of hot compressed water through hydrolysis reaction. Generally, hydrochar has a higher H/C molar ratio and lower aromatic structure than the biochar, and it has less fused aromatic structures [5]. The hydrothermal refinery can also develop more oxygen-functional groups (OFGs) on the char’s surface [9]. Likewise, typical the oxygen/carbon and hydrogen/carbon molar ratio of the hydrothermal char is considered higher when compared to the pyrolytic char. Nevertheless, the most previous reports in hydrothermal carbonization extend the potential of corncob as solid fuel application [10-11].

Activated carbon is considered as a highly porous substance which the carbonized char has undergone the activation so that it should be treated chemically or physically to develop pores structure or interconnected pores inside the carbon structure. The commonly used feedstocks for traditional activated carbon production include wood, coal, petroleum residues, peat, lignite and polymers. Those
kinds of products are very expensive and non-renewable [12]. Activated carbon is well known for its adsorption properties and is used in many applications and has a relate high market value. Hence, the bio-based activated carbon is always expected target materials produced from renewable material. The in-depth characteristics can have an increase in the correct upgrading. Therefore, the purpose of this study aims to explore the crucial characteristics including physical and chemical of carbonized corncob derived from hydrothermal and pyrolysis process that can be used to identify the potential of the renewable material for further surface enhancement.

2. Materials and methods

2.1 Materials
Corncob, is one of the immense amounts of agricultural wastes in Northern Thailand. It can be classified into 2 types as corn for consumer purpose and maize for animal feed purpose which has more amount than sweet corn. Corncob is used as feedstocks (see Figure 2). The input material is processed for size reduction and sieved with 2 - 0.84 mm. The prepared material is then dispersed in deionized water (DI) for the hydrothermal process.

2.2 Experiment
The slow pyrolysis conversion includes laboratory and mobile plant scale and yields the biochar. Laboratory scale pyrolysis is normally heated at 10°C/minute, 15 minutes of holding time and 1.5 l/minute of the N₂ flow rate of the rate (see Thermal System Research Laboratory, Chiang Mai University for more detail). The reaction temperature is performed at 480°C [13] and the previous study reported in the intersection of TGA and DTGA plot of corn stover at 420-470°C [14]. The mobile pyrolysis plant is operated in 2°C/minute with 190 minutes of holding time, as shown in Figure 3. As can be seen from Figure 4, the hydrochar is produced from 10 litres pressurized fixed vessel reactor at 250°C with the suspension of sieved corncob and deionized water (1:20 w/w). Consistent with the literature, this research found that the higher temperature tended to decrease a specific surface and produced a maximum S$_{BET}$ of 8.033 m$^2$g$^{-1}$ at 250°C, 20 min of residence time [8]. The holding time and heating rates are 100 minutes and 5°C/minute respectively. The hydrochar was rinsed by DI and dried in oven at 105°C, 24 hours. The processed chars are collected tightly for in the characterising step.

2.3 Physical and Chemical Characterization
Fibre analysis, Brunauer-Emmett-Teller surface area (BET surface area, S$_{BET}$) and Fourier Transform Infrared (FT-IR) analysis are characterized for feedstock and carbonized feedstock. The fibre analysis
and BET surface area are defined as physical characters. Analysing of fibre using a detergent method or is so-called the Neutral Detergent Fibre and the Acid Detergent Fibre and Acid Detergent Lignin were applied. Regarding the surface area analyzer, the model quanta chrome with model autosorb 1 MP was also employed to determine the BET surface area ($S_{\text{BET}}$). The $S_{\text{BET}}$ determination was operated with N$_2$ gas as adsorbate at 0.05-0.35 relative vapor pressure ($P/P_0$) with the temperature of the outgas at 150°C, and the outgas time spent was four hours. The operating time was at 46.8-57.9 minutes. The FT-IR is a crucial qualitative chemical characterization that has an estimation OFGs on the surface material.

![Mobile Pyrolysis Plant (Supported by ERDI-CMU)](image)

**Figure 3.** Mobile Pyrolysis Plant (Supported by ERDI-CMU).

![Hydrothermal fixed vessel reactor (Supported by ERDI-CMU)](image)

**Figure 4.** Hydrothermal fixed vessel reactor (Supported by ERDI-CMU).

### 3. Results and discussion

The four samples of Corncob with 2 - 0.84 mm, Corncob, Biochar-480” (pyrolyzed from the laboratory scale reactor), Biochar-380 (pyrolyzed from the Mobile Pyrolysis Plant) and “Hydrochar-250” (produced through hydrothermal conversion). They were then tested.

The physical appearance of Hydrochar-250 is slightly dark brown comparing to the corncob sample with a yellowish colour. The Biochar-480 and Biochar-380 are black as provided in Figure 5.
3.1 Fibre analysis

The determination of fibre constituents results in % of NDF, ADF and ADL. The interpretation of these compositions is the % of cellulose, hemicellulose and lignin as illustrated in Table 2.

| Sample          | NDF% | ADF% | ADL% | Cellulose | Hemicellulose | Lignin |
|-----------------|------|------|------|-----------|---------------|--------|
| Corncob         | 85.09| 44.30| 7.22 | 37.15     | 40.73         | 7.22   |
| Biochar-480     | 77.65| 74.95| 89.36| 89.36     | N/A           | 89.36  |
| Biochar-380     | 80.33| 74.89| 83.48| 83.48     | 2.51          | 78.78  |
| Hydrochar-250   | 91.91| 56.38| 10.26| 46.12     | 35.23         | 10.26  |

\[\text{Table 2. Fibre constituents}\]

a\text{NDF defined Neutral Detergent Fibre (cellulose, hemicellulose, lignin)}
b\text{ADF defined Acid Detergent Fibre (cellulose, lignin)}
c\text{ADL defined Acid Detergent Lignin (lignin)}

The current study found that the fibre constituents of feedstocks corncob are cellulose (37.15%), hemicellulose (40.73%) and lignin (7.22%) respectively. The composition of holocellulose includes cellulose and hemicellulose as a majority. Regarding fibre, the results indicate that the content of the hemicellulose is close to the cellulose. Biochar-480 and Biochar-380 that produced from pyrolysis have 89.36% and 78.78% of the lignin. However, both biochar differs in terms of the reaction temperature and can result in the retain lignin contents. The absolute decomposition of cellulose was found to be pyrolysis process of Biochar-480 and Biochar-380. The highest lignin with 89.36% produced from higher temperature pyrolysis process at 480°C is fully carbonized. The results of the detected hemicellulose through both pyrolysis process did not show a significant increase when compared to the lignin of Hydrochar-250. It shows a slight increase compared to the origin of raw material. Nevertheless, the holocellulose of Hydrochar-250 still has a high portion. The hydrothermal conversion, cellulose significantly started a hydrolysis at 200°C while hemicellulose fraction decomposed about 180°C and lignin that thermally more stable started a degradation at 280°C [15]. The study also suggested that the decomposition temperature should be under a hydrothermal of three components following the previous study illustrated the strong adaptation and optimization requirement. For this 250°C hydrothermal temperature, hemicellulose constituent decrease compared to origin of raw material during a slight increase of the lignin slightly increase. Although the findings from the fibre analysis indicate the better degradation for holocellulose (cellulose and hemicellulose), this study set out with the aim of the degradation of hemicellulose component to emerge from the analysis.

3.2 BET surface area ($S_{\text{BET}}$)

$S_{\text{BET}}$ analysis plays a crucial role in physical adsorption aspect of gases and vapours on porous carbon shown via actual adsorption isotherm [16]. The BET analysis directly measures surface area and pore size distribution. The $S_{\text{BET}}$ of both higher temperature pyrolysis (Biochar-480 and Biochar-380) are lower than the hydrochar, Hydrochar-250, while higher in BET C-constant (see Table 3).
Table 3. $S_{\text{BET}}$, BET C-constant and fibre composition.

| Sample          | $S_{\text{BET}}$ (m$^2$ g$^{-1}$) | BET C-constant | Cellulose (%) | Hemicellulose (%) | Lignin (%) |
|-----------------|----------------------------------|----------------|---------------|------------------|------------|
| Corncob         | 16.13                            | 2.49           | 37.15         | 40.73            | 7.22       |
| Biochar-480     | 7.66                             | 6.46           | N/A           | 2.69             | 89.36      |
| Biochar-380     | 6.12                             | 8.11           | N/A           | 2.51             | 78.78      |
| Hydrochar-250   | 11.53                            | 3.98           | 46.12         | 35.23            | 10.26      |

The hydrothermal carbonized of Palm Empty fruit bunches (EFB) developed $S_{\text{BET}}$ of 6.079, 8.033 and 2.043 m$^2$ g$^{-1}$ with 150, 250 and 350°C of reaction temperature and 20 minutes of the reaction time. The results compared with the EFB shown 1.478 m$^2$ g$^{-1}$ of $S_{\text{BET}}$ [7]. The $S_{\text{BET}}$ of corn stover’s carbonized char derived at 550°C, 15 mins pyrolysis and 250°C, 4 hours hydrothermal are 12 and 4 m$^2$ g$^{-1}$ respectively [17]. As can be seen from Table 3, there are the different trend in this study. Notably, the characters of surface material still combined the point of view of physical properties (fibre contents and $S_{\text{BET}}$) and chemical properties.

3.3 FT-IR Characteristics

FT-IR technique is crucial chemical characterization and aims to find the OFGs on material surface. The acidic carbon-oxygen surface groups of activated carbons make the carbon surface hydrophilic behaviour and polar in character [18]. The vibration of the functional group in the material that absorbed the infrared radiation at a specific frequency will be detected. These FT-IR spectrums plot the relation of wavenumber (cm$^{-1}$) and % transmittance.

From the FT-IR spectrums in Figure 6, it represents the distinction of corncob and biochar. Vibrational band of Biochar-480 and Biochar-380 were quite flat and is in the range of 3500-1500 cm$^{-1}$ especially Biochar-480 corresponding with the higher reaction temperature (O-H stretching representing the Hydroxyl, 3200 cm$^{-1}$). The spectra range of 1300-500 cm$^{-1}$ indicates the aromatic chemical skeleton and its result relate to 89.36% and 78.78% lignin in Biochar-480 and Biochar-380 respectively differ vividly from corncob. The band of 1205 and 1103 cm$^{-1}$ indicated the functional group of C-O stretching and it was found the vibration in lignin. The range was at 875-850 cm$^{-1}$ to testify the aromatic region.

Figure 6. FT-IR spectrums of Corncob, Biochar-480 and Biochar-380
FT-IR spectra of Hydrochar-250 represents in Figure 7 was very similar to the spectra of Corncob given in this study. The region at 1725 cm\(^{-1}\) of C=O stretching functional group represents the vibration band in hemicellulose. This can be found in corncob which can decreases in the intensity of the Hydrochar-250. The FT-IR result of pure cellulose also indicated the higher C=O compound containing while hemicellulose contained the O-H and C-O composition [19]. The interpretation of this result can be verified by 35.23% of hemicellulose in Hydrochar-250 and was found to be lower than the 40.73% of hemicellulose in Corncob. It can thus be suggested that can enhance the increasing of the oxygenated surface functional group.

Figure 7. FT-IR spectrums of Corncob and Hydrochar-250

3.4 Discussion
The comparison of FT-IR spectrums of 4 samples involved Corncob, Biochar-480, Biochar-380 and Hydrochar-250. As shown in Figure 8, we can see the critical disparity of carbonized corn cob material from the thermochemical biomass conversion process are the pyrolysis and hydrothermal carbonization. Figure 8 presents the blue dash line as it showed the C=C stretching and C-H bend functional group interpreted as the aromatic skeletal in lignin which has less polar properties. Oxygenated functional groups (OFGs) on surface material has the polar behaviour can be represented in following bands with red dash line: 3200 cm\(^{-1}\) (O-H stretching representing the hydroxyl, carbonyl groups (acid properties), alcohol (cellulose) or phenol (lignin)), 1725 cm\(^{-1}\) (C-O stretching representing the vibration in hemicellulose) found in the origin of raw material. Also, it showed a decrease of the intensity of the Hydrochar-250 but has less in Biochar-480 and Biochar-380 corresponding to fibre content results, 1240 cm\(^{-1}\) (C-O stretching representing the hemicellulose esters), 1205 cm\(^{-1}\) (C-O vibration in lignin). Besides, it has a more distinct peak of both biochar with higher lignin content and polymerized new aromatic portion.

The biochar through both high-temperature pyrolysis has a high lignin content and it demonstrated complete carbonized char with the S\(_{BET}\) range of 7.66 and 6.12 m\(^2\) g\(^{-1}\) for laboratory scale and mobile plant respectively. The hydrothermal char is partially carbonized with the S\(_{BET}\) of 11.53 m\(^2\) g\(^{-1}\), resulting in the degrading of the hemicellulose. Therefore, this is a critical point for optimization the degradation of hemicellulose component. The quantity of oxygen component on the surface of the carbon material is related to the increase in hydrophilic behaviour. The aromatic skeletal of both biochars demonstrated new polymerized aromatic structure.
4. Conclusion

A limitation of this study is that physical and chemical characteristics of carbonized corncob in producing precursor material for the bio-based activated carbon was an uncontrolled factor. The evidence from this study suggested that the identification of the potential of the material for surface enhancement should be taken into consideration. The findings of this study suggest that the analytical method and the optimization process includes the fibre compositions, $S_{BET}$ and FT-IR. The oxygenated functional surface groups (OFGs) of biochar and hydrochar has also analysed to provide the baseline for carbon activation. The adsorption ability does not only relate to the surface area defined as physical property but it also strongly involves the OFGs defined as chemical property which prominent electrostatic interaction in nature. The higher OFGs and higher $S_{BET}$ of hydrothermal char show significant results than biochar. This study set out with the aim of optimizing the hydrothermal conversion and analysing the crucial physical and chemical characteristics with a providing of the baseline for carbon surface activation of the renewable material.

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References

[1] Chen H 2014 Biotechnology of Lignocellulose: Theory and Practice (Dordrecht : Springer Netherlands) pp 25-71
[2] Dinjus E, Kruse A and Tröger N 2011 Chem. Eng. Technol. 34 2037-2043
[3] Dimitriadis A and Bezergianni S 2017 Renew. Sust. Energ. Rev. 68 113-125
[4] Version 2.1 of the IBI Biochar Standards International Biochar Initiative 2015 https://biochar-
international.org/characterizationstandard/, accessed on 1 December 2020
[5] Kambo H S and Dutta A 2015 Renew. Sust. Energ. Rev. 45 359-378
[6] Qian K Kumar A Zhang H Bellmer D and Huhnke R 2015 Renew. Sust. Energ. Rev.
[7] Srilek N and Aggarangsi P 2020 IOP Conf. Ser.: Earth Environ. Sci. 495 012026
[8] Parshetti G K Hoekman S K and Balasubramanian R 2013 Bioresource. technol. 135 683-689
[9] Liu Z Zhang F S and Wu J 2010 Fuel. 89 510-514
[10] Arellano O Flores M Guerra J Hidalgo A Rojas D and Strubinger A 2016 Chem. Eng. Trans.
[11] Nakason K Panyapinyopol B Kanokkantapong V Viriya-empikul N Kraithong W and Pava-
kesant P 2018 Biomass. Convers. Biorefin. 8 199-210
[12] Chen Y Zhu Y Wang Z Li Y Wang L Ding L and et al. 2011 Ad. Colloid. Interfac. 163
[13] Srilek N and Aggarangsi P 2019 Int.J.Eng.Adv.Technol. 8 1089-1098
[14] Kumar A Wang L Dzenis Y A Jones D D and Hanna M A 2008 Biomass. Bioenerg. 32 460-467
[15] Funke A and Ziegler F 2010 Biofuel. Bioprod. Bior. 4 160-177
[16] Wang T Zhai Y Zhu Y Li C and Zeng G 2018 Renew. Sust. Energ. Rev. 90 223-247
[17] Sohi S P Krull E Lopez-Capel E and Bol R 2010 Adv. Agron. 105 47-82
[18] Zhang L Wang Q Wang B Yang G Lucia L A and Chen J 2015 Energ. Fuel. 105 872-876
[19] Yang H Yan R Chen H Lee D H Zheng C 2007 Fuel. 86 1781-1788