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Research Article

Low cost activated carbon prepared from *Dipterocarpus alatus* fruit

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ABSTRACT

Dipterocarpus alatus tree grows prolifically throughout Thailand and can be tapped to yield significant quantities of oil to be used as natural diesel. However, such practices lead to waste dried fruit dropping from the tree. At present, there is no utilization of this dropped fruit, therefore cost-effective processes need to be applied to obtain higher value products from this waste. A possible to utilization is the conversion to activated carbon for adsorption applications including the removal of heavy metals, dyes, and other contaminants in water purification and other decontamination process. A major challenge of current commercial activated carbon is the high production cost and recently it has been shown that chemical activators comprise a significant proportion of these costs. This feasibility study investigates the use of *Dipterocarpus alatus* fruit as raw material to produce low cost activated carbon adsorbents. Activated carbon was prepared from *Dipterocarpus alatus* fruit: endocarp, mesocarp, and wing by chemical activation with $ZnCl_2$, $FeCl_3$, and KOH. Each part of the fruit was impregnated with 30 wt% activating agent at a ratio of 1:2 for 1 h and then carbonized at 500 ^oC for a further 1 h. The surface area, pore volume, and average pore size of the resulting carbons were characterized by nitrogen gas adsorption. Activation of mesocarp with $ZnCl_2$, KOH, and $FeCl_3$ gave activated carbons with the surface area of 447, 256, and 199 m^2/g, respectively. In the same way, $ZnCl_2$ activation gave a maximum surface area of 312 and 278 m^2/g for wing and endocarp, respectively. All of the aforementioned samples have an average pore size of around 2 nm. In contrast, KOH and $FeCl_3$ activation of wing and endocarp produced activated carbon with very low surface area (below 25 m^2/g), but with an average pore size of 5-14 nm. The maximum surface area of activated carbon prepared from *Dipterocarpus alatus* fruit was higher than some literature examples for activated carbon from other biomass. Consequently, *Dipterocarpus alatus* fruit demonstrated significant potential as a feedstock for the preparation of low cost activated carbons.

Key words: Dipterocarpus alatus fruit, activated carbon, chemical activation, surface area

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INTRODUCTION

Dipterocarpus alatus tree grows prolifically throughout Thailand and can be tapped to yield significant quantities of oil to be used as natural diesel. However, such practices lead to waste dried fruit dropping from the tree. At present, there is no utilization of this dropped fruit, therefore cost-effective processes need to be applied to obtain higher value products from this waste.

A possible to utilization is the conversion to activated carbon for adsorption applications including the removal of heavy metals, dyes, and other contaminants in wastewater treatment [1].

A major challenge of current commercial activated carbon is the high production cost and recently it has been shown that chemical activators comprise a significant proportion of these costs [2]. Significant research has focussed on reducing the production cost of activated carbon. Efforts to identify of low cost alternative precursors to traditional feedstocks such as coal have been extensively investigated. Agricultural and forest wastes such as corncob [3], cola nut shell [4], *Ficus carica* bast [5], plantain fruit stem [6], Macoré fruit shell [7], date seed [8] and *Eucalyptus camaldulensis* wood [9] have demonstrated great interest due to their accessibility and abundant availability. To the best of the author's knowledge no research on the preparation of activated carbon prepared from *Dipterocarpus alatus* fruit have been reported in the literature.

There are two methods for activated carbon production can be employed, physical and chemical activation. Physical activation consists of carbonization of the raw material followed by activation with steam, carbon dioxide or air at high temperature of 800–1000 ^oC. In the chemical activation method, the feedstock is soaked in a chemical activating agent such as

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H_3PO_4, $ZnCl_2$, KOH, NaOH and H_2SO_4 prior to carbonisation at temperatures in the range of 400–800 ^oC.

This preliminary study aims to demonstrate feasibility of the using of *D ipterocarpus alatus* fruit as raw material for the preparation of low-cost activated carbon. A one-step process, with lower activation temperature will be employed that leads to higher yields and development of extensive porosity [10]. The chemical activators $ZnCl_2$, $FeCl_3$ and KOH were selected for production of activated carbon in this work. In order to ensure that cost are kept low a maximum activator to biomass ratio of 2:1, was utilised in this study. The resultant activated carbons were determined their pore structure and proximate analysis.

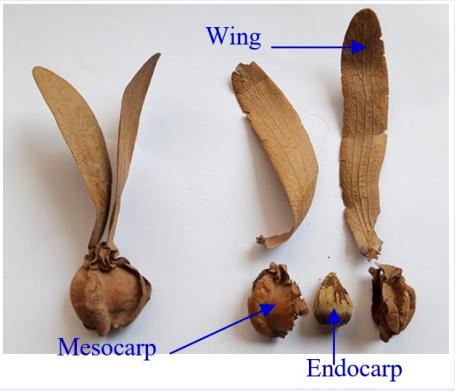

Figure 1: *D ipterocarpus alatus* fruit and its part.

MATERIALS AND METHODS

Materials

D ipterocarpus alatus fruits were collected from Khon Kaen University. The fruits divided into 3 parts: endocarp, mesocarp and wing as shown in Figure 1. Each part was cut into small piece and sieved with the size lower than 4 mm (mesh no. 5).

Preparation of activated carbon

10 g of the of *D ipterocarpus alatus* fruit sample was mixed with 30 wt% $ZnCl_2$, $FeCl_3$ or KOH at a impregnation ratio of sample:activating agent 1:2 for 1 h. It was noted that, at this ratio the chemicals were able to promote activation within the raw material, while leading to no excess unutilised activator. No drying step as employed and the resulting sample was carbonized inside fixed-bed stainless steel reactor (5 cm in the diameter and 30 cm in the height) at 500 ^oC for 1 h under high purity flow of nitrogen (200 cm^3/min). The chosen carbonization temperature was found from thermal analysis as explained in section 3.1. The sample was washed with distilled water until the solution was pH neutral. The carbon was then oven dried at 110 ^oC for 3 h and kept in air tight pack for further analysis. The yield of the activated carbon is defined as the ratio of mass of final activated carbon to that of the dried original sample (10 g).

Characterization

Thermal stability of endocarp, mesocarp and wing of *D ipterocarpus alatus* fruit samples were investigated by thermogravimetric analyser or TGA (TGA-50 Shimadzu). A typical analysis was conducted by heating a 10 mg sample up to 700 ^oC at a heating rate of 10 ^oC min^{-1} under N_2 at a purge rate of 10 ml min^{-1}.

In order to characterise the BET surface area, pore volume and average pore size of activated carbon, N_2 adsorption isotherm at –196 ^oC was determined by gas adsorption analyser (ASAP2460, Micromeritics). Adsorption data were obtained over the relative pressure or P/P^o ranging from 0.01 to 0.99. The sample was degassed in a vacuum at 250 ^oC for 5 h before adsorption test. Specific surface area (S_{BET}) was calculated using the Brunauer-Emmett-Teller equation. The total pore volume (V_T) was estimated at a P/P^o of 0.99. Micropore volume (V_{mic}) was determined using t-plot method. Mesopore volume (V_{meso}) was calculated by the different between total pore volume and micropore volume. Average pore size (D_P) was obtained by applying Barrett-Joyner-Halenda or BJH method.

Proximate analysis that include moisture, ash, volatile matters and fixed carbon of the raw material and activated carbon was carried out using standard method. The contents of volatile matters and moisture were determined based on ASTM D5832-98 by heated sample at 950 ^oC for 30 min and ASTM D2867 by heated sample at 150 ^oC for 3 h, respectively. For ash content, sample was heated at temperature of 800 ^oC for 2 h [11]. Finally, fixed carbon content calculated by the difference as 100 – moisture(%) – ash(%) – volatile matters(%).

RESULTS AND DISCUSSION

Properties of raw materials

The proximate analysis of each part of the *Dipterocarpus alatus* fruit based on the average of three samples was demonstrated in Table 1. For all parts, the content showed similar values; with a moisture content of 8 wt%, volatile matter content of 72–73 wt%, ash 2 wt% and fixed carbon of 16–17

wt%. *D ipterocarpus alatus* fruit exhibit low ash and high volatile contents, similar to other biomass wastes that have already been reported in literature. The fixed carbon content is also higher or comparable with those materials such as oil palm wood (9.63 wt%)[12], kenaf core fibre (11 wt%)[13], waste tea (11.34 wt%)[14], *Eucalyptus camaldulensis* wood (14.65 wt%)[9], bagasse (16.4 wt%)[15], barley straw (17.3 wt%)[16] and rice-straw (17.8 wt%)[17]. Therefore, *D ipterocarpus alatus* fruit is a suitable feedstock for preparation of activated carbon.

The thermal behaviour as analysed by TGA for the endocarp, mesocarp and wing of *Dipterocarpus alatus* fruit are presented in Figure 2. The TG curve of *D ipterocarpus alatus* fruit is like that of any other biomass comprised mainly of cellulose, hemicellulose and lignin. It indicates three mass loss steps: the evaporation of adsorbed moisture up to 110 ^{o}C, the decomposition of hemicellulose in the biomass at 200–340 ^{o}C and the cellulose decomposition at about 380–500 ^{o}C[9]. It can also be seen that the moisture the evaporated from the structure 10 wt%, which is consistent with the results of proximate analysis. Moreover, the main decomposition occurring between 200–480 ^{o}C is the devolatilisation process resulting in the remaining of carbon content in the structure. Therefore, the suitable temperature for preparation of activated carbon from this fruit should be higher than these temperatures, therefore 500 ^{o}C was used to prepare activate carbon in this work.

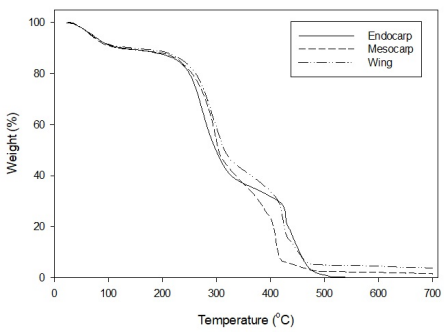

Figure 2: Thermogravimetric analysis plot of each part of the *D ipterocarpus alatus* fruit

N_2 adsorption isotherms and pore structure development

Figure 3 shows the nitrogen gas adsorption-desorption isotherms at –196 ^{o}C of the prepared activated carbons. It is noted that adsorption-desorption isotherms of KOH activation for endocarp part and $FeCl_3$ activation for wing part were not shown due to very low adsorption volumes. All the adsorption isotherms are of type I according to IUPAC or the International Union of Pure and Applied Chemistry classification, which is characteristic of microporous structures[16]. The adsorption rapidly increases at low relative pressures (P/P^o < 0.1). The isotherms also exhibited small hysteresis loops implying the existence of mesoporosity. Therefore, all prepared activated carbons are of a micro-mesoporous structure. Although the adsorption isotherms of all samples are similar classification, the adsorption capacities are different depend on type of activating agents. It was observed that $ZnCl_2$ activation had higher N_2 adsorption than that of $FeCl_3$ and KOH activation. The low N_2 adsorbed amount for KOH activation of wing was observed, indicating a less porous structure. Table 2 is summarised the yield, S_{BET}, V_{mic}, V_{meso}, V_T and D_P of all resulting activated carbons. A maximum yield of 43–51 wt% obtained from $FeCl_3$ activation while $ZnCl_2$ gave the yield of 32–38 wt%. The minimum yield of 16–25 wt% was recorded for KOH activation. As mentioned before, *D ipterocarpus alatus* fruit is a lignocellulosic material, with cellulose, hemicellulose and lignin as the main components. In activation and carbonization steps, these components decompose and liberate the non-carbon elements that is hydrogen, oxygen and nitrogen in the form of liquids and gases, remaining the carbon content[18]. This causes a decrease in mass of the resulting activated carbon when compare with the original material.

For all parts of the *Dipterocarpus alatus* fruit, textural analysis showed that the activated carbons synthesized with $ZnCl_2$ had greater porosity in term of surface area and total pore volume compare to $FeCl_3$ and KOH activated samples. It was demonstrated that activated mesocarp with $ZnCl_2$ provide best properties of activated carbon, with BET surface area of 447 m^2/g and total pore volume of 0.265 cm^3/g. Furthermore, $ZnCl_2$ and $FeCl_3$ activation produced activated carbon with mostly micropore except in the case of $FeCl_3$ activation of wing part. For KOH activation, resulting activated carbons demonstrated mainly mesoporous except for the mesocarp materials.

The results from Table 2 demonstrate that chemical activation of endocarp and wing with KOH and activation of wing with $FeCl_3$ obtaining activated carbons with low surface area and pore volume but with a pore size of 5–14 nm. It is suggested that large pore size adsorbent is suitable for adsorbed large molecule adsorbate in adsorption processes. Therefore, the use of such materials for the adsorption of large molecules

Table 1: Proximate analysis (wt%) of each part of *Dipterocarpus alatus* fruit

	Endocarp	Mesocarp	Wing
Moisture	8.26	8.74	8.12
Volatile Matter	73.02	72.35	72.08
Ash	2.70	2.21	2.54
Fixed carbon	16.02	16.70	17.26

may overcome diffusion limitations resulting from the small pore size of traditional activated carbons.

The adsorbent pores are classified into three groups: micropore (diameter < 2 nm), mesopore (diameter 2–50 nm) and macropore (diameter > 50 nm) according to the definition of IUPAC. Table 2 demonstrates that the average pore diameter of all activated carbons is between 2 and 14 nm, indicating they are a microporous and mesoporous materials.

For all activating agents, different parts of *D ipterocarpus alatus* fruit produced activated carbons with varying surface areas and pore volumes. This may be due to the different physical structure of each part. For example, mesocarp is hard compared to the wing part which is very thin.

The maximum surface area of activated carbon prepared from mesocarp of *Dipterocarpus alatus* fruit (447 m^2/g) was higher than some chemical activated carbons from biomass by such as palm flower (9.57 m^2/g) [19], branches of walnut wood (32 m^2/g) [20], oak wood (68 m^2/g) [21], peanut shell (89 m^2/g) [22], pine nut shell (296 m^2/g) [23], kenaf core fiber (299 m^2/g) [13], macauba seed endocarp (371 m^2/g) [23] and carnauba palm leave (431 m^2/g) [23].

Proximate analysis

According to Table 3, the volatile matters in activated carbon decreased from starting material while fixed carbon increased. This was expected as devolatilisation leads to the loss of oxygen and hydrogen in the form of water during carbonisation and activation resulted in sample containing predominantly carbon. Furthermore, ash content increased from starting material while moisture content decreased. These results were similar to that reported in the work of Ahmad et al. [12]. Low amounts of moisture, volatile matter and ash contents indicate that the activated carbon should be a good raw material for adsorbents [6]. Ash content reduces the activity of activated carbon the lower the ash content; the better activated carbon will be for adsorption [6].

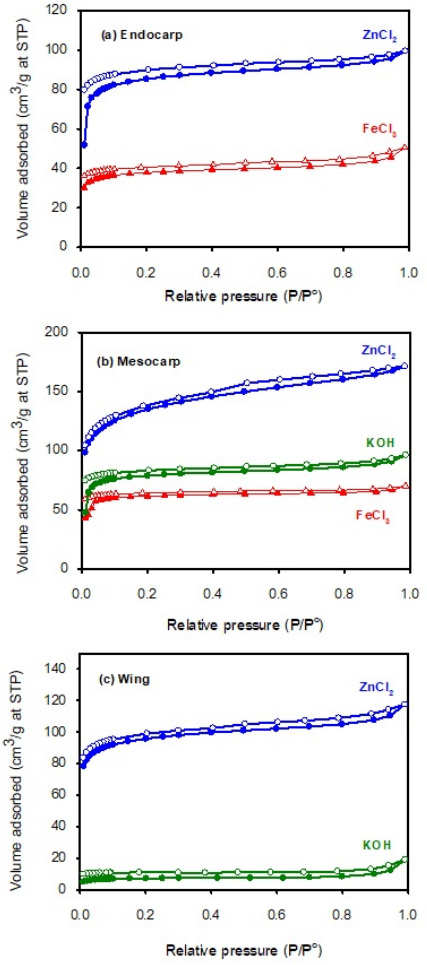

Figure 3: N_2 adsorption-desorption isotherms of the prepared activated carbon

CONCLUSION

In this preliminary study, the production of activated carbon from *Dipterocarpus alatus* fruit using the chemical activation method with $ZnCl_2$, $FeCl_3$ and KOH, has been investigated. The maximum BET surface area obtained by $ZnCl_2$ activation was 447, 312 and 278 m^2/g for mesocarp, wing and endocarp, respectively. In the case of $FeCl_3$ activation, activated

Table 2: Yield and porous texture of the prepared activated carbon

Sample	Yield (wt%)	SBET (m^2/g)	Vmic (cm^3/g)	Vmeso (cm3/g)	VT (cm3/g)	DP (nm)
Endocarp						
$ZnCl_2$	35	278	0.101 (66%)	0.053 (34%)	0.154	2.22
$FeCl_3$	51	122	0.045 (58%)	0.033 (42%)	0.078	2.55
KOH	16	2	0.001 (25%)	0.003 (75%)	0.004	13.84
Mesocarp						
$ZnCl_2$	32	447	0.117 (44%)	0.148 (56%)	0.265	2.37
$FeCl_3$	45	199	0.080 (74%)	0.028 (26%)	0.108	2.18
KOH	25	256	0.096 (64%)	0.053 (36%)	0.149	2.33
Wing						
$ZnCl_2$	38	312	0.112 (62%)	0.070 (38%)	0.182	2.33
$FeCl_3$	43	6	0.002 (15%)	0.011 (85%)	0.013	8.84
KOH	19	24	0.009 (30%)	0.021 (70%)	0.030	4.95

Table 3: Proximate analysis (wt%) of activated carbon prepared by $ZnCl_2$ activation

	Endocarp	Mesocarp	Wing
Moisture	7.00	6.50	7.14
Volatile Matter	25.71	26.36	27.77
Ash	8.53	7.32	8.29
Fixed carbon	58.76	59.82	56.88

carbon with surface area of 199 and 122 m^2/g were produced from the mesocarp and endocarp, respectively, but no porosity was formed for the wing part of the fruit. Regarding the activation with KOH, surface area of activated carbon from mesocarp was 256 m^2/g. However, KOH activation of the endocarp and wing parts could not develop porosity in activated carbon structure. The activated carbon prepared under the described experimental conditions demonstrates the potentiality of *Dipterocarpus alatus* fruit as low cost material for the preparation of activated carbon, resulting a surface area higher than that of activated carbons obtained from some biomass wastes.

Future studies will utilise *Dipterocarpus alatus* fruit activated carbons for adsorption of dye or heavy metal molecules. The preparation conditions such as activator ratio, impregnation time, carbonization temperature and carbonization time should also be investigated.

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AUTHOR CONTRIBUTIONS

All authors contributed equally to this work. All authors have read and agreed to the published version of the manuscript.

CONFLICT OF INTEREST

We declare that there is no conflict of whatsoever involved in publishing this research.

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