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PREPARATION OF POROUS CARBON FROM POPPED RICE VIA
IMPREGNATED WATER COUPLED WITH FREEZE-DRYING PROCESS

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จุฬาลงกรณ์มหาวิทยาลัย
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ถ่านกัมมันต์เป็นวัสดุที่มีความน่าสนใจ เนื่องจากมีพื้นที่ผิวสูงจากโครงสร้างที่มีรูพรุนสูงจึงทำ ให้เหมาะสำหรับใช้เป็นสารดูดซับที่ดี เหมาะสำหรับการประยุกต์ใช้ในงานที่หลากหลาย เช่น การบำบัด น้ำเสีย การดูดซับแก๊สต่างๆ หรือใช้เป็นยา วิธีการผลิตถ่านกัมมันต์โดยทั่วไปนั้นประกอบด้วย 2 ขั้นตอน คือ การเผาถ่าน และ การกระตุ้น ตามลำดับ โดยใช้วัตถุดิบเหลือทิ้งจากภาคการเกษตรเป็นแหล่งคาร์บอน งานวิจัยนี้สนใจศึกษาการผลิตถ่านกัมมันต์จากข้าวตอก เพราะข้าวตอกมีแป้งเป็นองค์ประกอบหลัก และ ภายในโครงสร้างที่รูพรุนสูง จึงมีศักยภาพในการประยุกต์ใช้ผลิตถ่านกัมมันต์หากได้รับการกระตุ้นผิว อย่างเหมาะสม นอกจากนี้งานวิจัยนี้ได้ศึกษาความเป็นไปได้ของวิธีทางเลือกในการผลิตถ่านกัมมันต์โดย การกระตุ้นผิวก่อนแล้วจึงค่อยเผาเป็นถ่าน โดยใช้วิธีการจุ่มชุ่มข้าวตอกด้วยน้ำควบคู่กับการทำแห้งแบบ แช่เยือกแข็งเป็นการกระตุ้นผิวให้รูพรุน ผลการทดลองพบว่าวิธีนี้ ทำให้เกิดรูขนาดเล็กขึ้นบนพื้นผิวของ คาร์บอนที่ได้จากข้าวตอก ซึ่งรูที่เกิดขึ้นนี้จะเกิดในเฉพาะวิธีการทำแห้งแบบแช่แข็งเท่านั้น เมื่อนำข้าวตอก ที่ได้จากการเผาไปทดสอบประสิทธิภาพการดูดซับสีย้อมเมทิลีนบลูพบว่ามีประสิทธิภาพการดูดซับด้อย กว่าถ่านกัมมันต์เชิงพาณิชย์ จากผลของพื้นที่ผิวและปริมาตรของรูที่วิเคราะห์ด้วยวิธีบรูเนอร์ เอลเม็ท เทล เลอร์ พบว่าคาร์บอนของข้าวตอกที่ผ่านกระบวนการกระตุ้นผิวด้วยวิธีจุ่มชุ่มด้วยน้ำควบคู่กับการทำแห้ง แบบแช่เยือกแข็งกลับมีค่าต่ำกว่าแบบไม่ผ่านกระบวนการทั้งๆที่ผิวของคาร์บอนที่ได้มีรูเกิดขึ้น ถ่านกัม มันต์ที่ผลิตขึ้นทั้งสองแบบมีประสิทธิภาพต่ำกว่าถ่านกัมมันต์ที่มีจำหน่ายเชิงพาณิชย์ เมื่อวิเคราะห์ โครงสร้างของข้าวตอกที่ผ่านกระบวนการจุ่มชุ่มควบคู่กับการทำแห้งแบบแช่เยือกแข็งก่อนเผาเป็น คาร์บอนพบว่าการเติมน้ำเข้าไปในระบบส่งผลให้โครงสร้างของข้าวตอกเกิดการพังและเป็นโครงสร้างที่ ซ้อนทับกันทำให้พื้นที่ผิวของข้าวตอกลดลงเป็นอย่างมากตั้งแต่ก่อนขั้นตอนเผาถ่าน ทำให้ถึงแม้เมื่อเผา แล้วคาร์บอนที่ได้มีพื้นที่ผิวเพิ่มขึ้นจากรูที่เกิดขึ้นแต่คาร์บอนที่ได้ยังไม่สามารถเทียบเท่ากับถ่านกัมมันต์ ในเชิงพาณิชย์ได้ งานวิจัยนี้น่าจะเป็นประโยชน์สำหรับการพัฒนาวิธีการผลิตถ่านกัมมันต์โดยการกระตุ้น ให้เกิดรูก่อนที่จะทำการเผาในอนาคตต่อไป

สาขาวิชา   ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์   ลายมือชื่อนิสิต ....

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Activated carbon is an interesting material due to its high surface area derived from the highly porous structure. This material is suitable for using as a good adsorbent in various applications such as wastewater treatment, gas absorption and medicine. Production of activated carbon typically consists of two steps which are carbonization and activation. Agricultural wastes are used as carbon sources. This research focuses on the production of activated carbon from popped rice due to its appropriate chemical and structural characteristics, including highly starch content and connected-pore structure. Therefore, it should potentially be applied to produce activated carbon if the surface of popped rice is activated properly. Herein, this work aims to study the feasibility of an alternative way to produce activated carbon, which is activation-then-carbonization method. Water impregnation coupled with freeze-drying method is as used an activation technique. The results show that the proposed activation method can create small pores on the surface of the carbon derived from popped rice. The pores appear after the freeze-drying process. Adsorption capacity of methylene blue on the popped rice-derived carbon was less than that of the commercial activated carbon. Brunauer–Emmett–Teller (BET) indicates that the surface area and pore volume of the popped rice-derived carbon is smaller than the one without activation despite having additionally generated pores on the surface. Again, both types of the popped rice-derived carbon have much smaller surface area and pore volume than the commercial product. The reason is that, the structure of the popped rice with water impregnation collapsed and became overlapped, resulting in overall decreased surface area. Therefore, although the proposed activation method can induce the formation of small pore, the obtained carbon black cannot provide adsorption capacity comparable to the commercial product. This research may be useful for further developing procedures that use water activation before carbonization in the future.

Field of Study:	Petrochemistry and Polymer	Student's Signature	....
	Science	Advisor's Signature	....
Academic Year:	2017	Co-Advisor's Signature	....

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CONTENTS

LIST OF FIGURES

LIST OF TABLES

จุฬาลงกรณ์มหาวิทยาลัย
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LIST OF SYMBOLS AND ABBREVIATIONS

OM	: optical microscope
SEM	: scanning electron microscope
SEI	: secondary electron imaging
FT-IR	: Fourier-transform infrared
UV-Visible	: ultra violet-visible
DSC	: Differential scaning calorimeter
XRD	: X-ray diffraction
BET	: Brunauer-Emmett-Teller
ATR	: attenuate total reflection
FD	: freeze-drying
DI	: de-ionized
IUPAC	: international union of poure and applied chemistry
N_2	: nitrogen
AC	: activated carbon
CO_2	: carbon dioxide
$ZnCl_2$	: zinc chloride
H_3PO_4	: phosphoric acid
KOH	: potassium hydroxide
HCl	: hydrochloric acid
EtOH	: eethanol
3D	: three dimension
h	: hour
min	: minute
s	: second
g	: gram
mg	: miligram
cm	: centimetre
mm	: milimeter
μm	: micrometer

nm	: nanometer
cm^{-1}	: reciprocal centimetre
m^2	: square centimeter
cm^3	: cubic centimetre
mL	: millilitre
ppm	: part per million
kV	: kilovolt
eV	: electron volt
Hz	: hertz
Pa	: pascal
atm	: atmosphere
$\propto$	: alpha
^{o}C	: degree Celsius
p	: pressure
V	: volume
V_{mic}	: micropore volume
V_t	: total volume
S_{BET}	: specific surface area
%w/w	: percent weight by weight
%v/v	: percent volume by volume

CHAPTER I

INTRODUCTION

Rice is a necessary food for people in Asian since the past. It was used in many applications such as sweet foods, flour, noodles, fertillizers, animal foods and cosmetics. Currently, Thai rice is suffering with problems such as low quality rice, high moisture content or insect-damage which effecting the price of rice. These rice cannot be sold as food. Furthermore, it also created storage problems to control the spoilage rice. In this work, we transform these rice into high value products, activated carbon. Due to rice is a carbohydrate in the form of starch or polysaccharide of glucose, which have two types of molecules: straight chain of amylose (20-25 % w/w) and branch chain of amylopectin (higher than 25 % w/w), it has been known that rice has a high carbon content in form of glucose [1]. Therefore, it is considered that rice is suitable to use as a raw material in the production of activated carbon.

Activated carbon (AC) is a sorbent material which is employed in many applications. Because of its porous structure and high surface area, AC is suitable for adsorption application. Most applications of activated carbon are water treatment whether it is adsorbing dyes or heavy metal from the factory before releasing to nature or use as a medicine. AC can be generated by two methods, physical and chemical activations [2].

The production of activated carbon consists of two main steps: carbonization under inert conditions and activation by physical or chemical activations. The physical activation is a process combine with carbonization of material followed by activating with steam or carbon dioxide at high temperature, this process needs high energy. For chemical activation, the material was carbonized first and then activated by chemical activating agent such as zinc chloride [3-4], potassium hydroxide [5-7] or phosphoric acid [8]. The chemical activation required lower energy than physical activation, but this method leave a lot of waste from chemical removal. The protocol of making activated carbon often used raw material from agricultural waste such as coconut shell, bagasse, rice husk or starch and transformed to activated carbon using physical and chemical activations [6, 9-12].

Rice is a suitable carbon source wherewith it consist of starch which can be used for activated carbon production. Especially, rice in form of 'popped rice', which was generated from waxy un-milled heating process, is a fantastic material because it has porous structure.

Recently, L. Ting proposed the production of porous carbon from 'Popcorn' to use as energy storage and CO_2 absorber by using KOH as chemical activating agent [6]. The structure of popcorn is similar to popped rice which are displayed an open character with a honeycomb-like structure. Therefore, we suggest that it would be possible to turn the popped rice to activated carbon as well. However, the generation of pores in the first step was not reported. Thus, we are aware that if we generate the pores before carbonization, it can reduce the amount of waste that is caused by washing process, and reduce the step of production process as well.

Some researches has studied the effect of freeze-drying process on microporous structure of starch granule [13]. The results showed that the microporous occurred in the freeze drying process was because the water in starch granule try to escape from inner to outer structure. From the above research, we suggest that freeze-drying process is a way to generate small porous structure. In the same way, freeze-drying together with a water system, are likely to generate the small porous and can go through a carbonization process to produce AC.

In this work, we focus on pore formation in activated carbon process. Pore formation was generated before carbonization by using freeze-drying process to create a porous structure on popped rice wall. We investigated the feasibility of using this method to produce activated carbon. In addition, this method is chemical free, and also require less energy than physical and chemical activation. We hope that this synthetic protocol can lead to the new way of making high value products from low quality rice.

1.1 Objective of this research

To synthesize activated carbon from popped rice by water impregnation together with freeze-drying process.

1.2 Scope of research

1. To study the changing of morphology and chemical structure of popped rice before and after carbonization.
2. To produce the activated carbon from popped rice by using water impregnation together with freeze-drying process.
3. To compare the adsorption efficiency of synthesized carbon with commercial activated carbon.

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CHAPTER II
THEORETICAL BACKGROUND

2.1 Rice

The main ingredient in rice grain is endosperm (90%) which consists of polygonal-shaped starch granule with diameter 2-15 μm (Figure 2.1) [14]. Starch granule consists of two close-packing polymers, amylose and amylopectin. The structure of amylose chains is essentially linear chain linked by $\propto$-1, 4-glycosidic bonds which show amorphous characteristics. The crystalline is amylopectin, a branch chain structure, contain $\propto$-1,4 and $\propto$-1,6-glycosidic bonds (Figure 2.2) [15]. The ratio of amylose and amylopectin in rice grain depends on the type of rice. The ratio of amylose and amylopectin can be classified into 5 types based on percentage of amylose: waxy (1-2% amylose), very low amylose (2-12%), low amylose (12-20%), intermediate amylose (20-25%) and high amylose (25-33%) [1]. In addition, many compounds in rice grain such as fats, crude fiber and organic materials are also in starch granule. In this work, we focus on waxy rice in form of 'popped rice'.
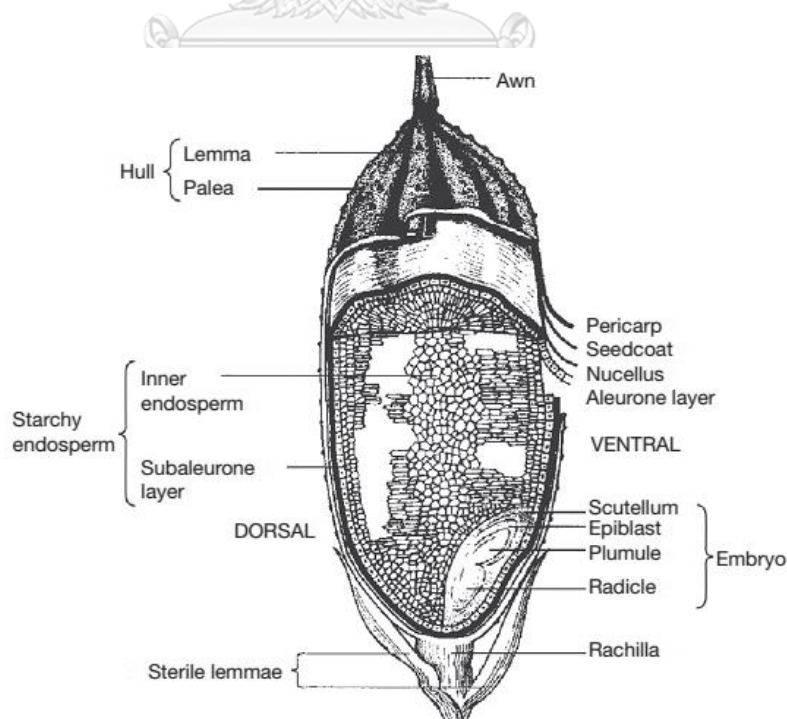
Figure 2.1 Important part of rice grain [14]. Copyright: © Academic Press 2009.
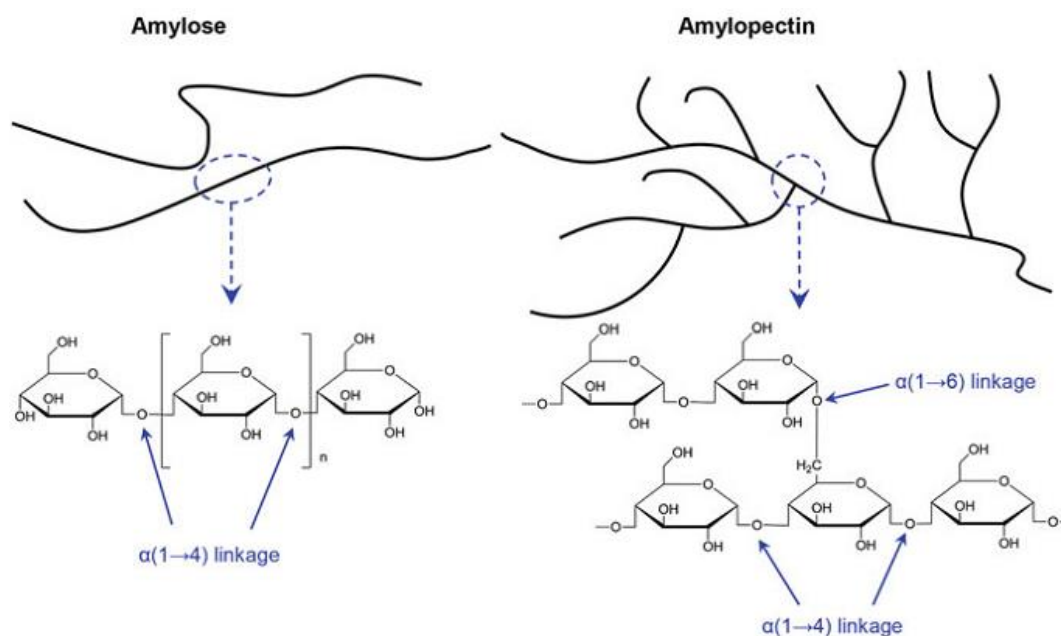
Figure 2.2 Chemical structure of amylose and amylopectin [15]. Copyright © 2014,
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2.2 Popped product of rice (Popped rice)

Popped rice is the most popular snack in India. The popped rice are made from several way such as hot air, microwave or conductive heating (roasting). Popping process is a simultaneous starch gelatinization and expansion of starch. The popped product occurred when the rice grain was heated. When the un-milled rice grain was heated for 40-60s, the moisture in the starch granule (10%) was evaporated and trapped in the husk. The starchy in the granule transformed to partial gel structure. The continuous heating, made the liquid water transform into superheated water steam and create the pressure buildup in the granule. The starch granule is exploded due to the instantaneous hull ruptures. The hull ruptures created the driving force for expansion of starch granule into popped rice. The 4.5% of water retained as moisture in the grain after the popping process. After the popping process, a grain was expanded into a sponge-like structure with thin wall [16].

2.3 Gelatinization and retrogradation of starch

Starch granule is the complex hierarchical structure which contain semi-crystalline areas in growth rings (Figure 2.3). The crystalline regions is derived from the arrangement of chains in the molecular layer of amylopectin in the form of clusters. Each cluster consists of a disorderly arrangement of linear chain from amylose and crystalline parts are branched chain of amylopectin. Both of these areas are resulted from the gelatinization of starch when the starch is heated [17].
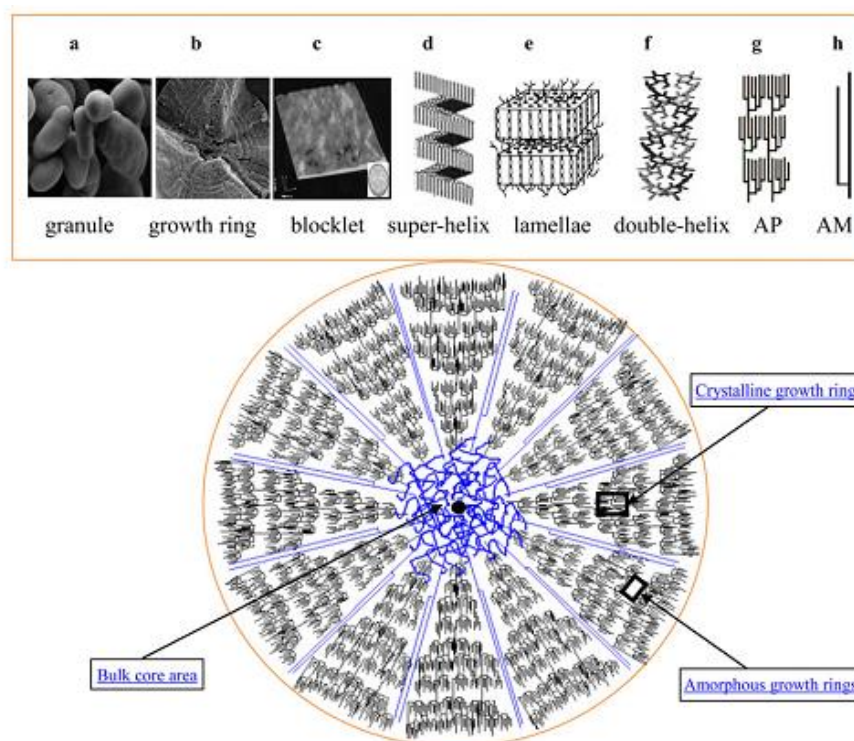
Figure 2.3 Schematic drawing of hierarchical structure of starch granules [17]. Copyright © 2015, John Wiley and Sons.

2.3.1 Starch gelatinization

The gelatinization is a process that break down the intermolecular in starch granule in the presence of water and heat. When native starch was heated, their semi-crystalline structure are destroyed, which transformed the ordered into disordered structure (loss of birefringence). The amorphous regions was transform as follows: the water in system breakdown the hydrogen bonds in starch granule, making the granule

swell and the water acts as a plasticizer for hydration and swelling process which affect the mobile of chain in granule. Due to the high water system (Figure 2.4), when undergo the cook rice process, the water within starch granule was boiled, which make the granule swell. The amylose chain are leaked out from granule by swelling process and amylopectin chain is condensed in the granule matrix of amylose and forming the gel structure, while the amylopectin collapsed within granule and held by gelatinous amylose.

In my work, the water was not added into system. The only water in the system are from moisture content in starch granule. Because of the limit of water in granule, make it difficult to destroy the strong crystalline regions. The heating cannot turn starch into gelatinized starch completely. Therefore, the heating process in this work increased the mobility of starch chain only and also destroyed the crystalline regions [4, 15, 17-19].

Raw starch granules made up of amylose (helix) and amylopectin (branched)

Addition of water breaks up amylose crystallinity and disrupts helices. Granules swell

Addition of heat and more water cause more swelling. Amylose begins to diffuse out of granules.

Granules, now containing mostly amylopectin, have collapsed and are held in a matrix of amylose forming a gel

Figure 2.4 Gelatinization mechanism in starch granule [15]. Copyright © 2014, Springer International Publishing Switzerland

2.3.2 Retrogradation process

When the gelatinization process is finished, the temperature are rapidly cooled down. The chain of amylose and amylopectin created the hydrogen bonds. The aggregation of double helices in polymer chain change into different reorganization before partially recrystallized starch. The recrystallization process of polymer chains are called 'Retrogradation'. The changing appearance are shown in Figure 2.5. The retrogradation process transform amylose to inelastic structure occurred in a short time (over minutes to hours), whereas amylopectin is slowly retrogradated (over hours to days). Generally, the storage of gelatinized starch refer to amylopectin recrystallization. Many researches used DSC, XRD or FTIR techniques to observe the retrogradation of gelatinized starch [17-19].

Figure 2.5 Retrogradation of native starch during heating, cooling and storage [17]. Copyright © 2015, John Wiley and Sons.

2.4 Activated carbon

Activated carbon is a carbon material which has a high porosity [20-21], high adsorptive capacity (over 0.2 cm^3/g) [22], high stability [23], and high degree of surface reactivity with large surface area (over 400 m^2/g) [24]. Because of its porous property, it was used in many applications including water treatment, purification, energy stora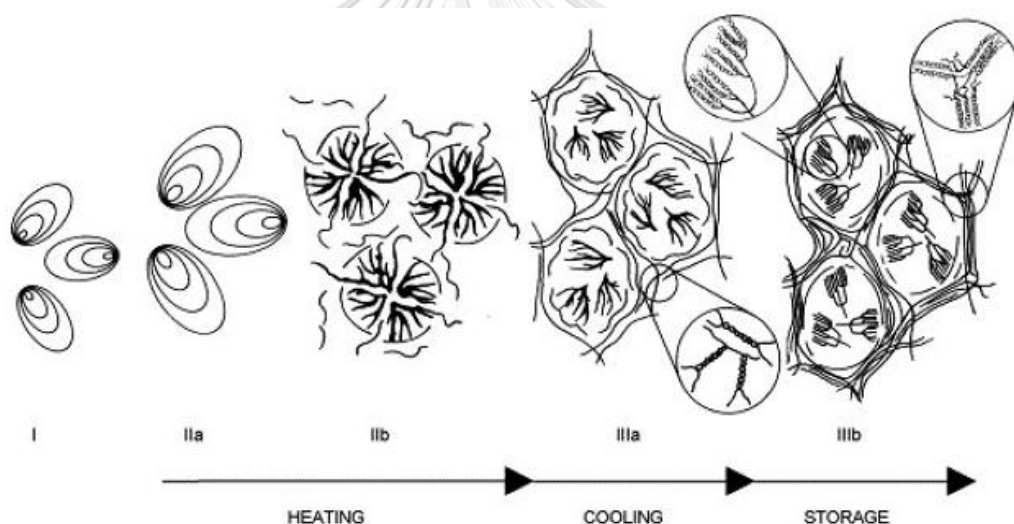ge, pharmaceutical and others. The materials for production of activated carbon are natural or synthetic carbonaceous materials which has high carbon content. Commercial activated carbon basically used coal, lignite, and peat as raw material which are expensive and non-renewable. Recently, many researches used the agricultural waste such as coconut shell, corncob, sugarcane, and bagasse or rick husk. However, the yields of activated carbon is lower than coal or peat, but they are more effective and inexpensive [2].

The production of activated carbon consists of two process: physical activation and chemical activation. Both activation result in various size and shape of activated carbon. The physical activation involves two steps: carbonized the raw material at 400−850 ℃ followed by activation with steam or carbon dioxide around 600−900 ℃. Many researches commonly used CO_2 to produce uniform pores in activated carbon. While, the chemical activation, raw materials are impregnated with activating agents and followed by pyrolysis under inert conditions. This process requires lower temperature of 300 to 800 ℃. The activating agents that usually used are $ZnCl_2$, H_3PO_4, or KOH. The activating agents act as dehydrating agents and oxidants, which can prevent the formation of tar and improve carbon yields. The chemical activation required washing process to remove the impurities from the activating agents by using HCl and water. The advantages and disadvantages of each activation process are shown in Table 1.1 [4, 7, 25].

For carbonization of starch, it is similar to cellulose due to its similar chemical composition. The mechanism of carbonization included four steps, as shown in Figure 2.6. First step, the physical adsorbed water is desorbed when the temperature was heated up to 150 °C. Second step, the AGU is dehydrated in range 150 °C to 240 °C. The cellulose is decomposed by severance of glycosidic and other C−O bonds as well

as C−C bonds when heated up to 400 °C. Last step above 400 °C, aromatization of the remaining residue with four carbon atoms occurs. [26]
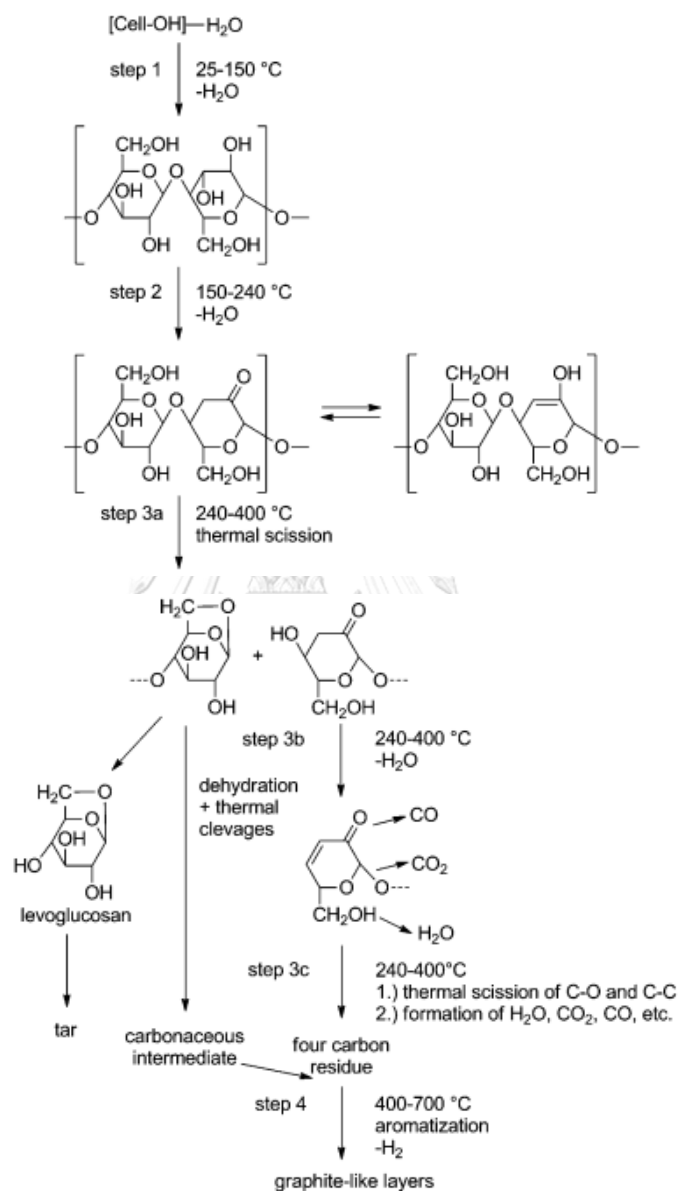

Figure 2.6 Pyrolysis mechanism of cellulose [26]. Copyright © 2014, John Wiley and Sons.

Table 1.1 Advantage and disadvantage of physical and chemical activation

activation process	advantage	disadvantage
Physical activation	▪ easy to handle and can controlled temperature in activation process ▪ clean process ▪ not required washing process ▪ produce the uniform pores	▪ need a high temperature above 700 ℃ ▪ two-step process
chemical activation	▪ need a lower temperature ▪ produce in one step ▪ higher product yields ▪ create well developed micro pores ▪ produced higher surface	▪ required the washing process to induce the activated carbon ▪ corrosive the reactor

Many researches studied the effect of carbonization conditions on porosity development from agricultural waste by using physical and chemical activation. Both activations can produce the effective activated carbon, which has a high surface area, micropore volume and total pore volume, are shown in Table 1.2 [2].

Table 1.2 Characteristic pore from activated carbon using physical and chemical activation

Material	Activation process	S_{BET} (m^2/g)	V_{mic} (cm^3/g)	V_t (cm^3/g)	Pore size (nm)	reference
coconut shell	CO_2, 600 ℃/2 h	1700	0.88	1.14	2.7	[10]
coconut shell	Steam, 1000 ℃/2 h	1926	0.93	1.26	2.6	[11]
sugar cane	Steam, 900 ℃/2 h	320	-	0.17	2.1	[27]
almond shell	Steam, 850 ℃/30 min	601	0.34	0.37	-	[28]
rice husk	$ZnCl_2$	927	-	0.56	0.80	[9]
corncob	$ZnCl_2$	1410	-	0.486	1.2	[4]
cotton stalk	H_3PO_4	1720	0.71	0.89	-	[3]
bamboo	KOH	1533	-	0.5	-	[5]
popcorn	KOH	1489	-	0.71	0.57	[6]

The pore sizes of activated carbon depends on type of application; micropore (pore size < 2 nm), mesopore (2 nm < pore size < 50 nm) and macropore (>50 nm). Basically, micropores mainly contribute to surface area and macropore contribute as a channel to micropore surface. Pore distribution depends on degree of initial impregnation of activating agent used. The shape and size of pores in activated carbon depend on the mechanism of activation, which produce by burn-off the disorganized carbon. The important factors, which affect the production of pores in activated carbon are the starting material, carbonization conditions, and activation process. The pore volume and surface area are also important properties of activated carbon [11, 29].

2.5 Freeze drying process

Freeze drying is process which dehydrates frozen materials by turning the water into ice crystals and subsequently triggering the sublimation process by lowering the pressure and temperature below the triple point (4.579 mmHg and 0.0099 ℃). As shown in Figure 2.6, ice crystals are formed during the freezing process by reducing the temperature below the freezing point. The sublimation process can be divided into two steps of primary drying and secondary drying. Primary drying is a sublimation of ice crystals under a vacuum (10^{-4} to 10^{-5} atm) and a product temperature (-45 ℃ to -20 ℃). In secondary drying, the materials are heated under a low pressures and the water vapor are drawn off. Subsequently, the hole made by the ice crystals are formed within the material structures [13, 30].
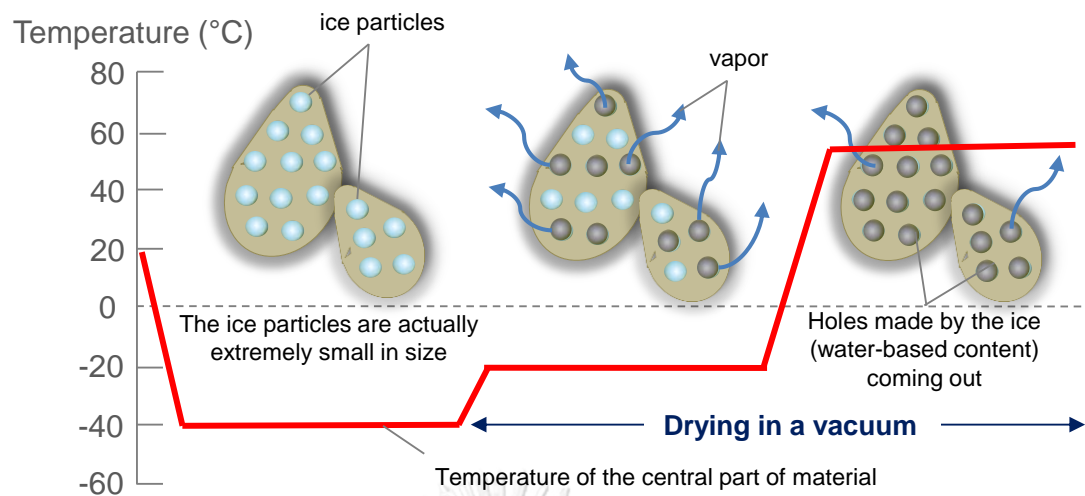
Figure 2.7 Mechanism of freeze-drying process [39]. Available at: http://www.ulvac. com, Accessed June 6, 2018.

2.6 N$_2$ adsorption-desorption isotherm

Nitrogen adsorption-desorption is important analysis technique using the physical adsorption of nitrogen gas molecules on a solid surface. This molecule are filled on sorbent surface and desorb from surface again. Adsorption-desorption isotherm is related to the pressure and volume of adsorbate. This technique was used to measure the specific surface area, pore size, pore volume or pore size distribution by analyze with Brunauer−Emmett−Teller (BET) method. The adsorption isotherm was classified into six types by IUPAC recommendation, as shown in Figure 2.8 [31].
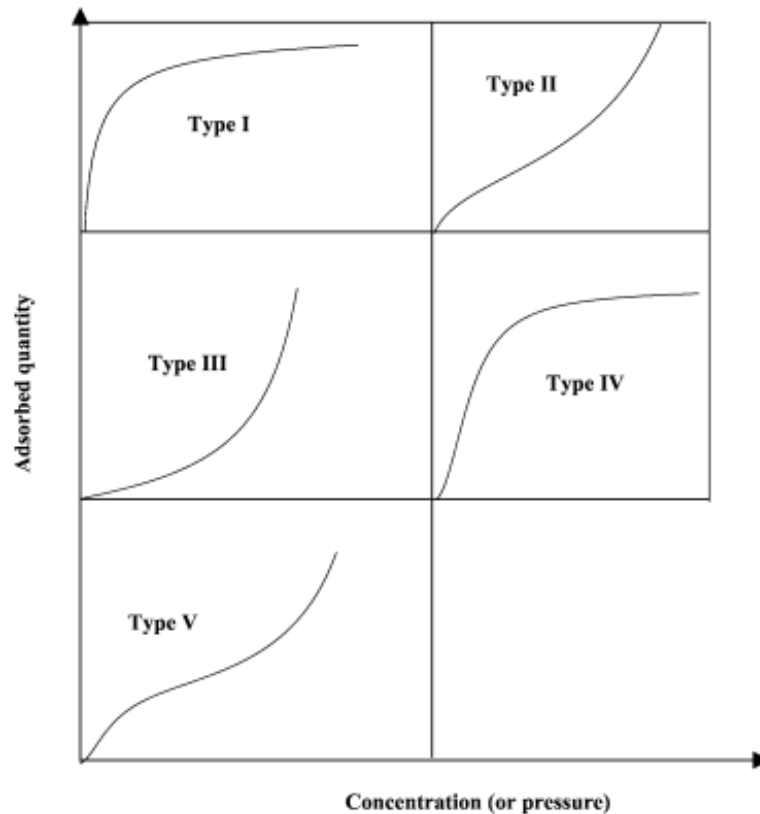
Figure 2.8 Type of adsorption isotherm [31]. Copyright © 2005 Springer-Verlag US.

Type I   Isotherm shows character of microporous material, which relate to the adsorption of monolayer material.

Type II   Isotherm shows character of nonporous material, which related to the adsorption of multilayer material.

Type III   Isotherm shows character of nonporous material, which have the weak interactions of adsorbent and adsorbate.

Type IV   Isotherm shows mesoporous materials, which relate to multilayer adsorption. The hysteresis loop refers to capillary which desorption.

Type V   Isotherm shows monolayer-multilayer adsorption which is presence mesoporous structure.

Type VI   Isotherm represents multilayer adsorption on a uniform non-porous structure.

CHAPTER III
EXPERIMENT

3.1 Materials and Chemicals

- Un-milled waxy rice called 'Laow-taek' (*Oryza sativa L.*) from Yasothon Province

- Methylene blue (MB) (Merck, Thailand)

- Ethanol (EtOH, C_2H_6O) (Merck, Thailand)

- Activated carbon (AC) (CA-R-BON, Greater, medical grade)

3.2 Instruments

- Optical microscope (OM), Carl Zeiss Axio Scope. A1 with a CCD camera (Carl Zeiss, AxioCam HRc)

- Scanning electron microscope (SEM), JEOL JSM-6510

- Nitrogen adsorption-desorption analyzer, BEL Japan, Inc. Belsorp mini II analyzer

- UV-visible spectrometer, Ocean Optics USB4000 Fiber Optic Spectrometer coupled with a Halogen light source from Mikripack.

- Fourier-transform infrared (FT-IR) spectrometer, Nicolet 6700

- Thermal gravitation analysis (TGA), Perkin Elmer, Pyris 1-TGA

- Freeze dry/shell freeze system, LABCONCO

- Filter holder (Millipore, swinnex 47) with membrane filter (pore size 5μm/diameter 47 mm) (Millipore).

- Electric pan cooker from Imaflex with 220 volt 50 Hz power consumption and 1050 watt.

3.3 Popping process

The un-milled waxy rice are heated at 200 °C for 2-3 min in electric pan with continuous stirring. The amylose and amylopectin in starch granule were exploded due to the superheated water in granule. The granule expanded into sponge-like structure which called "popped rice", then remove the rice husks from popped rice. Popped rice was dried in oven at 150 °C for 2 h to get rid of humidity and kept in desiccator for further investigation.

3.4 Activation process

3.4.1 Treatment of popped rice

In general, activation process induce pore surface in material after carbonization using physical and chemical activations. However, in this work we need to create porous structure from the begining by adding water into popped rice instead of using chemicals. In this method, popped rice was impregnated with water, but it cannot be directly impregnated due to popped rice is sensitive to water. So, we have to use ethanol as the main solvent for protection popped rice structure from collapsing and add water into ethanol at 5, 10, 15 and 20% v/v. Then, popped rice was immersed into solution for 10 min and dried with filter paper for 5 min before freeze drying.

3.4.2 Drying process

Freeze drying is a drying process by using a low temperature and pressure to remove water in the material. This process has 2 steps: formation of ice crystals (freezing), water will be expand in volume after phase change to ice crystal and the sublimation of ice crystals under vacuum (drying). The wet popped rice after treatment were frozen in acetone-dry iced (-78 °C) for 15 min and dried using freeze drying process at 100 Pa and -52 °C for 3 h. In this work, we expected that this process combined with adding water can create pore structure on wall surface of popped rice.

3.5. Pyrolysis process

Pyrolysis process is used to transform material to carbon structure by using high temperature without oxygen in system. Firstly, popped rice after freeze drying was placed in crucible and purged with N_2 gas for 20 min to make oxygen-free system. The thermal set in system consists of 2 steps: ramping temperature from room temperature to 500 ºC with heating rate of 10 ºC/min and hold on at 500 ºC for 1 h. After that we get activated carbon (AC) from this process.

3.6 Characterizations

3.6.1 Morphological characterizations

3.6.1.1 Microscopy

The samples (virgin popped rice, freeze-dried popped rice, popped rice with EtOH treatment, popped rice with 5, 10, 15 and 20% water in EtOH) were prepared by cross-section and set onto the aluminum stub covered with carbon tape. The morphology (wall thickness, pore size and wall surface) was observed by optical microscope (OM) (magnification 200X, 500X and 1000X) and scanning electron microscope (SEM), with an accelerating voltage of 1 kV using secondary (SEI) detector. Wall thickness and pore size were investigated using ImageJ software on 200 individual pores and 50 individual wall thickness from different SEM images.

3.6.1.2 Adsorption efficiency of AC

The adsorption efficiency of AC was determined by MB adsorption. The 10 ppm MB solution was prepared by dissolved 0.01 g MB in 1000 mL DI water. Each AC (0.01 g with sieve size of 45 μm) prepared by different conditions was added into a 50-mL MB in 50-ml syringe and injected through the membrane filter (pore size 5 μm). The 2 ml of solutions were collected every minute from 1 min to 10 min into test tube and detected by UV-Vis spectroscopy at 666 nm.

3.6.1.3 Nitrogen adsorption-desorption isotherm

Prior to measure isotherm, the sample (approximately 40 mg) were degasses at 300 ℃ for 3 h by Belprep-vac II (BEL Japan, Inc.). The specific surface area and porosity were analyzed by nitrogen adsorption-desorption analyzer (BEL, Japan, Inc. Belsorp-mini II analyzer) at -198 ℃ with high purity nitrogen (99.998%) and measured by Brunauer-Emmett-Teller (BET) method.

3.6.2 Chemical and reorganization of starch chain (FTIR measurement)

All absorbance spectra were collected by Nicolet 6700 FT-IR spectrometer with a deuterated triglycine sulphate (DTGS) detector using attenuated total reflection (ATR) accessory with a diamond crystal. All samples were measured directly after pressing on diamond crystal. The absorbance spectra were obtained at a resolution of 4 cm^{-1} with 128 number of scans in the spectral range 4000-700 cm^{-1}. All of spectra were baseline-corrected between 1067 cm^{-1} and 950 cm^{-1} by drawing a straight line. Measuring the reorganized of starch chain were obtained by ratios of absorbance intensity at 1047 cm^{-1} (crystalline) and 1022 cm^{-1} (amorphous).

3.6.3   Decomposition profiles of popped rice

The decomposition profile of popped rice was determined using thermal gravimetric analysis (TGA, Perkin Elmer Model: pyris 1TGA). The process was carried under nitrogen. The weight of sample (1-10 mg) was placed into TGA pans. The sample was heated from 30.00 °C to 600 °C at a rate of 20.00 °C/min. The weight loss at the beginning of the process (100 °C) was due to the evaporated moisture from the grains.

CHAPTER IV
RESULTS AND DISCUSSION

To increase the porosity of the structure, we used the freezing method together with adding water to the system. We expected that this process can created a small porous structure on the surface of the structure. This may make it possible to produce effective activated carbon.

4.1 Morphology of popped rice

Cross-section optical microscopy (OM) images reveal that structure of popped rice consists of numerously 3D interconnected starch balloons (Figure 4.1A1) forming honeycomb-like macrostructure (Figure 4.1A2). As shown in Figure 4.2, SEM image analysis shows that the balloon have an average cavity size of 93.60 ± 28.86 μm and wall thickness of 2.85 ± 0.80 μm, respectively. It should be noted that the standard deviation of the cavity size was relatively high not only due to characteristic of balloon cavity size itself but also the variance caused by randomly cross-section positions where the popped rice specimen was sliced. These measured values were used as reference values of non-treated popped rice for observing morphology changes after treatments in further studies.
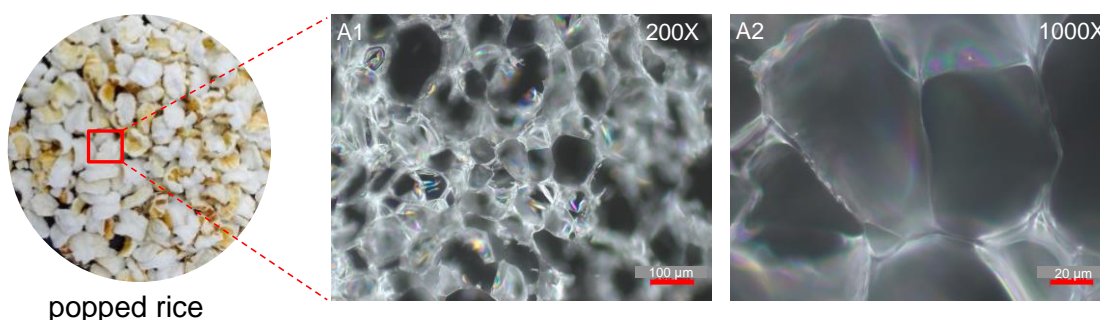

popped rice

Figure 4.1 Cross-section OM images of popped rice with difference magnifications. (A1) 200X and (A2) 10000X.
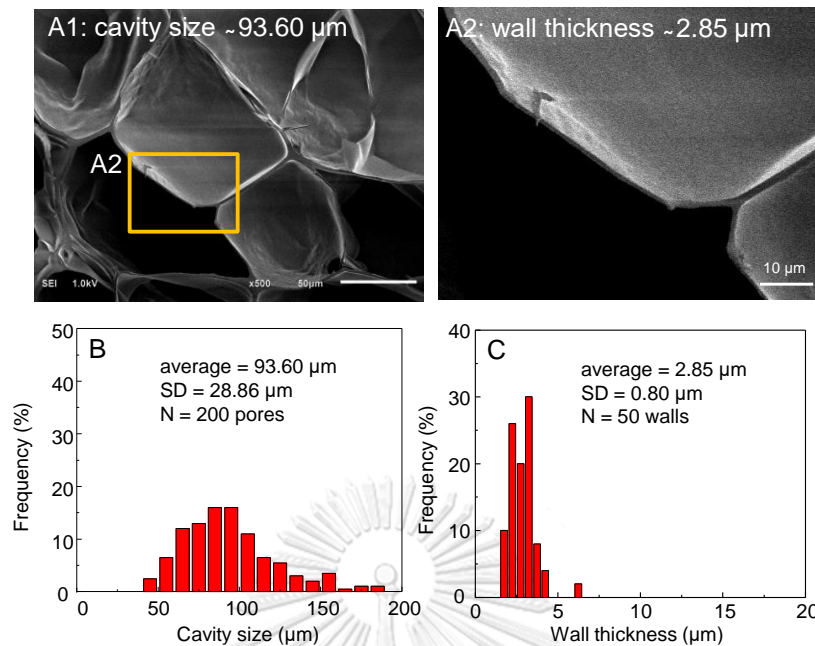
Figure 4.2 Cross-section SEM images of popped rice. (A) Cavity and wall structure of the starch balloon. Size distributions of starch balloon cavity (B) and wall thickness (C).

4.2 Effect of freeze-drying process on morphology of dried popped rice

As known that freeze-drying process involves freezing of water content in samples followed by drying the frozen mass under vacuum. Both freezing and drying can cause various physical stresses such as ice crystal damage and dehydration stress to samples [30, 32]. In some cases, these effect may lead to the loss of their initial morphologies [32-33]. Therefore, it is interesting to observe whether freeze-drying process affects the morphology of popped rice.

After freeze-drying, the structure of the freeze-dried popped rice was still retained as indicated by cross-section OM images (Figure 4.3). As clearly seen, no significant difference on their structure can be observed when compared to those of the virgin popped rice wall. In addition, SEM images (Figure 4.4) not only confirmed the OM image results but also showed that freeze-drying process cause no damages on the surface of the popped rice. Surprisingly, SEM image analysis implied that a slight collapse of the honeycomb-like structure of the popped rice is occurred. As shown in Figure 4.5, the cavity size decreased from 93.60 ± 28.86 to 88.25 ± 28.38 μm and the

wall-thickness increased from 2.85 ± 0.80 to 3.37 ± 1.06 μm after freeze-drying. This structural shrinkage was probably due to the residual moisture in popped rice which play an important role in supporting the popped rice structure.
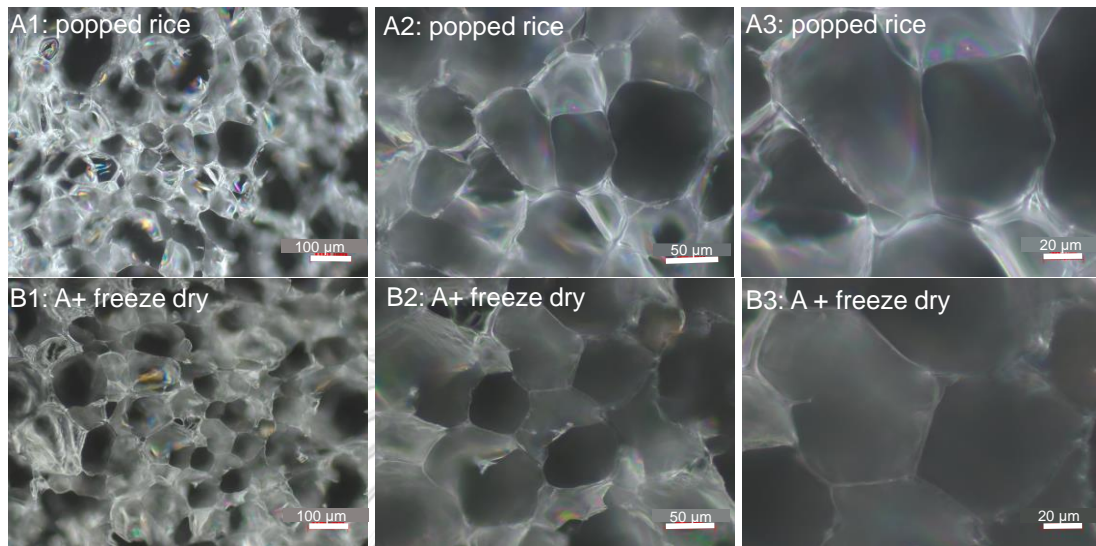

Figure 4.3 Cross-section OM images of popped rice before (A1-A3) and after (B1-B3) freeze drying with different magnifications 100X, 500X and 1000X, respectively.
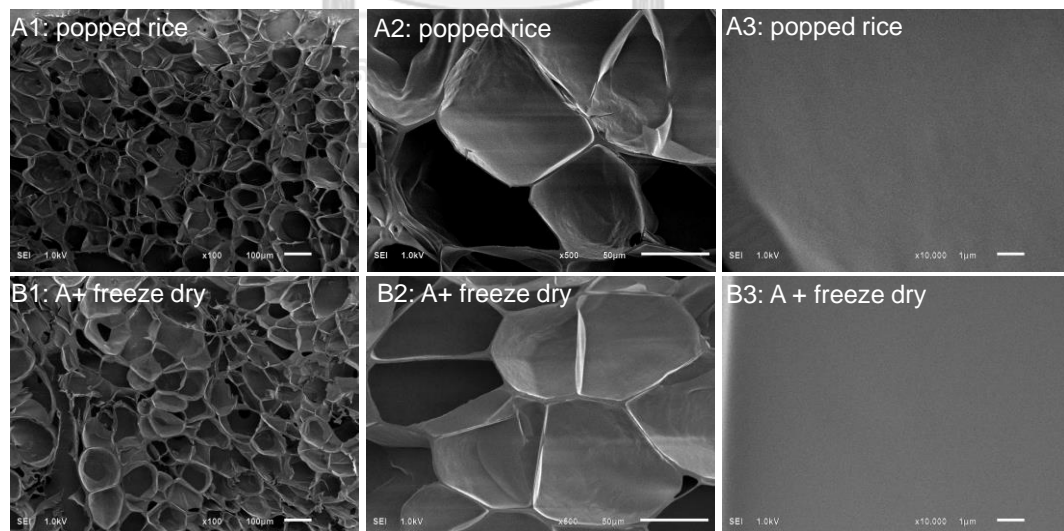

Figure 4.4 Cross-section SEM images of popped rice before (A1-A3) and after (B1-B3) freeze drying process with different magnifications 100X, 500X and 1000X, respectively.
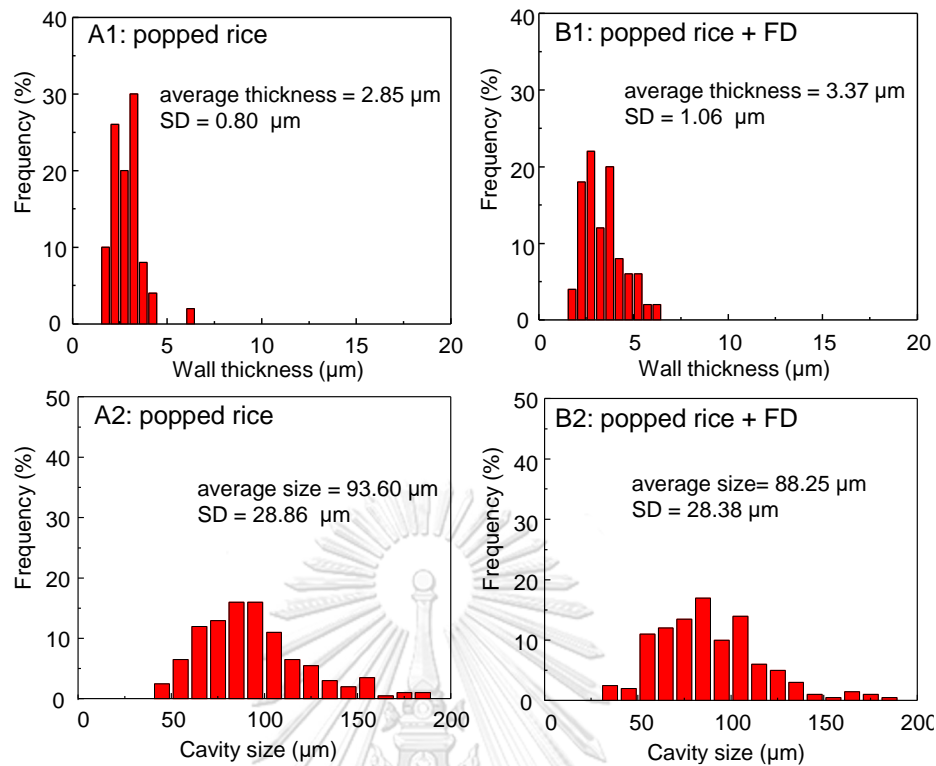
Figure 4.5 Size distributions of wall thickness (A1−B1) and starch balloon cavity (A2−B2) before and after freeze-drying (FD).

4.3 Effect of water impregnation treatment of popped rice before freeze-drying process

As observed in previous section, freeze-drying process did not affect the morphology of popped rice. It might be attributed to insufficient amount of ice crystal, which derived from water content in popped rice, to breaking the starch balloon wall. We hypothesized that if the popped rice contained a greater amount of water, it might create a significant change in the morphology when the popped rice underwent freeze-drying process. Therefore, in this section, popped rice was impregnated with water in order to increasing water content prior to freeze-drying treatment. However, it should be mentioned that the popped rice impregnated with water alone could not be prepared. Immersion of popped rice in water leads to softening the popped rice, causing loss of its honeycomb-like structure. On the contrary, using of a small amount of water also impossible for consistently impregnated the popped rice. To overcome the limitation, ethanol was considered to be a good candidate for using as an intermediate, which can

assist impregnation of water into popped rice while maintaining the structure due to its poor solubility of starch in ethanol [34].

After ethanol immersion, as shown in Figure 4.6B, the popped rice was neither softened nor wet and its appearance was similar to the virgin popped rice (Figure 4.6A). This result suggested that ethanol can be used an intermediate as expected because of having no effect to the original structure of popped rice. Subsequently, where added water to ethanol for water impregnation, the white parts of the popped rice tended to shrink upon increased water contents which can be clearly seen in Figure 4.6C−F. These results suggest that water in ethanol could impregnate inside the popped rice, thereby causing the alteration of the popped appearance.
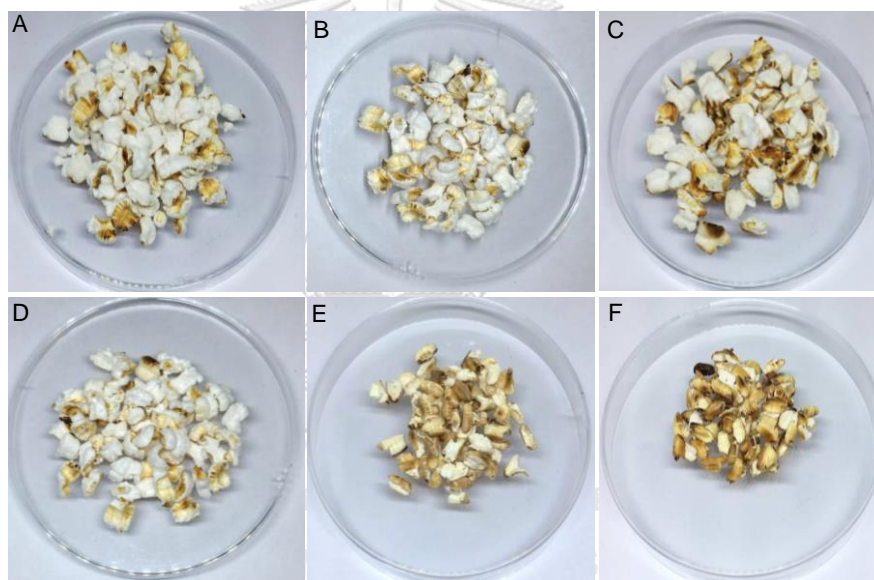

Figure 4.6 Photograph of popped rice (A) popped rice with freeze dry, (B) popped rice with EtOH treatment, (C) popped rice with 5% (v/v) of water in EtOH, (D) popped rice with 10% (v/v) of water in EtOH, (E) popped rice with 15% (v/v) of water in EtOH and (F) popped rice with 20% (v/v) of water in EtOH.

Accordingly, the popped rice structures with different water impregnation levels were further investigated after subjected to freeze-drying process. Noted that those impregnated samples could not directly be cross-sectioned due to limitations from their softness. While using freeze-drying treatment to those impregnated popped rice could fairly maintain the structure after cross-sectioned, as suggested by the previous results. Interestingly, OM images showed that the inter-balloon region was thicker while the balloon cavity size decreased with the increased of water contents in ethanol (Figure 4.7). These observations of the morphology changes were confirmed again by SEM images, as shown in Figure 4.8. SEM image analysis showed that impregnated pop rice with 0, 5, 10, 15, 20% (v/v) of water content in ethanol resulted in the wall thickness (Figure 4.9) as 1.95 ± 1.20, 4.17 ± 1.57, 3.42 ± 1.57, 6.46 ± 2.50 and 6.04 ± 2.75 μm, respectively. In addition, the measured cavity sizes of those (Figure 4.10) were 80.45 ± 16.89, 40.29 ± 13.53, 50.68 ± 15.87, 38.84 ± 18.23 and 27.69 ± 12.39 μm, respectively.
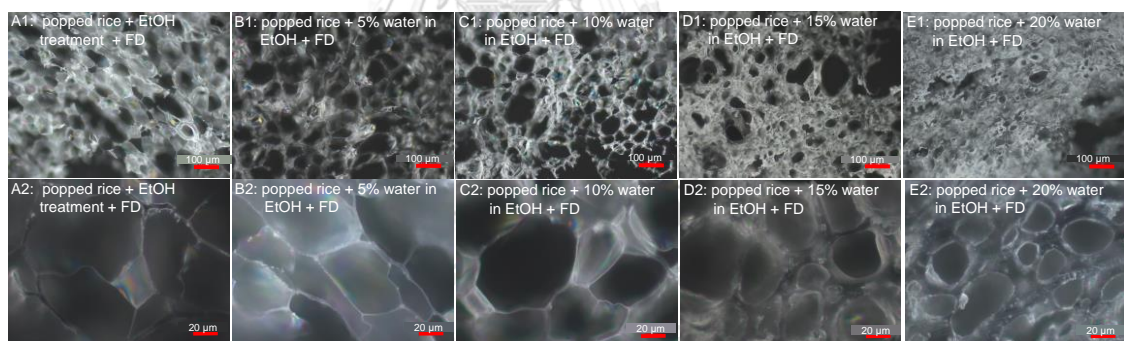
Figure 4.7 OM images show pore morphologies of popped rice with wall thickness after freeze drying process: (A) popped rice with EtOH treatment, (B) popped rice with 5% (v/v) of water in EtOH, (C) popped rice with 10% (v/v) of water in EtOH, (D) popped rice with 15% (v/v) of water in EtOH and (E) popped rice with 20% (v/v) of water in EtOH.
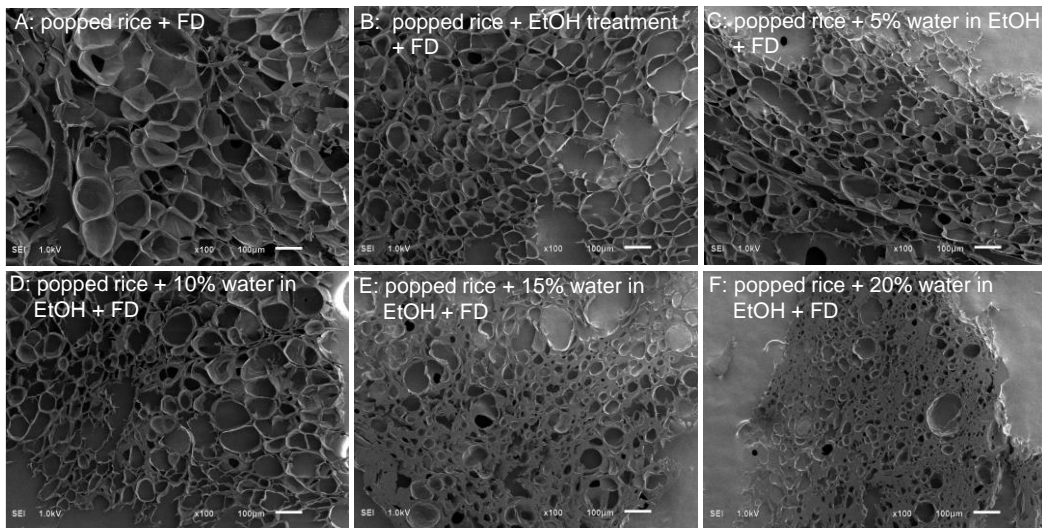
Figure 4.8 SEM images show pore morphologies of popped rice with wall thickness after freeze drying process.
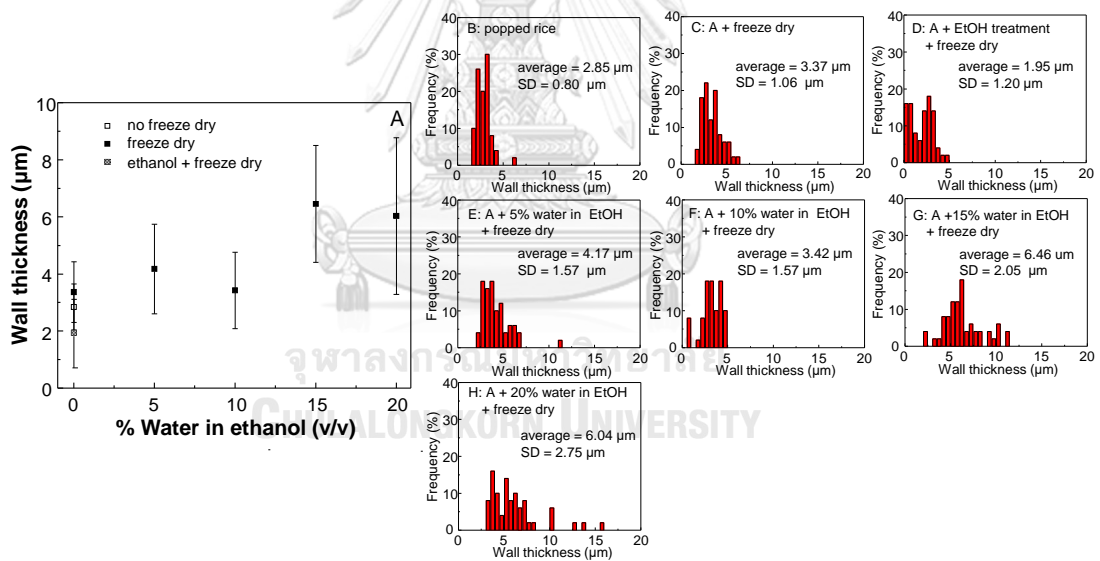

Figure 4.9 Plot between water content and wall thickness of popped rice (A) with distributions of wall in each water content (B−H).
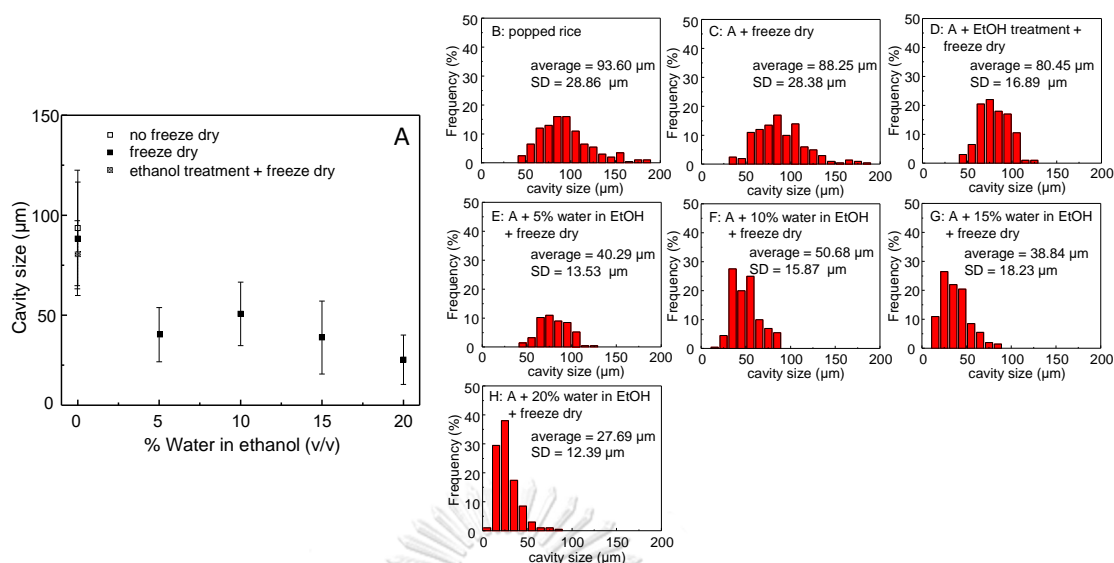
Figure 4.10 Plot between water content and cavity size of popped rice (A) with distributions of cavity in each water content (B–H).

Furthermore, SEM images showed that wrinkles occurred on the surface of the balloon wall of which all popped rice impregnated with water, while impregnation with ethanol alone could not cause any change to the surface morphology (Figure 4.11). These results suggested that when popped rice impregnated with water, molecules of water are preferentially absorbed into the inter-balloon region, leading to shrinking of the starch balloon. Because the structure of popped rice basically is gelatinized starch, which is their amylose partially diffused out of the starch granule to the inter-balloon region after popping process [15]. Amylose initially provides strength and resistance to solubility of the starch balloon. Therefore, popped rice structure is susceptible to water that can leach more amylose of the inter-balloon region and form gel. Once, popped rice was further impregnated with water, the starch balloon mostly lost amylose and now contained only amylopectin. The structure thus collapsed and the wall was thickened with wrinkles.
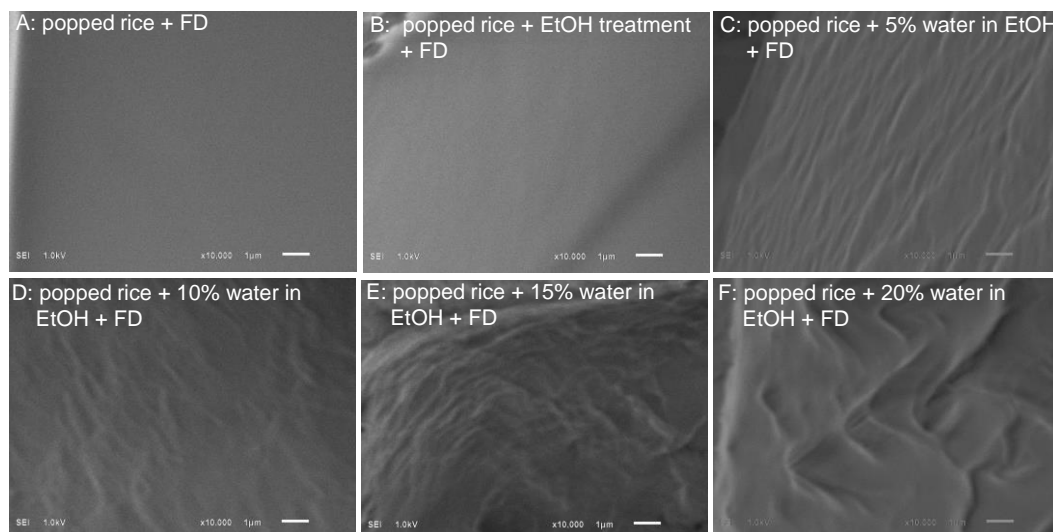
Figure 4.11 SEM images show wall surface of popped rice freeze drying process: (A) popped rice with freeze dry, (B) popped rice with EtOH treatment, (C) popped rice with 5% water in EtOH, (D) popped rice with 10% water in EtOH, (E) popped rice with 15% water in EtOH and (F) popped rice with 20% water in EtOH.

Next, according to the freeze-drying step, retrogradation effect was further investigated via ATR-FTIR to clearly understand physical properties of freeze-dried/impregnated popped rice before undergoes carbonization process. Retrogradation is a recrystallize process of the amylose and amylopectin molecules in gelatinized starch such as popped rice, where stored in a cooling environment. If retrogradation occurs in popped rice, it probably affect to the structure of the carbon obtained after carbonization. ATR-FTIR spectra were collected in the region of 1200-900 cm^{-1} containing C−C and C−O stretching modes of the polysaccharide backbone. The bands in this region include 1047 and 1022 cm^{-1}, which are a characteristic of retrograded crystalline starch and a feature of amorphous form, respectively [35-36]. Hence, a greater band ratio of 1047: 1022 cm^{-1} indicates a greater degree of crystallization. This parameter has been used to follow the retrogradation of starches in different studies [37]. To compare the results, another set of non-freeze-dried samples was prepared by drying impregnated popped rice at 110 °C for 3 h prior to measure FTIR. This step is necessary because of removing of the remained water molecules inside the popped rice

structure capable of preventing error from the further progressive collapse and signal interference from water. Figure 4.12A-B illustrated the difference of FTIR spectra of wet and dried impregnated popped rice. The summarized band ratio of 1047:1022 cm^{-1} (I_{1047}/I_{1022}) was shown in Table 4.1. For non-freeze-drying popped rice, FTIR spectra (Figure 4.12B) support the previous results that water impregnation affect the crystallinity of the popped rice structure as can be observed by a slight decrease of 1047: 1022 cm^{-1} ratio. Then, FTIR spectra of the impregnated popped rice after freeze-drying process (Figure 4.12C) show no significant change. Therefore, in this case, freeze-drying process does not induce retrogradation on impregnated popped rice.
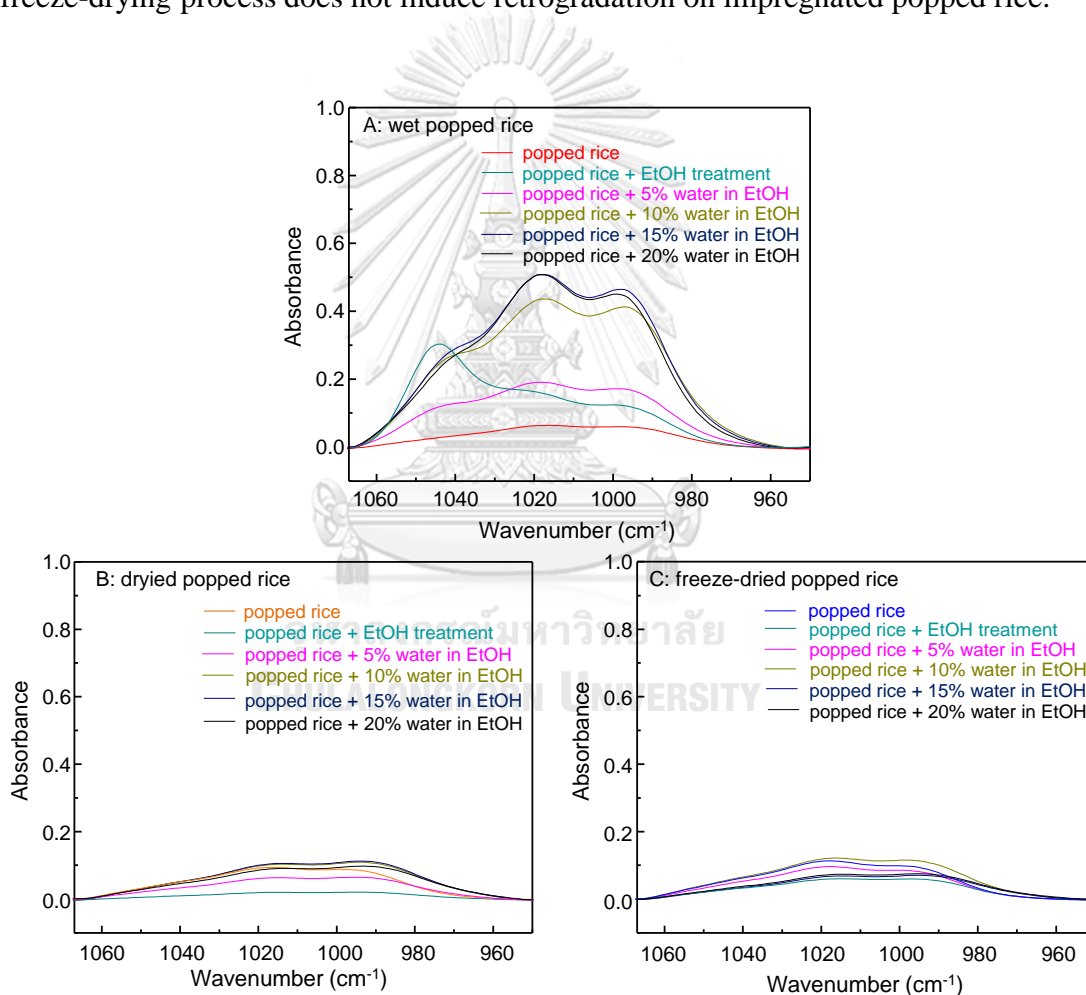

Figure 4. 12 FTIR-spectra of popped rice with difference process, (A) wet popped rice, (B) dried popped rice and (C) freeze−dried popped rice.

Table 4.1 Absorbance ratio (I_{1047}/I_{1022}) of popped rice each conditions

sample/condition	original	wetted popped rice	dried popped rice	freeze-dried popped rice
virgin popped rice	0.4013	-	0.4234	0.4237
5% water in EtOH	-	0.5645	0.4193	0.4162
10% water in EtOH	-	0.5035	0.3921	0.4194
15% water in EtOH	-	0.4359	0.3843	0.3961
20% water in EtOH	-	0.3955	0.4061	0.4093
EtOH treatment	-	1.690	0.3571	0.4342

Overall, it could be summarized that water impregnation treatment directly affects the morphology of popped rice during the water exposure period. While freeze-drying process, which turn water molecules into ice crystals, insignificantly cause damages, ruptures, or retrogradation on the wall structure of the popped rice.

4.4 Morphological study on porous activated carbon from popped rice via carbonization process

Before studying the carbonization of the treated-popped rice, the thermal degradation profile of popped rice was examined using thermogravimetric analysis (TGA). TGA thermogram of popped rice was shown in Figure 4.13. Derivative thermogram (blue line) showed two weight loss profiles possessing the onset temperatures at 80.92 °C and 318 °C, and level-off at higher than 500 °C. The weight loss profile with the onset at 80.92 °C related to the evaporation of the absorbed water molecules in popped rice while the onset at 318 °C was from the decomposition of

organic materials [38]. Therefore, 500°C was selected as the carbonized temperature in this study.
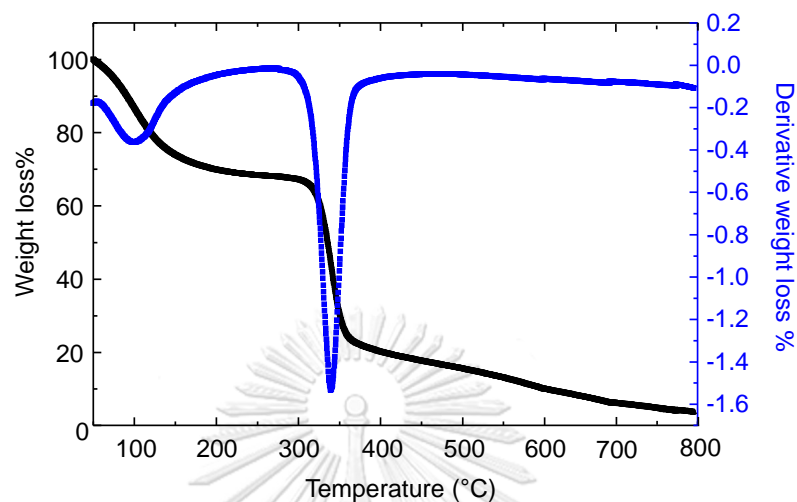

Figure 4.13 TGA thermograms of popped rice (black line) and derivative thermograms (blue line).

After surface activation of popped rice, all impregnated samples were then carbonized at 500 °C for 3 h. The appearance of the both obtained carbons from popped rice with and without freeze-drying/impregnation treatment were similar (Figure 4.14). The structure of those carbons can easily be broken off when cross-sectioned or forcedly touched due to their brittle and crisp texture. Hence, for the morphological study, only part of the carbons which retained their original morphology was carefully sampled and the observation focused on changing on the carbon surface.
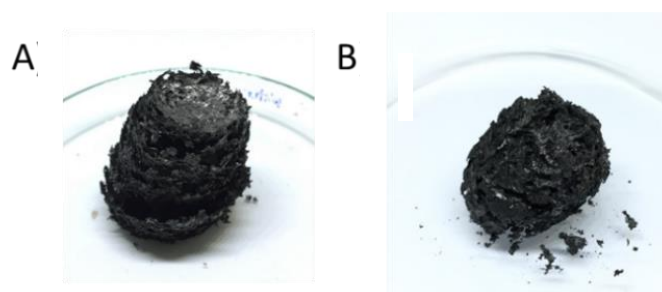

Figure 4.14 Photograph of porous carbon derived from (A) popped rice and (B) popped rice pre-treated with 20% water content impregnation and freeze-drying process.

As shown in Figure 4.15, SEM images show that the structures of both virgin and freeze-dried popped rice were collapsed as expected. Carbonization caused the loss of moisture and the decomposition of popped rice components. However, wall surface of the carbons was still smooth similar to those before carbonized, as previously shown in Figure 4.11. The results suggest that carbonization process could not alter the surface morphology. In contrast, freeze-dried/impregnated popped rice clearly induced the formation of micropores on wall surface of the carbons (Figure 4.16). The micropore generation could probably due to be a rupture process on the weakest spot, which is amorphous part, of wall starch impacted from the thermal decomposition of popped rice. Accordingly, these results raised an assumption that the rupture may be necessarily attributed to the synergistic effect of water impregnation and freeze-drying process that weaken the polymeric structure against the carbonization process. Neither water impregnation nor freeze-drying alone could give rise to the mircropore generation, as suggested by the previous studies.
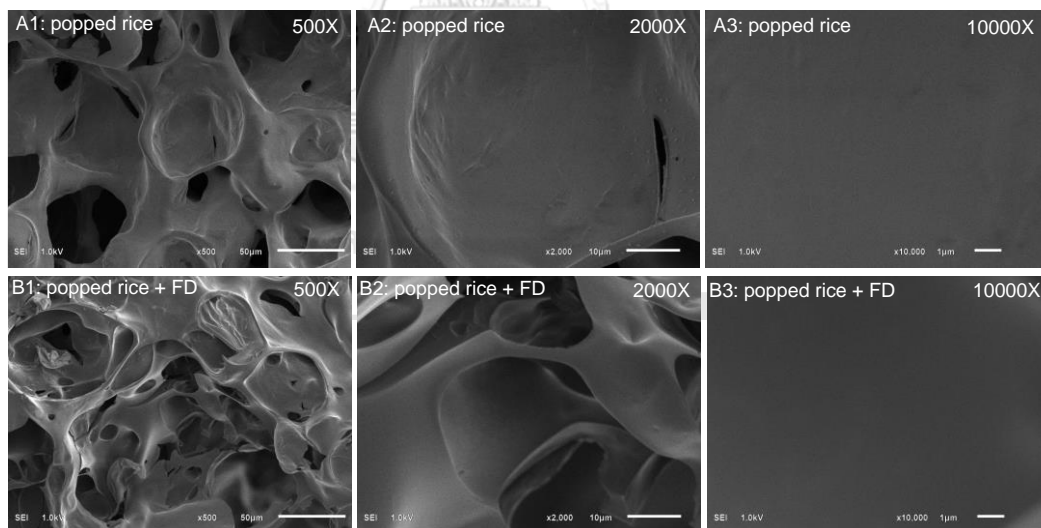

Figure 4.15 SEM images of wall surface of popped rice after pyrolysis process: (A) popped rice before freeze dry and (B) popped rice after freeze dry.
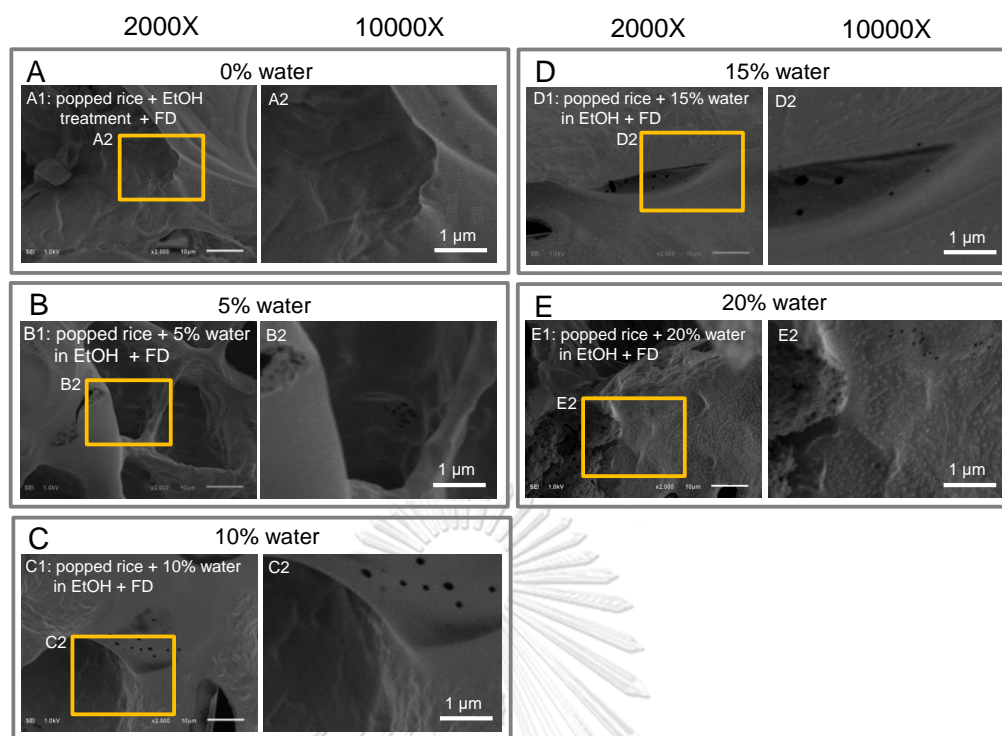
Figure 4.16 SEM images of popped rice wall with internal and external wall after pyrolysis process with magnification at 2000X and enlarge SEM images.

To emphasize the synergistic effect, the impact of water impregnation was further investigated. We considered that water molecules could penetrate and surround the starch balloons of the popped rice structure. Therefore, if ice crystals involve weakening the wall surface, the generated micropores should be visible on any sides of the carbon wall. The carbon samples were carefully cracked to allow observation of the surface in different positions. The carbon derived from freeze-dried/ethanol impregnated (0% water content) popped rice did not exhibit micropores on its surface for both area-B and area-C (Figure 4.16A). When the impregnation system contained water contents from 5 to 20% (v/v), micropores at the internal surface can also be observed similar to those appeared in Figure 4.16. When comparing the pore size on the internal to external surface (Figure 4.17B−C), it was found that they were similar as approximately ~0.3 μm. The measurement of pore size distributions was shown in Figure 4.17D. These results implied that the generation of micropores, which occurs on both sides of the wall, was induced by the impregnated water.
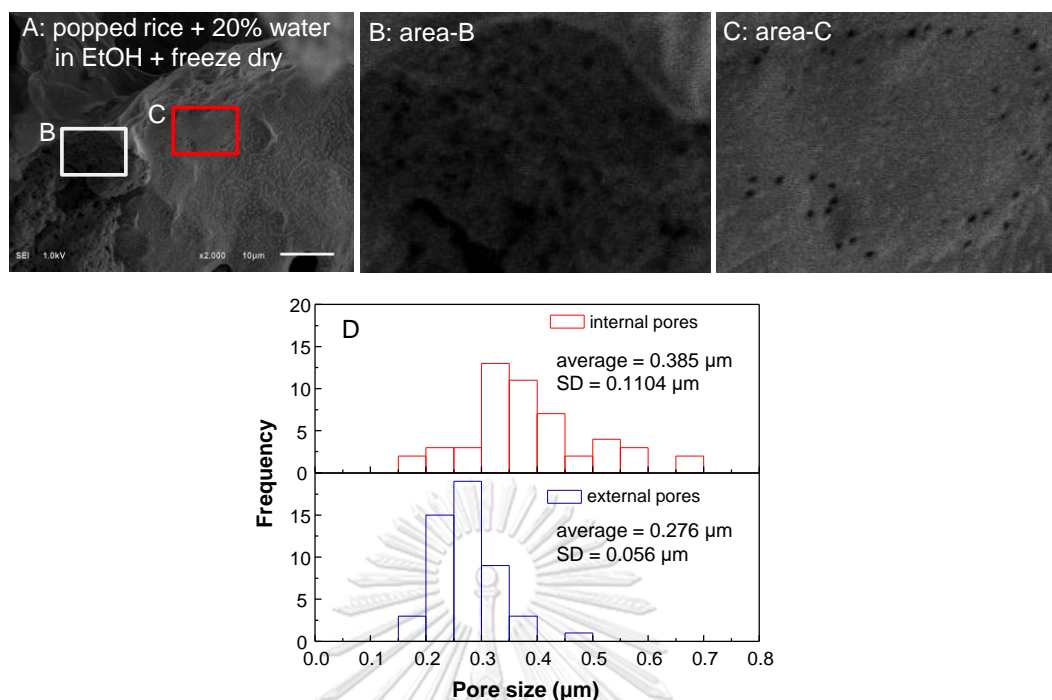
Figure 4.17 SEM images of internal and external wall of popped rice impregnated in
        20% of water after pyrolysis with magnification at 10000X (A−C).
        Distribution of void between internal and external surface (D).

Furthermore, the role of freeze-drying process in micropore generation after carbonization was investigated. The study was performed by drying impregnated popped rice in oven at 110 °C, instead of using freeze-drying method. Water impregnation at 20% water content was selected in this study because of providing most obvious effect from water impregnation. As expected, physical appearances, and morphologies of the impregnated popped rice, which resulted from either oven-drying or freeze-drying methods, were similar. Figure 4.18 shows the structural collapse, thickened starch wall, and wrinkles. After carbonization, the sample was cracked to again observe the micropore generation on the wall surface. SEM images (Figure 4.19) show that there was no appearance of micropores on the wall surface, which differs to the results observed from freeze-drying method. This result indicated the necessity of using freeze-drying method in order to activate micropore on the surface of starch wall.
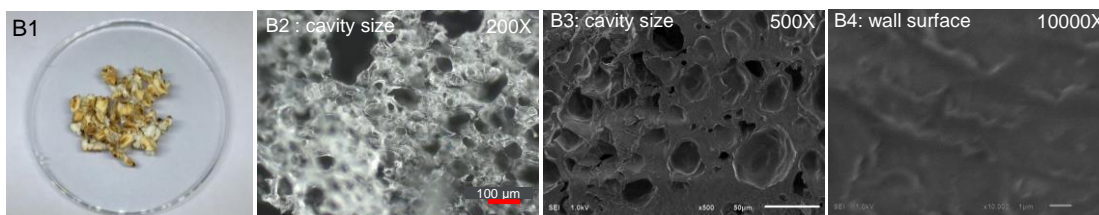
Figure 4.18 popped rice impregnated with 20% water content after dried in oven at 110 °C, 3 h.
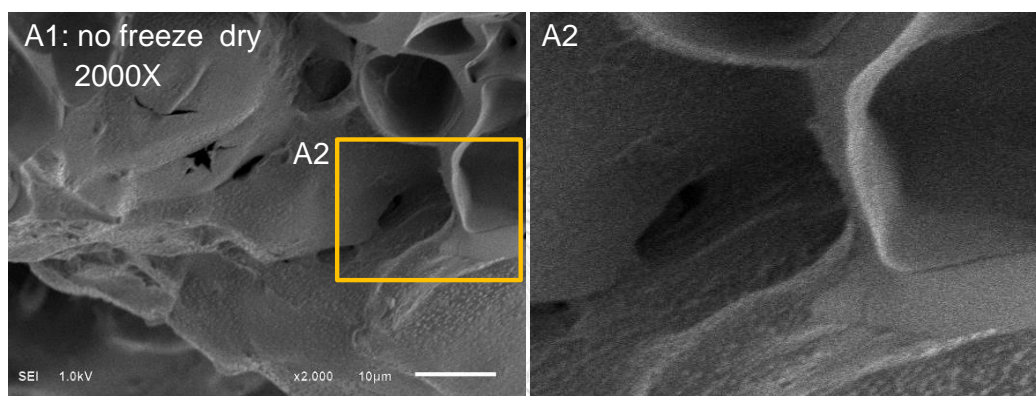

Figure 4.19 SEM images of wall of carbon after pyrolysis process with magnification at 2000X: carbon from popped rice without freeze dry (baked in oven at 110 °C, 3 h) (A1) and enlarge SEM images (A2).

4.5 The effect of treatment process (added water, baked and freeze dry) to the crystallization of starch

Since, water impregnation combined with freeze-drying process can be used to activate micropores on the popped rice surface, appearing after carbonization. Thus, it likely suggests that micropore generation may sufficiently increase surface area to the popped rice-derived carbon conferring activated carbon capability. Therefore, it is necessary to determine total surface area of the carbons, which is related to the effect of the freeze-drying/impregnation treatment. Brunauer-Emmett-Teller (BET) analysis was employed through N_2 adsorption-desorption isotherm. Prior to measurement, different kinds of carbons including virgin, treated, and commercially activated carbon were grounded and sieved to obtain the controlled particle size as approximately 45 μm in diameter. Dark field OM images confirmed the similar size of the obtained particles from different carbons, as shown in Figure 4.20.
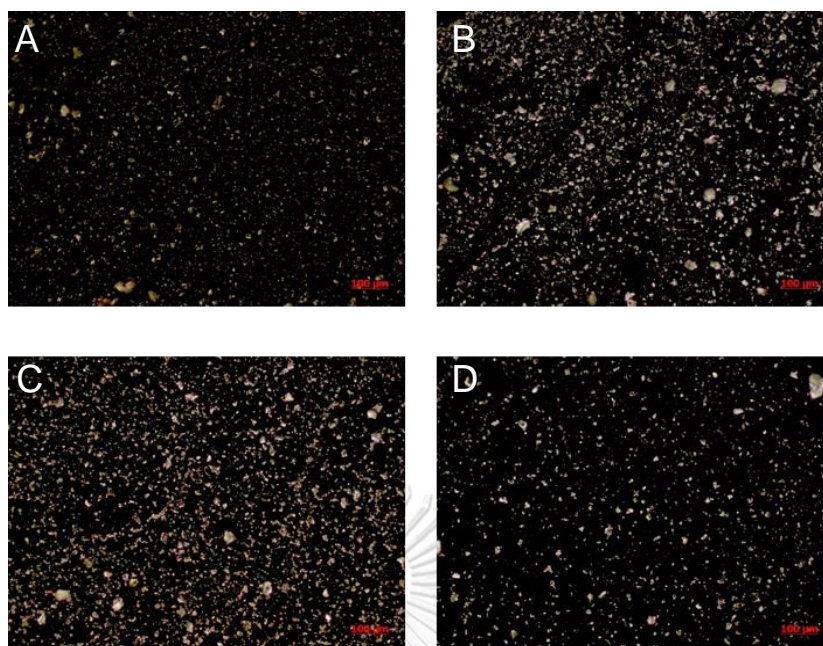
Figure 4.20 Dark-filed OM images of different kinds of carbon particles: (A) commercially activated carbon, (B) virgin popped rice-derived carbon, (C) freeze-dried popped rice carbon, and (D) freeze-dried/impregnated (20% water content) popped rice-derived carbon.

The adsorption-desorption isotherms of all popped-rice derived carbons, as shown in Figure 4.21A, were fitted to type I, indicating microporous structure [31]. By following the isotherms, surprisingly, BET calculations revealed that both total surface area and pore volume decreased as the water content in the impregnation solutions increased. The opposite outcome is probably due to water molecules collapsing the popped rice structure, thus resulting in reduced effectiveness of the carbonization process.
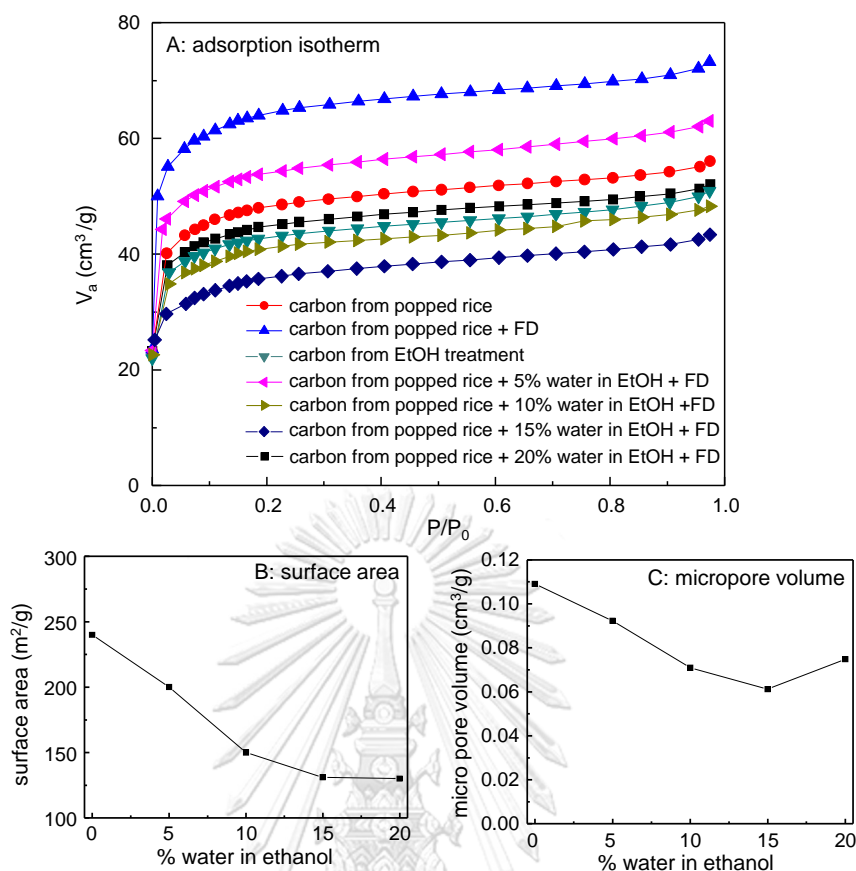
Figure 4.21 Adsorption-desorption isotherm of popped rice after pyrolysis at 500°C
(A). Plot of surface area between water content (B). Plot of surface area
between water content and plot of micropore volume between water
content (C).

4.6 Activated carbon captivity of popped rice-derived carbon

After surface properties of popped rice-derived carbons were studied, we further
tested that weather the pretreatment method, which is water impregnation coupled
freeze-drying process, can be used to convert popped rice to activated carbon after
carbonization. Adsorption test of methylene blue was performed to demonstrate their
activated carbon capability.

The results showed that the MB absorption capacity of the treated and untreated
samples was not significantly different. When comparing the treatment samples with
commercial activated carbon, the absorbance was significant, as shown in Figure 4.22
The adsorption capacity of carbon from this popped rice (30.52%), popped rice with
freeze dry (32.16%) and impregnated with water (23.95%), which lower than that of

the commercial activated carbon (~100%), as shown in Figure 4.22B. These results suggest that freeze-drying/impregnation treatment is not effectively enough to confer activated carbon capability to the popped rice-derived carbon. This unsuccessful method for activated carbon production may be deduced to the structural collapse of the popped rice during the activation treatment. The structural shrinkage due to water impregnation dominantly causes a reduction of the surface area and pore volume of the carbons, despite eventually gaining the micropores on the surface. Overall, for activate-then-carbonize method, preservation of original starch structures is more important than creating marginal surface area to prevent the opposite effect of the surface activation due to the structural collapse, which can be explained in Figure 4.23. The adsorption isotherm from treated sample (20% of water) has a lower than commercial activated carbon due to the surface area and total pore of treated sample are much smaller when comparing with commercial activated carbon (Table 4.2).
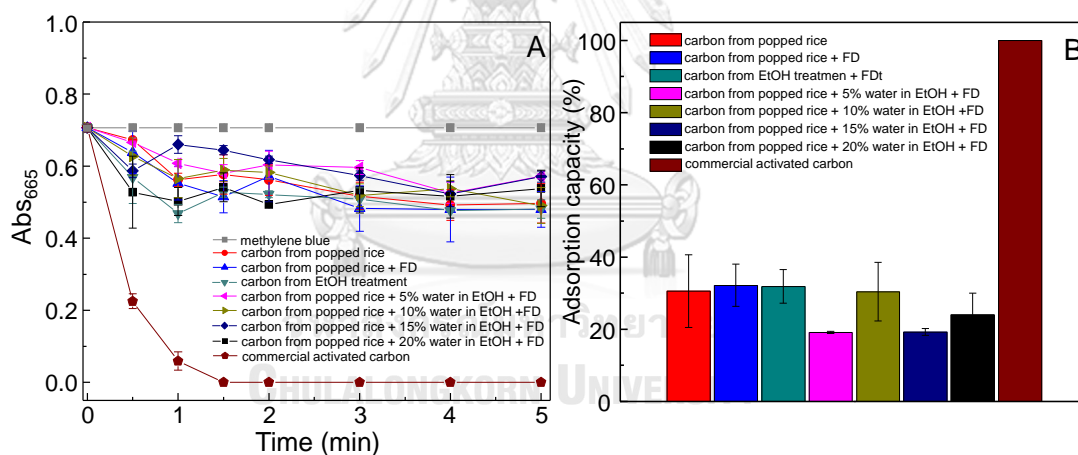
Figure 4.22 Methylene blue adsorption of carbon from popped rice each conditions
compare with commercial activated carbon.
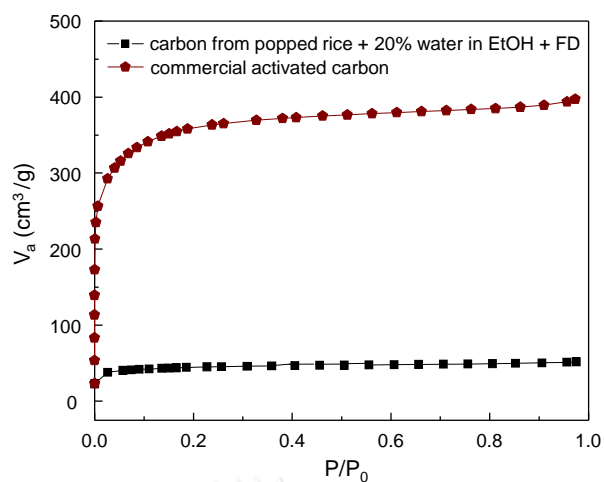
Figure 4.23 Adsorption isotherm of carbon from popped rice with 20% water in EtOH and commercial activated carbon.

Table 4.2 Surface area and pore volume of AC from popped rice with 20% water in EtOH and commercial activated carbon

Sample	S_{BET} (m^2/g)	V_{total} (cm^3/g)
20% water in EtOH + FD	130	0.0065
commercial activated carbon	1287	0.6146

CHAPTER V
CONCLUSIONS

In this work, the effect of the freezing method together with water adding into the system was studied to create the small pores on popped rice wall and transformed to activated carbon with pyrolysis at 500 °C for 1 h. In the system with water, the wall thickness were increased while the cavity pore of popped rice was shrunk. The structural collapse, due to the effect of water, corresponds to the wrinkle on popped rice wall. The small pores were observed after pyrolysis. When increase the water from 5 to 20 % (v/v), the number of pores increased. The small pores both inside and outside of the wall are similar in size about 0.3 μm. This is due to the water that penetrates the inner and outer walls. Although, the water was added, baked or freeze-drying, the retrogradation did not occur in the system. In addition, the water impregnation cause decreasing of total surface area due to surface area also decreased when the amount of water increased even with the occurrence of the pores in the structure. The methylene blue absorption was used to evaluate the sorption efficiency of activated carbon by comparing the carbons from treated-popped rice to the commercial activated carbon. The absorption efficiency show no significant difference among of treated-samples, but much lower when comparing with commercial activated carbon. Therefore, the freezing method together with adding water to the system can create the small pores on popped rice wall after pyrolysis, but this method cannot turn carbon to the activated carbon because of structural is collapsed when the water is added.

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