

Preparation of Activated Carbons From Teak Sawdust Using Chicken Dropping Compost and Empty Fruit Bunch

Boodsakorn Kongsomart^{1,*}, Liuyun Li² and Takayuki Takarada¹

¹ Department of Environmental Engineering Science, Graduate School of Science and Technology, Gunma University, 1-5-1 Tenjin-cho, Kiryu, Gunma, 376-8515, Japan

² Department of Chemistry and Chemical Engineering, Niigata University, 2-8050, Ikarashi, Niigata, 950-2181, Japan

Abstract

In this paper, the preparation of the activated carbon (ACs) from teak sawdust (TS) biomass mixed with chicken dropping compost ash (CCA) and empty fruit bunch ash (EFBA) as activating agents were studied. The carbonization was done in pure N₂ and N₂/CO₂ stream gases by temperature variations between 600 to 1000°C. The concentration of CO₂ in N₂/CO₂ gas was varied from 2 to 10%. The specific surface area (SSA) of TS mixed with CCA (1:1 wt%) carbonized at 1000°C in N₂ and N₂/2%CO₂ gas ambient was 930 and 1094 m²g⁻¹, respectively. Larger SSA of carbonization in N₂/2%CO₂ gas ambient is due to the reaction between CO₂ gas and the carbon content in TS during pyrolysis. This can increase pores and widen the pore size in ACs. Finally, the EFBA is more efficient in increasing the SSA up to 30% compared to the CCA with the same process conditions.

Keywords: Activated Carbon, Activating Agent, Ash, Biomass, Surface Area

1. Introduction

In recent years, agricultural by-products are generally used as feedstock in fuel combustion. However, recycling agricultural waste as combustion fuel still lacks of profit and efficiency. Agricultural waste especially biomass is commonly used as raw materials to produce various value-added products in solid, liquid and gaseous forms from various conversion processes [1-4]. This is because biomass has high carbon content and is low-cost, renewable and environmental friendly. Among solid products, activated carbons (ACs) are the most attractive material due to its high microporous structure, high specific surface area (SSA) and good adsorption properties. The properties of ACs are excellent for various applications such as wastewater treatment, pollutant removal, solvent recovery, color removal and ground water improvement [5-9].

Typically, ACs can be produced by chemical activation and physical activation. The chemical activation method requires a single step of carbonization at a relatively low temperature between 400 to 700°C in the presence of chemical agents. The physical activation method is a thermal activation process that consists of carbonization of a precursor and the activation of a resolution char in the presence of some activating agents [10-12]. Generally, carbon dioxide (CO₂) and steam (H₂O) are preferred as activating gases due to the controllability of the oxidation process compared with O₂ and air [13].

In the past, synthesis chemicals such as KOH, ZnCl₂, H₂SO₄, NaOH and K₂CO₃ were used as activating agents. However, the by-products from synthesis activating agents are harmful and it

can contaminate the surrounding environment [14]. Therefore, some research groups reported that the ACs with large SSA can be produced by using natural activating agents obtained from agricultural wastes [5-6]. Unfortunately, much agricultural waste such as rice straw, wheat straw, pinewood and olive tree wood have SiO₂ as its main component (40 to 95%) [15]. Hence, utilizing agricultural waste still requires significant amounts of synthesis activating agents to produce ACs.

This paper focuses on the utilizing of two different agricultural wastes including chicken dropping compost ash (CCA) and empty fruit bunch ash (EFBA) as natural activation agents instead of synthesized chemicals. The low cost ACs production from teak sawdust (TS) was used as the carbon source. The effects of various parameters including the ash/biomass weight ratio, the concentration of CO₂ in reaction gas and the reaction temperature to the SSA, yield of ACs, adsorption volume, pore size and N₂ adsorption isotherm of the prepared ACs were investigated.

2. Experimental

2.1 Raw materials

Teak sawdust (TS) from Thailand with particle size of 0.25 to 0.50 mm was used as the raw material. The proximate and ultimate analyses of the initial material are shown in Table 1. The volatile matter and ash contents were measured by thermo

*Corresponding author.

E-mail address : boodsakorn.k@gmail.com, t13802381@gunma-u.ac.jp (Boodsakorn Kongsomart), Tel:+81 277 30 1699; fax: +81 277 30 1454

gravimetric analyzer (TGA 701, Leco Co., Ltd.). The content of C, H, N and O elements were determined using an elemental analyzer (TruSpec CHN, version 100, Leco Co., Ltd) and the content of sulfur element was analyzed by sulfur analyzer (Leco SC-432, Leco Co., Ltd). The TS was dried at 107°C for 1 hour before mixed with biomass ashes.

The chicken dropping compost (CC) was obtained from Kinsei Sangyo Co., Ltd., Japan. The CCA was prepared by TGA in oxygen

gas ambient with temperature variations from 500 to 815°C with the heating rate of 10°C/min and stabilized at 815°C for 30 min. The CCA was then cooled down to room temperature and was kept for further use. The empty fruit bunch (EFB) was obtained from Chemical Engineering Department, Universiti Teknologi Petronas, Malaysia. Note that the preparation condition of EFBA is similar to the process condition used for CCA.

Table 1 : Proximate and ultimate analysis of the teak sawdust

Proximate analysis (%wt)				Ultimate analysis (%wt, daf)				
Moisture ^{ar}	Volatiled	Ash ^d	Fixed carbon ^b	C	H	N	S	O ^b
7.48	76.77	0.83	22.40	50.02	9.49	0.29	0.12	40.08

ar: as-received, d: air-dried basis and b: by difference

2.2 Sample preparation

TS was mixed with two different biomass ashes, CCA and EFBA. Both CCA/TS and EFBA/TS weight ratio were varied from 0.6 to 1.0 and the mixtures were replaced to a horizontal fixed bed reactor. The char was produced by slow pyrolysis in a ceramic crucible at 600 to 1000°C for 30 min. The slow pyrolysis in a fixed bed reactor was done in different gas ambient including pure N₂ and N₂/CO₂ gas ambient by using the heating rate of 10°C/min.

To remove the ash components in CCA and EFBA, the char samples were put in the magnetic stirrer that contained 1M of HCl at 70°C for 2 hrs. In this process, metal oxide was converted to water-soluble Metal-Cl thus easily removed from char. After that, the carbon samples were rinsed with deionized water and filtered until the pH is 7. Then, the ACs were obtained by heating the carbon samples in an oven at 107°C for 24 hrs.

2.3 Characterization of the activated carbons

The SSA, pore size distribution and N₂ adsorption isotherm were characterized by nitrogen adsorption and desorption at -196°C using Brunauer-Emmett-Teller (BET) and micropore analysis (MP) methods (BELSORP-max, Japan), respectively. Note that all samples were degassed at 300°C for 3 hrs before the adsorption in N₂ gas ambient.

3. Results and discussion

3.1 Preparation of ACs from TS mixed with CCA activating agent

3.1.1 Effects of CCA activating agent

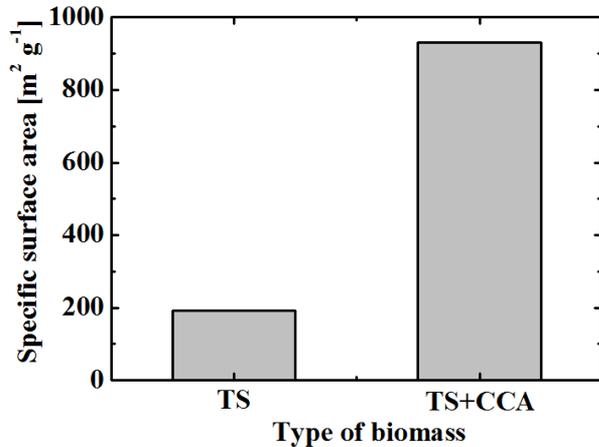
Fortunately, CCA and EFBA contains low amount of SiO₂ component (< 20%) as the information shown in Table 2. The composition of CCA contains high amount of calcium oxide, CaO (~ 85%) and the composition of EFBA contains high amount of potassium oxide, K₂O (~ 77%). Therefore, CCA and EFBA are very interesting activating agents to produce ACs without using any synthesized chemicals in the activating process.

Fig. 1 shows the SSA of TS and ACs obtained from TS mixed with CCA activated with N₂ gas stream at 1000°C. By adding the CCA catalyst, the SSA of TS has increased from 192 to 930 m²g⁻¹. This means the CCA is an effective catalyst to activate the TS to ACs with high SSA.

Typically, calcium oxide (CaO) in the CCA was deposited into the structure of porous materials during pyrolysis by a mechanism called "pore blocking effect". In this mechanism, the ash that contains a discrete inorganic compound (calcium atom) is capable to form an intercalation compounds with carbon by penetrating through an adjacent carbon layer and inserting into a graphite-like structure. The similar mechanism caused by different additives deposited on the porous materials have been widely reported [2, 16-18]. The pore blocking effect is widely used to describe the decreasing of textural parameters. Nevertheless, washing out the CaO from the porous materials is a simple way to substantially high porosity from micropores.

Table 2 : Composition of metal oxide in CCA and EFBA

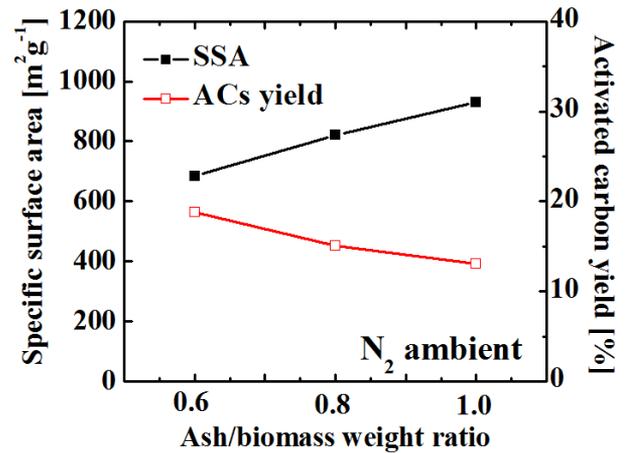
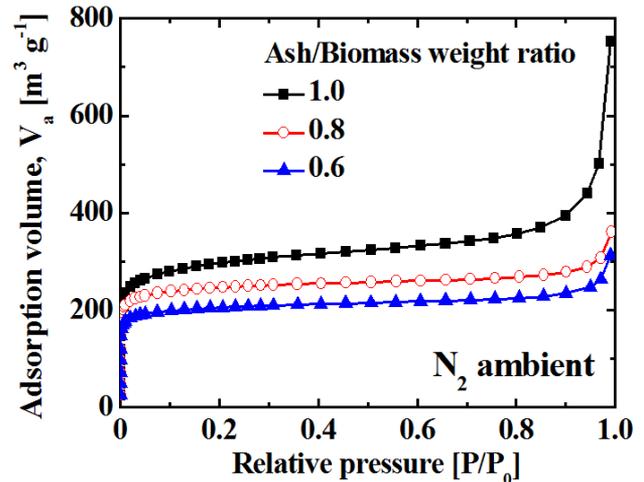
Biomass ash	Metal oxide composition (wt%, dry basis)					
	K ₂ O	SiO ₂	CaO	P ₂ O ₅	Fe ₂ O ₃	SO ₃
CCA	11.06	1.27	84.65	2.58	0.29	0.14
EFBA	76.94	18.17	3.46	0	1.01	0.16

**Figure 1** : Specific surface area of TS and TS mixed with CCA.

3.1.2 Effects of ash to biomass weight ratio

The results in Fig. 2 show the evolution of ACs produced by slow pyrolysis using the TS mixed with CCA. The amount of activation agent mixed with CCA and TS was varied at the weight ratio of 0.6 to 1.0. It was found that when the ash to biomass weight ratio has increased from 0.6 to 1.0, the SSA has increased from 684 to 930 m²g⁻¹ and carbon yield of ACs has decreased from 18.9 to 13.1%, respectively.

The decrease of ACs yield by increasing the ash to biomass weight ratio can be explained by the reaction rate of metal elements with the char and volatile matter. By using high ash to biomass weight ratio, the activation of TS has increased and the by-products can be quickly diffused out from the particles surface during activation process [19]. Therefore, the gasification of carbon atom surface becomes predominant that leads to decrease the weight loss and ACs yield. Fig. 3 exhibits the N₂ adsorption isotherm of ACs obtained from carbonization process in N₂ gas stream with different ash to biomass weight ratio. The appearance of isotherm clearly shows the Type I, which is the characteristic of microporous materials [20].

**Figure 2** : Specific surface area and yield of ACs with different CCA to biomass weight ratio.**Figure 3** : Adsorption isotherm of ACs with different CCA to biomass weight ratio.

3.1.3 Effects of carbonization gas ambient using CCA activating agent

The results in Fig. 4 show that the main effect of gasification with N₂/2%CO₂ gas is the creation and widening of the existing pores. This can improve the adsorption properties such as SSA. By using N₂/2%CO₂ activation at 1000°C, the SSA of TS has increased from 196 to 600 m²g⁻¹. The increasing of SSA can be explained by the "burn off" reaction. In the burn off reaction, CO₂ reacts with carbon to produce CO during the thermal activation by reaction mechanism in Eq. 1. The CO₂ can increase an amount of the activating gas in the reaction. Moreover, it can enhance the bulk mass transfer of the CO product from the burn off reaction [21].

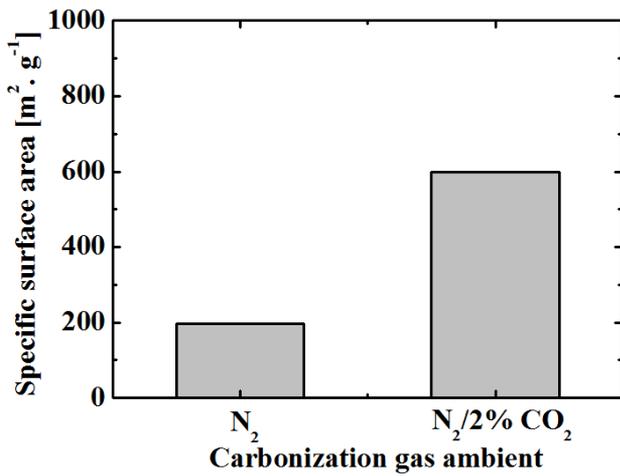
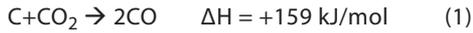


Figure 4 : Specific surface areas of the ACs from TS prepared in pure N₂ and N₂/2%CO₂ gas ambient at the carbonization temperature of 1000°C.

3.1.4 Effects of carbonization temperature using CCA activating agent on CO₂ gas

The results in Fig. 5 show the SSA and ACs yield obtained from TS and TS mixed with CCA using carbonization process with N₂/2%CO₂ gas ambient at various carbonization temperatures. When the carbonization temperature has increased from 600 to 1000°C, the SSA has increased from 400 to 1094 m²g⁻¹ but the ACs yield has decreased from 24.4 to 6.3%, respectively. By using the combination of chemical and physical activation, the SSA of ACs is higher than the one that obtained from chemical activation. Table 3 shows the characterization parameters of the ACs obtained from the carbonization process including yield of activated carbon (Y_{acs}), SSA, volume of microporous (V_{micro}), total volume of ACs (V_{total}) and average diameter of ACs (D_{avg}). The volume of microporous has increased by increasing the activation temperature. Fig. 6 show the pore size distribution of ACs obtained from carbonization process with N₂/2%CO₂ gas ambient at different carbonization temperatures. When the carbonization temperature has increased from 600 to 1000°C, the pore size distribution of ACs decreased from 0.7 to 0.5 nm, respectively. However, the pore size distribution of ACs in the range of 0.8 to 1.0 nm has increased as the carbonization temperature increased.

The carbonization is a complex reaction process that includes the decomposition of organic matter and the elimination of volatile matter in the remaining products. At the carbonization temperature of 450°C, the volatile matter start to accumulate in the particles undergoes the first cracking, which can generate pores on the materials surface. When the carbonization temperature is higher than 450°C, the volatile matters start to escapes from the particles undergoes the secondary cracking. It can form carbon to deposit on the char thus blocking the developed pore and leads to decrease the surface area of microspore [22]. The continuous of secondary cracking at higher carbonization temperature can collapse the micropores size of 0.4 to 0.7 nm and generate the bigger pore with the size of 0.8 to 1.2 nm.

The dependence of SSA, ACs yield and pore size distribution on the carbonization temperature can be explained by the burn off mechanism. The products burn off at low carbonization temperature is smaller than the high carbonization temperature. Therefore, the amount of volatile matter in the products that was obtained from high carbonization temperatures is smaller than the one that obtained from low carbonization temperature. The loss of volatile materials was related to the high SSA of ACs [23-24].

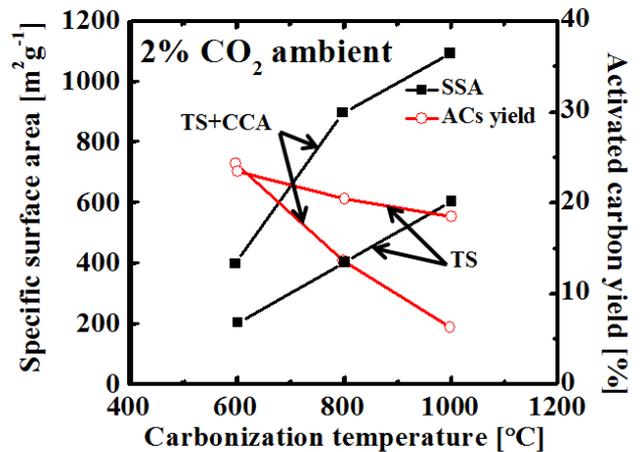


Figure 5 : Specific surface area and ACs yield obtained from carbonization process in N₂/2%CO₂ gas ambient by varied the carbonization temperature from 600 to 1000°C.

Table 3 : Characterization parameters of the activated carbon obtained from the carbonization process

Sample	Carbonization temperature [°C]	Gas ambient	CCA to TS ratio	Y_{ACs} [%]	SSA [m^2g^{-1}]	V_{micro} [cm^3g^{-1}]	V_{total} [cm^3g^{-1}]	D_{avg} [nm]
AC1	1000	N ₂	0.6	13.6	684	0.33	0.48	2.80
AC2	1000	N ₂	0.8	10.7	820	0.40	0.55	2.67
AC3	1000	N ₂	1.0	7.0	1006	0.42	1.15	2.55
AC4	600	N ₂ /2%CO ₂	1.0	24.4	400	0.16	0.34	2.39
AC5	600	N ₂ /5%CO ₂	1.0	23.6	482	0.22	0.36	2.94
AC6	600	N ₂ /10%CO ₂	1.0	21.8	554	0.22	0.40	3.21
AC7	800	N ₂ /2%CO ₂	1.0	13.7	897	0.43	0.57	2.30
AC8	1000	N ₂ /2%CO ₂	1.0	6.3	1093	0.51	0.63	2.31

Y_{ACs} : yield of activated carbon, SSA: specific surface area, V_{micro} : volume of microporous, V_{total} : total volume of ACs and D_{avg} : average diameter of ACs

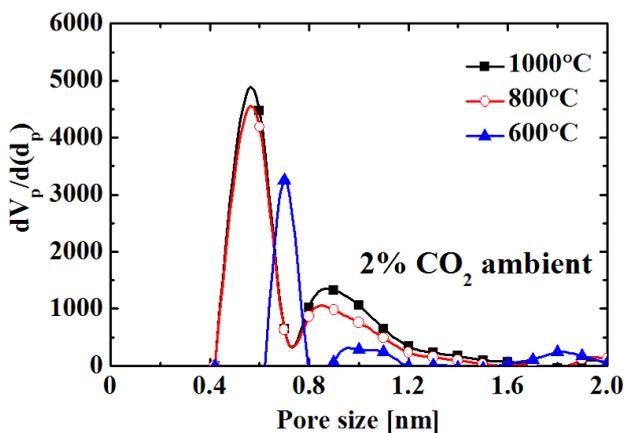


Figure 6 : Pore size distribution obtained from carbonization process with N₂/2%CO₂ gas ambient at different carbonization temperatures.

3.1.5 Effects of CO₂ concentration in carbonization process using CCA activating agent

The effects of N₂/CO₂ gas ratio to the SSA and the yield of ACs using the CCA activation agent at 600°C were investigated. In this experiment, the CO₂ concentration of N₂/CO₂ gas was varied from 2 to 10%. Fig. 7 show that when the CO₂ concentration has increased from 2 to 10%, the SSA has increased from 400 to 554 m²g⁻¹. However, the ACs yield has decreased by increasing the CO₂ concentration. This means, higher CO₂ concentration is more efficient in removing the volatile matters from the activating mass. This can be explained by the reaction between carbon and CO₂ in the activation process. The carbon was removed and then exposed to the aromatic carbon sheets to the action of CO₂ gas [25-27]. Based on the results in Fig. 7, it can be predicted that if the CO₂ concentration is less than 2%, SSA trends to decreases and ACs yield trends to increases, respectively. In contrast, if the CO₂ concentration is excessively

increases, the burn off reaction will be strongly occurred. Therefore, the CO₂ could react with all of carbon in TS and the ACs products will not remain after carbonization process.

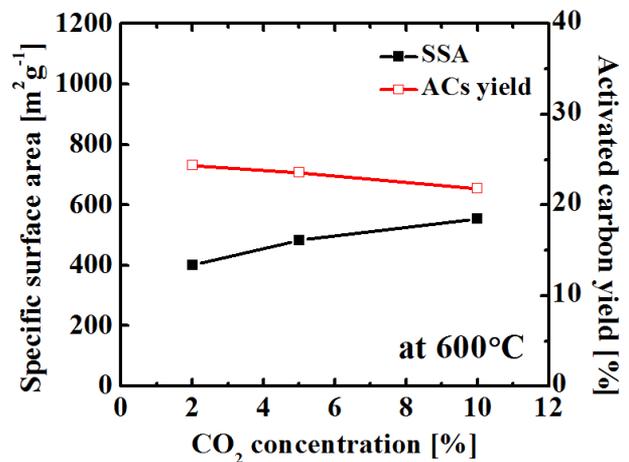


Figure 7 : Specific surface area and ACs yield with different CO₂ concentration in N₂/CO₂ gas ambient at 600°C.

3.2 Comparison of CCA and EFBA activating agents

Fig. 8 show the comparison of the SSA of ACs obtained from TS mixed with CCA and TS mixed with EFBA at different ash/biomass weight ratio. The carbonization was done in different gas ambient at 1000°C. By using an EFBA activating agent, the SSA has higher compared to CCA activating agent. This is related to the different composition of EFBA that contains potassium oxide (K₂O) and CCA that contains calcium oxide (CaO) as shown in Table 2. The ACs with high SSA can produce from biomass that contains the potassium compound. This could be explained by the carbon gasification of CO₂ by-

product to the decomposition of potassium compound.

Moreover, high SSA obtained from potassium compound can be attributed to the particle reaction of the potassium with the cellulose in biomass [28]. Due to the ionic strength of calcium cation being weaker than potassium cation, the catalytic activity during pyrolysis of calcium is less than potassium. Moreover, the combination of chemical activation and physical activation process can increase the SSA of TS by the reaction of metal oxide and CO_2 gas.

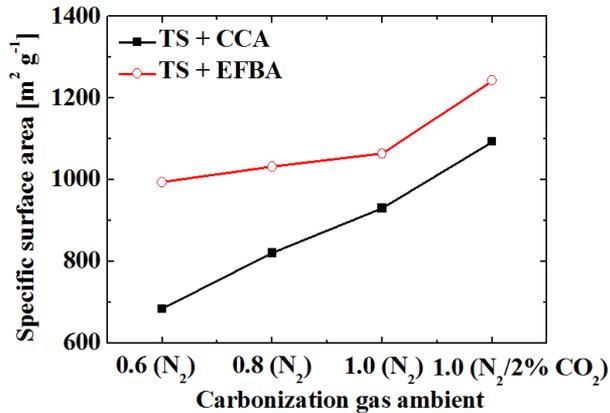


Figure 8 : Specific surface area of ACs from TS mixed with CCA and EFBA by varied the ash/biomass weight ratio from 0.6 to 1.0 and carbonized in different gas ambient at 1000°C.

Finally, the pore size distribution of the activated carbon obtained from TS mixed with CCA and TS mixed with EFBA is shown in Fig. 9. The pore size of ACs was varied from 0.4 to 2.0 nm. The maximum volume (means of normal distribution) of the pore size was located at 0.5 nm. Therefore, the average pore size of the ACs obtained from TS mixed with CCA and TS mixed with EFBA were 0.5 nm.

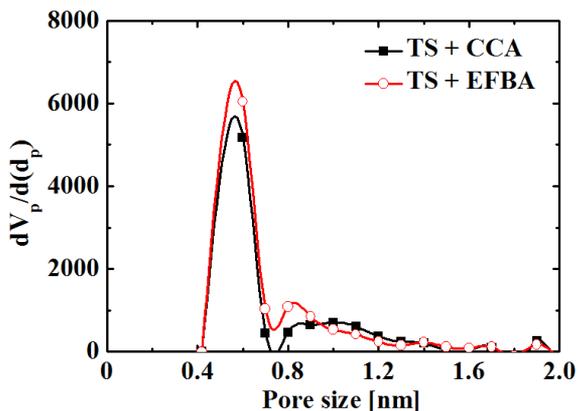


Figure 9 : Pore size distribution of ACs from TS mixed with CCA and EFBA with the ash/biomass weight ratio of 1.0 and carbonized in N_2 gas ambient at 1000°C.

4. Conclusions

Activated carbon (ACs) can be produced from teak sawdust (TS) mixed with two different biomass activation agents including chicken dropping compost ash (CCA) and empty fruit bunch ash (EFBA). The specific surface area (SSA) of ACs over $1000 \text{ m}^2\text{g}^{-1}$ can be obtained for both CCA and EFBA after physical activation process in $\text{N}_2/2\%\text{CO}_2$ gas ambient at 1000°C. However, the potassium compound (K_2O) in EFBA has more efficiency to increase the SSA compared to the calcium compound (CaO) in CCA.

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