Preparation of Activated Carbons from Hydrolyzed *Dipterocarpus alatus* Leaves: Value Added Product from Biodiesel Production Waste

Warangkana KHANGWICHIAN※1, Sudarat PATTAMASEWE※1, Atip LAUNGPAIROJANA※1, Rattanaporn LEESING※2, Andrew J. HUNT※3, and Yuvarat NGERNYEN※1†

(Received December 28, 2020)

A solid waste is generated in the production of biodiesel from the leaves of the *Dipterocarpus alatus* tree. This waste was hydrolyzed by oleaginous yeast and was employed as the precursor for preparing activated carbon by chemical activation. This work investigated the effect of types of chemical agent i.e. acid (H₃PO₄ and HNO₃), base (KOH and NaOH) and chloride (ZnCl₂ and FeCl₂) on the porous properties of the resulting activated carbons. The dry leaves prior to hydrolysis were also used for comparison. The experiment was conducted as an activator to a biomass impregnation ratio of 1:2 for 1 h, followed by carbonization at 500 °C for 1 h. The raw materials and activated carbons were analysed using proximate analysis and the porous properties by using nitrogen adsorption-desorption isotherms and thermogravimetric analysis (TGA). According to proximate analysis, fixed carbon contents of 9.27 and 16.25 dry wt% were found for the hydrolyzed material and dry leaves, respectively. This indicated that both materials served as good precursors to produce carbons. The results of porous properties show that the maximum surface area of 456 m²/g was produced using ZnCl₂ activation. The prepared carbons from hydrolyzed leaves had surface areas comparable with carbons prepared from dry leaves for ZnCl₂, H₃PO₄, HNO₃ and NaOH activation. However, activation of hydrolyzed leaves with FeCl₂ and KOH gave activated carbons with a lower surface area than dry leaves. Moreover, *Dipterocarpus alatus* leaf activated carbons had a higher surface area than several other literature examples of activated carbons. Therefore, hydrolyzed *Dipterocarpus alatus* leaves are a good precursor for the preparation of economical activated carbon.

Key Words

*Dipterocarpus alatus* leaves, Activated carbon, Chemical activation, Surface area

1. Introduction

*Dipterocarpus alatus* is a tree found in Thailand and other Southeast Asian countries. It is a medicinal plant used for the treatment of skin, rheumatism and liver diseases ¹. Its dry leaves can be hydrolyzed by acid to get hydrolysate which contains fermentable sugar. The hydrolysate is used as the carbon source of oleaginous yeast fermentation for biodiesel production. Then, the remaining hydrolysate from the fermentation process becomes biomass waste. Therefore, the sustainable conversion of this biomass waste into useful products is needed. Many researchers try to convert biomass waste from municipal, agricultural, forest or industry into a precursor to produce activated carbons due to their low-cost and wide availability.

Activated carbon is a widely used adsorbent due to its high surface area, high pore volume, large adsorption capacity and fast adsorption kinetics. The precursors used to produce activated carbons are materials that contain carbon such as coal, agricultural wastes, woody biomass, waste tires, sewage sludge, animal manure, bone, etc. In principle, there are two methods for preparing activated carbon: physical and chemical activation. Physical activation
has two steps, the raw material is firstly carbonized under atmosphere in the absence of oxygen. Then, the resulting carbonized material or char is activated in the presence of activating agents such as CO₂, steam or air. For chemical activation of the one step method, the raw material is impregnated with chemicals such as ZnCl₂, KOH, NaOH, H₂SO₄ or H₃PO₄, etc. Then, the impregnated material is carbonized under atmosphere in the absence of oxygen. The carbonization and activation step proceeds simultaneously in this activation method.

There has been some research that has used leaves of plants to produce activated carbons, for example, coconut leaves ⁵, Typha orientalis leaves ⁶, banana leaves ⁷, or sugar cane leaves ⁸. However, there has been no research that uses Dipterocarpus alatus leaves to prepare activated carbon. Moreover, the results obtained by previous researchers showed that different biomass materials have different reactivity to different activating agents. For example, Ravichandran et al. ⁶ studied the preparation of activated carbons from Casuarina equisetifolia fruit waste by activating with H₃PO₄, KOH and ZnCl₂. The results showed that H₃PO₄ was the best activating agent with the maximum surface area. In addition, Yagmur et al. ⁷ activated oleaster fruit with KOH and ZnCl₂ and found that ZnCl₂ gave activated carbon with a higher surface area. Therefore, the objective of this study is to determine the effect of different chemical activations on the preparation of activated carbons from hydrolyzed Dipterocarpus alatus leaves and for dry leaves as a comparison. The physicochemical properties of prepared activated carbons were investigated using proximate analysis and porous characteristics.

2. Experiments

Hydrolyzed Dipterocarpus alatus leaves (DL) were collected from acid hydrolysis before fermentation process of biodiesel production. Briefly, DL was subjected to dilute acid hydrolysis (1.5% v/v H₂SO₄) with a solid amount of 10% (w/v) at 120 °C for 15 min. DL solid residues or hydrolyzed leaves were then separated by filtration, then were washed with distilled water and dried at 70 °C for 6 h. These hydrolyzed leaves were shown in Fig. 1 (b) and used in their original form. For dry leaves (Fig. 1 (a)), these were cut and sieved to size 4 mm (mesh no. 5) as shown in Fig. 1 (c).

Activated carbons were prepared by using the one step activation method. The precursors were individually treated by direct impregnation with chemical activating agents including chloride (ZnCl₂ and FeCl₃), acid (H₃PO₄ and HNO₃) and base (KOH and NaOH). The conditions of activation and carbonization were 5 g leaves, 30 wt% activating agent, precursor: activator ratio was 1:2, impregnation time 1 h, then subjected to carbonization at 500 °C for 1 h under N₂ atmosphere. After activation, the samples were removed from the furnace and allowed to cool to room temperature. After that, the activated carbon was washed with distilled water to remove excess activating agent. Then the activated carbon was dried at 120 °C in an oven and stored in a zip lock bag. The activated carbon production yield (wt%) was determined through the mass of activated carbon divided by the mass of dry leaves.

The thermal properties of the precursors were studied by the thermogravimetric analysis (TGA, DTG-60H, Shimadzu) from room temperature up to 950 °C at a heating rate of 10 °C/min with a N₂ flow rate of 60 mL/min. The chemical compositions of the raw material and
activated carbon were determined by proximate analysis. The moisture content was determined using ASTM D2867 by drying the samples at 150 °C for 3 h in an oven (UNE 500, Memmert). For volatile matter determination, according to ASTM D5832-98, the sample was heated at 900 °C for 30 min in a muffle furnace (TM3-550, VULCAN). The sample was heated in a muffle furnace from room temperature to 800 °C and held for 2 h to determine ash content. Finally, the fixed carbon was estimated by difference.

The porosity properties of activated carbons were measured by nitrogen gas adsorption/desorption isotherms at –196 °C using Surface area and Porosity Analyzer (ASAP2460, Micromeritics). The BET surface area ($S_{BET}$) was obtained by the Brunauer–Emmett–Teller method. The total pore volume ($V_T$) was calculated from the adsorption amount of N$_2$ at a relative pressure ($P/P_0$) of about 0.99. The micropore volume ($V_{mic}$) was determined by the Dubinin-Radushkevich (DR) equation and the mesopore volume was obtained by deducting the micropore volume from the total pore volume. The average pore size was obtained by the Barrett–Joyner–Halenda (BJH) method.

### 3. Results and Discussion

Data from the proximate analysis of hydrolyzed and dry leaves are listed in Table 1. The analysis is given on a dry basis since the moisture content of both precursors was around 12 wt%. As can be seen from the table, the proximate compositions depend on the starting leaves. The hydrolyzed compositions show higher values of volatile matter and ash contents, consequently, lower fixed carbon. These carbon contents are comparable with other biomass that was used as raw materials to produce activated carbons such as 14.65 wt% of eucalyptus wood [8], 15.41 wt% of cedar sawdust [9], 15.67 wt% of teak saw dust [9] or 17.3 wt% of barley straw [10].

Fig. 2 presents the thermogravimetric analysis (TGA) of hydrolyzed and dry leaves. It is obvious that hydrolyzed leaves have a similar thermal behavior when compared to dry leaves. The mass loss can be divided into four stages: < 150 °C, 150–380 °C, 380–500 °C and > 500 °C. The first stage of mass loss is resulting from moisture elimination. As exhibited in the figure, hydrolyzed leaves had a higher moisture content than dry leaves which agrees with proximate analysis (Table 1). The second stage has a greater mass loss representing light volatile compounds, which resulted from the degradation of cellulose and hemicellulose. The third stage indicates the decomposition of lignin, which has a high stability structure. The weight loss of the final stage is very small indicating that the main structure of char is formed. Therefore, the proper temperature for preparation of activated carbon should be greater than 500 °C. Consequently, this study uses carbonization

| Sample          | Moisture (wt%) | Proximate analysis (wt%, dry basis) |  |
|-----------------|----------------|-----------------------------------|---|
|                 |                | Volatile matter | Ash | Fixed carbon |
| Hydrolyzed leaves | 12.61          | 78.51              | 12.22 | 9.27         |
| Dry leaves      | 12.09          | 74.50              | 9.45  | 16.05        |

**Fig. 2** TGA curves of hydrolyzed and dry leaves
temperature of impregnated samples of 500°C.

The N₂ isotherms of prepared activated carbons are shown in Fig. 3. The isotherms with a hysteresis loop of all samples are typical Type IV according to IUPAC classification. The amount of adsorbed nitrogen was found to increase rapidly at low relative pressure, then the slope of the plateaus gradually increases with higher relative pressures. This indicates that the prepared activated carbons are mesoporous materials. The hysteresis loop is associated with the capillary condensation of N₂ in mesoporous structure. The low N₂ adsorbed amount for KOH activation of hydrolyzed leaves and HNO₃ activation of dry leaves was observed, indicating that these samples have a low porosity structure.

Textural parameters of the prepared activated carbons are presented in Fig. 4 and Table 2. Based on the results, it is evident that different activating agents produced significantly different characteristics of activated carbons. The BET surface area of activated carbons prepared from hydrolyzed leaves follows the sequence ZnCl₂ > H₃PO₄ > NaOH ≈ FeCl₂ ≈ HNO₃ > KOH. The results obtained from the hydrolyzed leaves are then compared with the activated carbons prepared from the dry leaves. It is found that the surface area of hydrolyzed leaves activated carbons are higher than those for the dry leaves if activated with ZnCl₂, H₃PO₄, HNO₃ and NaOH. However, FeCl₂ and KOH
activation show the opposite trend. The different obtained surface area between hydrolyzed leaves and dry leaves may be due to the pre-treatment of leaves with H₂SO₄ during the hydrolysis process.

The analysis of the micropore and mesopore volumes presented in Table 2 shows a predominance of mesopore in the activated carbons produced with HNO₃, KOH and NaOH. The obtained results of total pore volume show a similar trend as with the results for the surface area. The IUPAC classifies the micropore, mesopore and macropore of the adsorbents depending on the pore size: < 2 nm, 2–50 nm and > 50 nm, respectively. Therefore, activated carbons prepared from HNO₃, KOH and NaOH activation have a mesoporous structure while ZnCl₂, FeCl₂ and H₃PO₄ produce mesoporous structure activated carbons with a tendency to be microporous. Adsorption process largely depends on the size matching between adsorbate molecules and activated carbon pores.

The production yields are also shown in Table 2. The obtained yields vary between 40 and 67 wt%. It is evident that hydrolyzed leaves give higher activated carbon production yields than dry leaves. These results agree with weight loss in final stage of TGA profiles (Fig. 2). In the activation and carbonization step, the raw materials were decomposed and liberated most of the non-carbon elements, leaving behind a rigid carbon skeleton in the form of aromatic sheets and strips. Generally, high carbon content favors high yields of activated carbon. As shown in Table 2, the yields of activated carbon obtained from both raw materials are in the range of 40–67 wt%. The yields are similar with activated carbons prepared from sawdust (30–50%) 12), sago palm bark (30–65%) 13), tamarind seed (52–82%) 14), soybean straw (78%) 15) that use chemical activation. The balance between the surface area and the yield of the obtained activated carbon should be considered to select the optimum activation conditions for the desired activated carbon pore structure and economic production 16).

It is interesting to note that chemical activation by ZnCl₂ resulted in an activated carbon with the highest surface area (456 m²/g) and demonstrated higher surface area than other activated carbons reported in the literature (Table 3). For example, Ravichandran et al. 6) activated Casuarina equisetifolia fruit waste with the one step process by using H₃PO₄, KOH and ZnCl₂ which resulted in activated carbons with surface areas of 263, 218 and 62 m²/g, respectively. Lacerda et al. 17) used carnauba palm leaves, 

### Table 2 Yield, pore volume and pore size of activated carbons prepared from hydrolyzed (H) and dry (D) leaves

| Activating agent | Yield (wt%) | Vmic | Vmeso | VT | DP (nm) |
|------------------|-------------|------|-------|----|--------|
|                  | H | D | H | D | H | D | H | D | H | D | H | D |
| ZnCl₂            | 66 | 44 | 0.22 (73%) | 0.19 (83%) | 0.08 (27%) | 0.04 (17%) | 0.30 | 0.23 | 2.63 | 2.28 |
| FeCl₂            | 58 | 48 | 0.03 (38%) | 0.11 (78%) | 0.05 (62%) | 0.03 (22%) | 0.08 | 0.14 | 4.47 | 2.99 |
| H₃PO₄            | 67 | 42 | 0.11 (52%) | 0.10 (67%) | 0.10 (48%) | 0.05 (33%) | 0.21 | 0.15 | 3.60 | 2.76 |
| HNO₃             | 50 | 42 | 0.03 (30%) | 0.02 (29%) | 0.07 (70%) | 0.05 (71%) | 0.10 | 0.07 | 5.89 | 5.13 |
| KOH              | 60 | 40 | 0.01 (20%) | 0.10 (71%) | 0.04 (80%) | 0.04 (29%) | 0.05 | 0.14 | 13.41 | 3.46 |

### Table 3 Comparison of surface area of obtained activated carbons with literature

| Raw material | Chemical activating agent | Surface area (m²/g) |
|--------------|--------------------------|---------------------|
| Hydrolyzed Dipterocarpus alatus leaves | ZnCl₂ | 456 |
| Casuarina equisetifolia 6) | ZnCl₂ | 62 |
| | KOH | 218 |
| | H₃PO₄ | 263 |
| Carnauba palm leaves 17) | H₃PO₄ | 402 |
| | CaCl₂ | 431 |
| Endocarp of macauba seeds 17) | H₃PO₄ | 371 |
| | CaCl₂ | 265 |
| Pine nutshell 17) | H₃PO₄ | 296 |
| | CaCl₂ | 290 |
| Rice husk 18) | H₃PO₄ | 420 |
| | KOH | 514 |

J. Jpn. Inst. Energy, Vol. 100, No. 10, 2021
endocarp of macauba seeds and pine nutshell as raw materials to prepare activated carbons using H$_3$PO$_4$ activation. They found that the surface area of resulting activated carbons were 402, 371 and 296 m$^2$/g, respectively. Moreover, activation of these materials with CaCl$_2$ resulted in activated carbons with surface areas of 431, 265 and 290 m$^2$/g, respectively. Therefore, the activated carbon obtained in this study could be applicable as an adsorbent for the adsorption process.

4. Conclusions

In this study, hydrolyzed and dry Dipterocarpus alatus leaves were used as precursors to prepare activated carbons. The type of chemical activating agents (ZnCl$_2$, FeCl$_2$, H$_3$PO$_4$, HNO$_3$, KOH or NaOH) had great effects on the porous properties of the prepared activated carbons. The BET surface area was found to be higher in the case of activated carbons prepared from hydrolyzed leaves with ZnCl$_2$, H$_3$PO$_4$, HNO$_3$ and NaOH activation. The activation with ZnCl$_2$ produced a high surface area and pore volume for both raw materials. The BET surface area and total pore volume were achieved in their highest value of 456 m$^2$/g and 0.30 cm$^3$/g, respectively, with ZnCl$_2$ activation of hydrolyzed leaves. As a conclusion, hydrolyzed Dipterocarpus alatus leaves, waste from biodiesel production, can be utilized as a cheap raw material to produce activated carbon.

Acknowledgement

The authors gratefully acknowledge the support of the National Research Council of Thailand for funding this research.

References

1) Yongram, C.; Tadtong, S.; Weerapreeyakul, N.; Puthongking, P., *Journal of Thai Traditional&Alternative Medicine*, 17, 437-446 (2019)

2) Rashid, R. A.; Jawad, A. H.; Ishak, M. A. B. M.; Kasim, N. N., *Sains Malaysiana*, 47, 603-610 (2018)

3) Anisuzzaman, S. M.; Joseph, C. G.; Daud, W. M. A. B. W.; Krishnaiah, D.; Yee, H. S., *Int. J. Ind. Chem.*, 6, 9-21 (2015)

4) Martín-González, M. A.; Susial, P.; Pérez-Pena, J.; Dona-Rodríguez, J. M., *Revista Mexicana de Ingeniería Química*, 12, 595-608, (2013)

5) Patil, D.; Chavan, S.; Barkade, S., *International Journal of Engineering Research & Technology*, 2, 1-5 (2013)

6) Ravichandran, P.; Sugumaran, P.; Seshadri, S.; Basta, A. H., *R. Soc. Open Sci.*, 5, 171578 (2018)

7) Yagmur, E.; Golce Y.; Tekin S.; Semerci, N. I.; Aktas, Z., *Fuel*, 267, 117232 (2020)

8) Heidari, A.; Younesi, H.; Rashidi, A.; Ghoreyshi, A., *J. Taiwan Inst. Chem. Eng.*, 45, 579-588 (2014)

9) Ramírez, A. P.; Giraldó, S.; Ulloa, M.; Florez, E.; Acelas, N. Y., *IOP Conf. Series: Journal of Physics: Conf. Series*, 935, 012012 (2017)

10) Pallerés, J.; González-Cencerrado, A.; Arauzo, I., *Biomass and Bioenergy*, 115, 64-73 (2014)

11) Peng, P.; Li, J.; Wang, H.; Xu, Z., *ACS Omega*, 5, 24064-24072 (2020)

12) Zhang, H.; Yan, Y.; Yang, L., *Adsorption*, 16, 161-166 (2010)

13) Erabee, I. K.; Ahsan, A.; Zularisam, A. W.; Idrus, S.; Daud, N. N. N.; Arunkumar, T.; Sathiyamurthy, R.; Al-Rawajfeh, A. E., *Engineering Journal*, 21, (2017), DOI: https://doi.org/10.4186/ej.2017.21.5.1

14) Mopoung, S.; Moonsri, P.; Palas, W.; Khumpai, S., *The Scientific World Journal*, Article ID 415961 (2015)

15) Yuliusman; Nasruddin; Nugroho, Y. W.; Na’fan, H.; Sinto J., E3S Web of Conferences, 67, 03019 (2018)

16) Wu, L.; Shang, Z.; Wang, H.; Wan, W.; Gao, X.; Li, Z.; Kobayashi, N., *Journal of Material Cycles and Waste Management*, 20, 1676-1688 (2018)

17) Lacerda, V. da S.; López-Soto, J. B.; Correa-Guimaraes, A.; Hernández-Navarro, S.; Sánchez-Bárcenas, M.; Navas-Gracia, L. M.; Martin-Ramos, P.; Martin-Gil, J. J., *Environ. Manag.*, 155, 67-76 (2015)

18) Kennedy, L. J.; Mohan das, K.; Sekaran, G., *Carbon*, 42, 2399-2407 (2004)

19) Khezami, L.; Chetouani, A.; Taouk, B.; Capart, R., *Powder Technology*, 157, 48-56 (2005)