การดูดซับสารอินทรีย์ระเหยง่ายด้วยคาร์บอนที่พัฒนาจากเส้นใยของเรโซซินอลฟอร์มาลดีไฮด์เจลซึ่งถูกปั่นด้วยไฟฟ้าสถิตย์

นางสาวอสมาภรณ์ ภูดินดาน

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
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ADSORPTION OF VOLATILE ORGANIC COMPOUNDS ON CARBON FIBER DERIVED FROM ELECTROSPUN RF-GEL

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อสมาภรณ์ ภูดินดาน : การดูดซับสารอินทรีย์ระเหยง่ายด้วยคาร์บอนที่พัฒนาจากเส้นใยของเรโซซินอลฟอร์มาลดีไฮด์เจลซึ่งถูกปั่นด้วยไฟฟ้าสถิตย์ (ADSORPTION OF VOLATILE ORGANIC COMPOUNDS ON CARBON FIBER DERIVED FROM ELECTROSPUN RF-GEL) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: รศ. ดร. วรงค์ ปวราจารย์, 73 หน้า.

โทลูอีนเป็นสารก่อมะเร็งและมลภาวะ การดูดซับโดยใช้เส้นใยถ่านกัมมันต์เป็นวิธีที่ถูกและมีประสิทธิภาพในการกำจัดโทลูอีน เรโซซินอล-ฟอร์มาลดีไฮด์ เจล หรือ อาร์เอฟเจล เป็นฟีนอลิคเรซินซึ่งเป็นสารตั้งต้นถ่านกัมมันต์ที่ให้ถ่านกัมมันต์ที่มีคุณสมบัติโดดเด่น เส้นใยอาร์เอฟเจลสามารถผลิตได้จากการปั่นเส้นใยด้วยไฟฟ้าสถิตย์แบบไม่ใช้เข็ม ชนิดแท่งเกลียวเหล็ก โดยเส้นใยถ่านสามารถได้จากกระบวนการคาร์บอไนเซชันของเส้นใยอาร์เอฟเจลที่ 650, 750 และ 850 องศาเซลเซียส การเพิ่มรูพรุนของเส้นใยถ่านสามารถทำได้โดยการกำจัดถ่านที่ไม่เป็นระเบียบอยู่ในโครงสร้างรูพรุนโดยกระบวนการกระตุ้นด้วยไอน้ำที่อุณหภูมิ 700, 800 และ 900 องศาเซลเซียส เป็นเวลา 30 นาที เส้นใยถ่านกัมมันต์ถูกใช้เป็นตัวดูดซับในกระบวนการดูดซับโทลูอีน ไอโซเทอมของการดูดซับของเส้นใยถ่านแสดงประสิทธิภาพการดูดซับสูงสุด 0.2 มิลลิกรัมโทลูอีน/มิลลิกรัมตัวดูดซับ และประสิทธิภาพการดูดซับสามารถเพิ่มขึ้น 0.3 มิลลิกรัมโทลูอีน/มิลลิกรัมตัวดูดซับหลังจากกระบวนการกระตุ้น และการดูดซับของ 1-ออคทานอลถูกศึกษาเพื่อแสดงรายละเอียดมากขึ้นในโครงสร้างของรูพรุนของเส้นใยถ่าน

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ASAMAPHORN PUDINDARN: ADSORPTION OF VOLATILE ORGANIC COMPOUNDS ON CARBON FIBER DERIVED FROM ELECTROSPUN RF-GEL. ADVISOR: ASSOC. PROF. VARONG PAVARAJARN, Ph.D., 73 pp.

Toluene is a carcinogen and a pollutant. An adsorption using carbon fiber is a cheap and effective method in elimination of toluene. Resorcinol-formaldehyde gel (RF-gel) is a phenolic resin carbon precursor which provides carbon with outstanding properties. RF-gel fibers can be fabricated from twisted-wire needle-less electrospinning. Carbon fiber can be obtained from carbonization of RF-gel at 650, 750 and 850 ˚C. An increase in porosity of carbon fiber can be achieved from removal of disorganized carbon in pore structure via steam activation at 700, 800 and 900 ˚C for 30 minutes. Activated carbon fiber was used as an adsorbent in adsorption of toluene. An adsorption isotherm of carbon fiber shows the highest adsorption capacity up to 0.2 mg toluene/mg adsorbent. The adsorption capacity can be increased up to 0.3 mg toluene/mg adsorbent after the activation. And 1-Octanol adsorption was investigated for more detail in pore structure of carbon fiber.

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CONTENTS

List of tables

List of figures

List of figures (cont.)

Figure Page

Chapter I
Introduction

1.1 Introduction

Volatile organic compounds or VOCs is an organic compound which easily evaporate at room temperature and atmosphere. VOCs are usually released from combustion or from many products in daily life. Its properties have many harmful effects on both human and environment as carcinogen and ozone layer destructor respectively [1]. Therefore, almost countries in this world have limitation of VOCs that were released to atmosphere [2].

Adsorption is a well-known green technology which used for VOCs capture [1]. Generally, porous solid and removed-gas/liquid are called as adsorbent and adsorbate in adsorption process respectively. There are many advantages of adsorption technology includes simple and low cost [3]. Moreover, an adsorbent can be recovered for reusing after VOCs adsorption [4].

Carbon materials generally use as an adsorbent because of its properties includes large surface area and high adsorption capacity [5, 6]. Carbon fiber is one type of carbon materials that have long thin strand [7]. Carbon fiber have many outstanding properties such as easily handling and higher surface area. Generally, the properties of carbon fiber are depend on many factors such as type of precursor, production, carbonization or activation.

Resorcinol-formaldehyde gel is a carbon precursor that have high mesoporosity [8-10]. So, carbon that was received from this precursor should be had high mesoporosity. Accordingly, carbon fiber which carbonized from resorcinol-formaldehyde gel is also expected to have high mesoporosity. Carbon fibers can be regenerated faster with an appearance of mesoporosity.

In this study, carbon fibers produced from combination of sol-gel process and twisted wire electrospinning. Effects of heating rate in carbonization, carbonization temperature and activation temperature on carbon properties are studied. Moreover, temperature of adsorption isotherm and liquid phase adsorption are also investigated for describing on porosity of carbon fiber.

1.2 Objectives

To investigate porosity and an adsorption behavior of carbon fibers which are resorcinol-formaldehyde gel as a precursor.

1.3 Scopes of study

There are 9 parameters that were studied for VOCs adsorption includes;

1.3.1 Carbon precursor was resorcinol-formaldehyde gel which R/F, R/W and R/C were fixed at 0.5, ∞ and 500 respectively. Sodium hydrogen carbonate ($NaHCO_3$) was used as catalyst.

1.3.2 Twisted wire needle-less electrospinning used in fiber production. All parameters of electrospinning were fixed at 12 cm of distance between twisted wire and plate collector, 30 kV of applied voltage, 45-50% of humidity and 20 ml/h of feed flow rate.

1.3.3 Heating rate of carbonization was studied at 1, 5 and 10 ˚C/min.

1.3.4 Carbonization temperature was studied at 650, 750 and 850 ˚C.

1.3.5 Steam activation temperature was varied at 700, 800 and 900 ˚C.

1.3.6 Toluene was selected as representative of toluene.

1.3.7 Adsorption isotherms were performed at 30,45 and 80 ˚C.

1.3.8 1-Octanol was chosen for a studying of liquid phase adsorption.

1.3.9 Liquid phase adsorption was performed at 30 ˚C

Chapter II

Theory and literature review

In this chapter, basic theories and literature review which related to this work are described. There are 5 parts of basic theory includes resorcinol-formaldehyde gel, activated carbon fiber, electrospinning, adsorption and VOCs.

2.1 Theory

2.1.1 Resorcinol-formaldehyde

A highly cross-linked polymer such as resorcinol-formaldehyde or RF-gel is a common type of aerogel. Because of a large internal void space, an aerogel made a high surface area and easy controllable porosity material [8-10]. Therefore, RF-gel usually uses as a carbon precursor which can be synthesized high surface area and high mesoporosity carbon adsorbent [10, 11].

RF-gel is produced by a polycondensation reaction which resorcinol reacted with formaldehyde under alkaline or acid conditions [12].

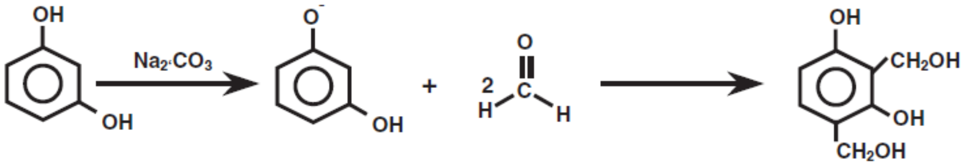


Figure 1 Addition reaction [13]

There are 2 steps of polycondensation reaction includes addition reaction and condensation reaction which shown as figure 1 and 2 respectively. Hydroxymethyl derivatives (-CH_2OH-) are formed by addition reaction which formaldehyde is added in 2-, 4-, or 6- position of resorcinol. Then, this derivatives are condensed to form methylene (-CH_2-) and methylene ether (-CH_2OCH_2-) bridged compound or resorcinol-formaldehyde compound [13].

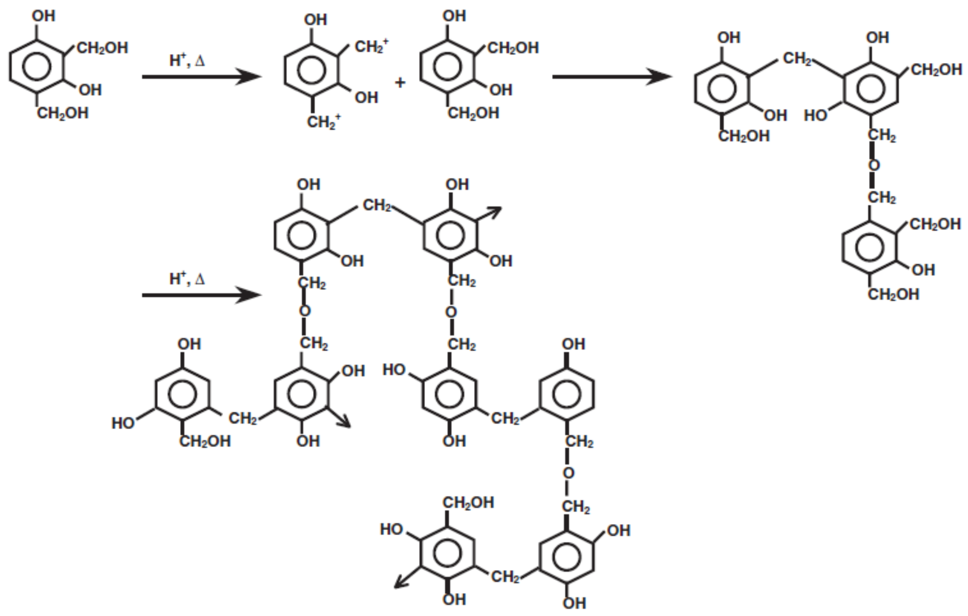


Figure 2 Condensation reaction [13]

Properties of RF-gel depend on various variables. An example of variables shown as table 1.

Table 1 Effect of each variable to RF-gel properties [10, 13]

Variables	Effect on
Initial pH	surface area and pore size
Resorcinol to water Ratio	pore size distribution and porosity
Resorcinol to catalyst Ratio	density, surface area, and mechanical properties

Table 1 (Cont.) Effect of each variable to RF-gel properties [10, 13]

Variables	Effect on
Acid catalyst	gelation time
Alkaline catalyst	

2.1.2 Electrospinning

One of the most popular methods to produce fibers is spinning. Fibers that produced from spinning process such as melt spinning, dry spinning, wet spinning and gel-state spinning have small diameters typically in range 5 to 500 microns [14]. However, there is a process which gives a smaller diameter such as an electrospinning.

An electrospinning generates an ultrafine fibers that have size of diameters in range of a few nanometers to a few microns [14]. Because of electrostatic field , an electrospun fibers have outstanding properties include high surface area per unit mass and lots of porosity [14]. In general, electrospinning that has single needle and single Taylor cone at a needle tip is called needle electrospinning [15]. Due to a low productivity, a development of needle electrospinning is occurred. An improved process is called a needle-less electrospinning.

2.1.2.1 Needle-less electrospinning

An equipment of needle-less electrospinning consists of grounded collector, voltage generator and spinneret which is different from needle electrospinning. A spinneret acts like a bunch of many needles. So, multiple Taylor cones are formed. There are various models of spinneret such as cylinder, cone, disc, ball or wire [15, 16].

For a twisted wire spinneret, a schematic diagram shown as figure 3. A polymeric solution which is contained in plastic syringe flows down along a twisted metal wire because of gravitational force. This spinneret is set in the center of a collector which is a cylindrical metal grid that wrapped with aluminum foil. When a voltage is applied, fibers are ejected simultaneously from multiple Taylor cone along a twisted metal wire.

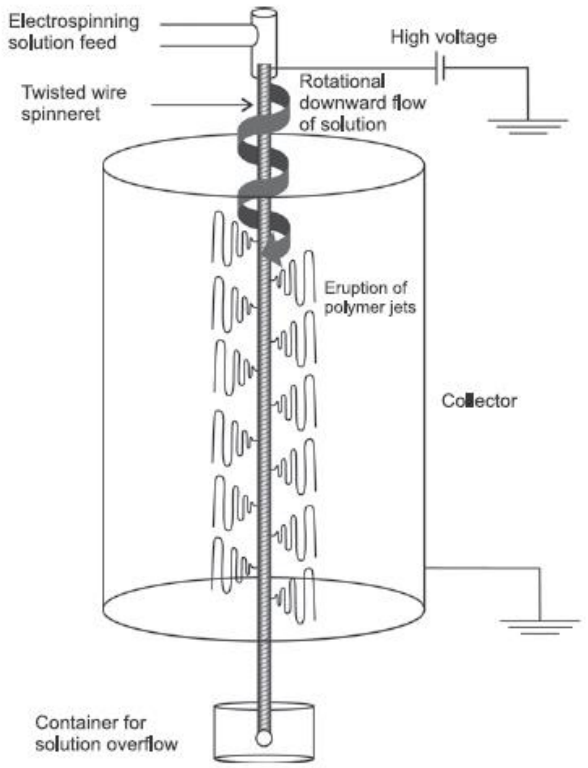


Figure 3 A schematic diagram of a needleless twisted wire electrospinning [15]

Next, There is more description for each Taylor cone that occurred in electrospinning process. During electrospinning, a droplet of solution charges by high voltage that applied to process [17]. A droplet configuration gently changes to conical known as a Taylor cone. While a potential increases until a driving force of electric charge increases more than a surface tension, [18, 19] a solution strand injects out of the end of the Taylor cone. A solvent of solution evaporated along distance between spinneret and collector. Then, an electrospun fibers deposit on a collector [18]. A diagram of fiber formation shown as figure 4.

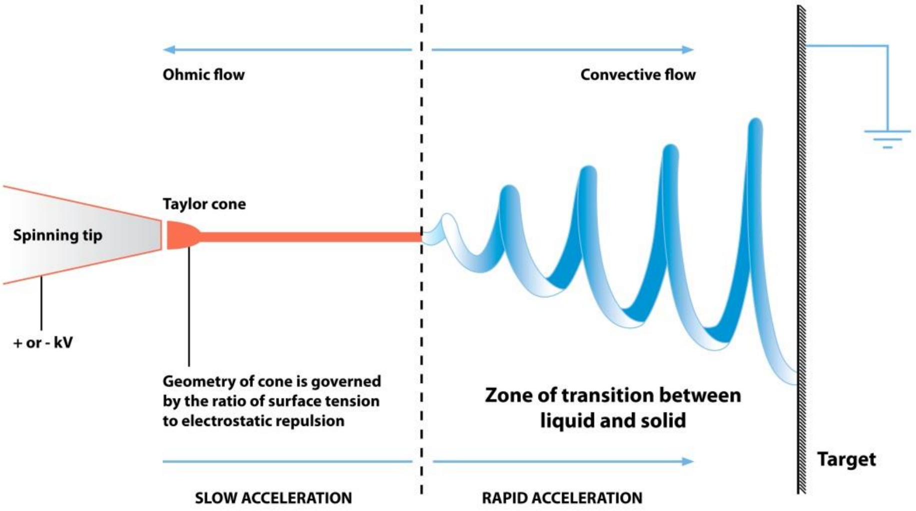


Figure 4 Fiber formation by electrospinning [20]

2.1.2.2 Parameters of electrospinning

There are many significant parameters that affected on fiber structure and properties. A detail of all parameters shown as table 2

First of all, shapes of collector affected on product collection. Plate collector makes thick-layer of electrospun fiber. So, electrospun fibers which attached on aluminium foil can be peel easily. In the other hand, Cylindrical collector has larger area. Electrospun fibers are spread out. So, product which attached on aluminium foil is difficult to collect. Next, A long electrospun fibers are taken when a distance between spinneret and collector equals 12 cm. If a distance is above 12 cm, electrospraying can be occur. Furthermore, diameter of electrospun fibers are bigger because there are no control of polymer solution flowing rate. A flowing rate of polymer solution must be set in range 10 to 20 ml/min. Moreover, A high voltage also affected on productivity of electrospun fiber. High productivity of long electrospun fibers receive when 30 to 35 kV of high voltage applied. Finally, humidity percent must be 45 to 50 %. Above or below a range, electrospraying and short electrospun fiber can be occurred.

Table 2 Parameters of twisted wire needle-less electrospinning [21]

Parameter	Type/range
Collector	Plate Cylindrical
Distance between spinneret and collector	12 cm Above 12 cm
Flowing rate of polymer solution	10 to 20 ml/min Above of range
Applied voltage	30 to 35 kV Above or below of range
Relative humidity	45 to 50% Above or below of range

2.1.3 Carbon fiber

In recent year, carbon fibers which discovered by Edison in1879 are popular material that widely used around the world [22]. In general, carbon fibers are filaments which consists of carbon over 90% and aspect ratios are higher than 10. Carbon fibers become widespread material because of its properties as following : [22, 23]

- High tensile strength
- High stiffness
- Low density
- High chemical resistance
- High thermal stability

Therefore, carbon fibers are used in many different fields such as aerospace, construction and especially adsorption [7]. However, process of activated carbon fiber production consists of 2 mainly steps include carbonization and activation. An overall process of carbon fiber production shown as figure 5.

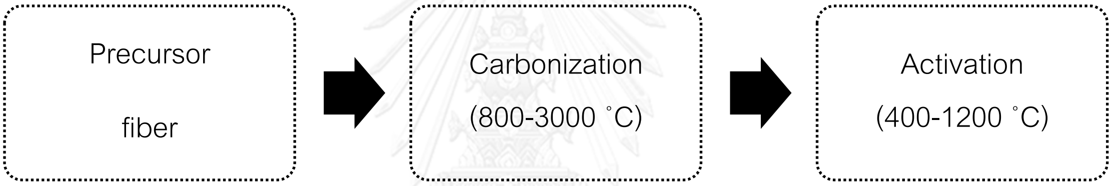


Figure 5 Overall process of activated carbon fiber production

2.1.3.1 Carbonization

Precursor fibers are changed to carbon fibers in this step. There are many precursor types which are widely used such as cellulose material, phenolic material and acrylic material. A process occurs at temperature 800-3000 ˚C in an inert condition and using tube furnace. In this process, chemical and physical composition change. Non-carbon substances are removed in form of volatile gases. Thus, diameter of fiber is decreased. There are many volatile gases which are eliminated such as methane, hydrogen, nitrogen, water, carbon dioxide or carbon monoxide. Finally, product which get from carbonization have weight loss up to 50% [22-24].

Carbonization is divided into 2 steps. The beginning period that temperature increases from room temperature to about 250 ˚C occurs endothermic reaction. At this step, 3% of mass are lost because adsorbed water are released. Next, releasing of other compounds occur in the second period that temperature are heated up from 250 ˚C to final temperature. Because of this releasing, there are 2 phenomena include decreasing of macropores and increasing of micropores and mesopores.

The yield of product from carbonization controlled by heating rate, final temperature and time [25].

2.1.3.2 Activation

After carbonization, Carbon fibers have pores which blocked by disorganized carbon. A disorganized carbon atoms can be removed from pore structure by activation process. In addition, an activation also creates new pore structure. So, properties of carbon fiber are developed include an increasing of pores and surface area [23-25]. In general, an activation is classified into 2 types includes physical activation and chemical activation.

A.) Physical activation

This activation type is simple and give high efficiency. Hot gases typically carbon dioxide (CO_2) and steam (H_2O) are used as an oxidizing gas. An activation occurs at high temperature in range 500 to 1200 ˚C. A reaction between carbon fiber and steam (representative as oxidizing gas) is heterogeneous reaction which can be described as equations (1). This equation is an endothermic reaction that releases 118 kJ/mole of heat. Moreover, Equations (2) to (6) show any intermediates which formed during reaction between carbon fiber and steam. Finally, any oxygen containing functional groups are presented on activated carbon fibers [24].

Reaction with H_2O :

$$C + H_2O \leftrightarrow CO + H_2 \quad (1)$$

$$C + H_2O \leftrightarrow C(H_2O) \quad (2)$$

$$C(H_2O) + C \leftrightarrow C(OH) + C(H) \quad (3)$$

$$C(OH) + C \leftrightarrow C(O) + C(H) \quad (4)$$

$$C(O) \leftrightarrow CO \quad (5)$$

$$C(H) + C(H) \leftrightarrow 2C + H_2 \quad (6)$$

For more detail, development of pore structure in steam activation can be divide to 2 steps. In the first step, volume of micropores are increased since disorganized carbon burned off. For the next step, there are occurrence of larger pore size includes mesoporous and macroporous because wall between adjacent pores are destroyed. Finally, increasing of pore volume and more wide pore size distribution are presented in activated carbon fiber [24, 25].

An activation process have many factors which effected to surface area and porosity of carbon fibers. All parameters are listed in table 3

Table 3 Factors of each activation type [24]

Physical activation	Chemical activation
Carbon structure of carbon fiber	Nature of carbon fiber
Impurities in carbon	Types of activation reagents
Types of activation gas	Mixing method
Activation temperature	Activation temperature
Flow rate of activation gas	Washing step

B.) Chemical activation

Chemical activation is an activation which used activation reagent in process instead of oxidizing gas. An activation reagent such as Potassium hydroxide (KOH) impregnated with carbon fiber. Then, this carbon fibers are heated at temperature in range 300 to 900 ˚C. After that, residue of activation reagents are removed from carbon fibers by washing with acid or base solution. Finally, an activated carbon fiber can be harvest after drying at 60 ˚C by hot air oven. Nevertheless, there are many advantages and disadvantages of chemical activation which describe in table 4 [23-25].

Table 4 Advantages and disadvantages of chemical activation

Advantages	Disadvantages
lower temperature	Difficulty in washing step
shorter activation time	More corrosive behavior
narrow pore size distribution	

2.1.3.3 Carbon and pore structure

Carbon structure are formed in carbonization process. When hydrogen, oxygen and nitrogen are eliminated in volatile gaseous forms, carbon atoms are grouped into stacks of aromatics sheet and cross-linked in random structure which shown in figure x. Because of this irregular structure, there are disorganized carbon atoms which occur from other decomposition product in free interstices [25, 26].

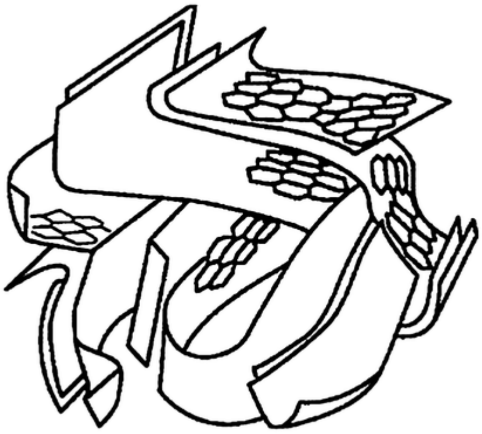


Figure 6 Carbon fiber structure[27]

However, porosity of carbon cleared by reaction between disorganized carbon atoms and oxidizing gases in activation process. So, activated carbon fibers generally are a good adsorbent. Normally, porosities are classified into 3 types which based on their size includes micropore, mesopore and macropore. Furthermore, sizes of each porosity are described in table 5 and nature of carbon porosity are shown in figure 7 [25, 28].

Table 5 Classification of pore [28]

Type of pore	Size
Micropore	< 2 nm
Mesopore	2-50 nm
Macropore	> 50 nm

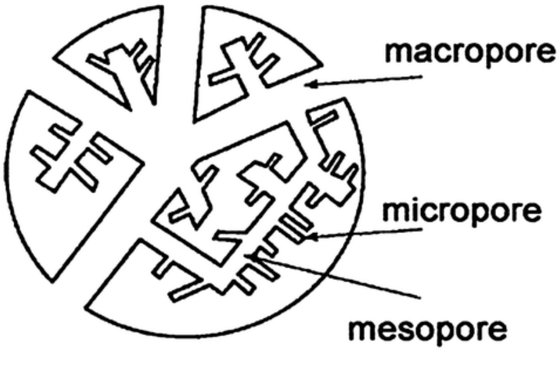


Figure 7 Porosity of carbon [26]

Because of an outstanding porosity characteristic, carbon materials generally use as an adsorbent in adsorption process. In general, an adsorption mainly occurs in microporous. However, the presences of macropore, mesopore and micropore make a faster adsorption. There is an explanation about this process by supposing macropore and mesopore as a motor-way, micropore as a local street and adsorbate molecules as car. If cars are driven through both motor-way and local street, those cars can be arrive home faster than using only a local street. In the same way, an adsorption process occurs faster with many pore types. Nevertheless, kinetics of this process do not affect to an adsorption capacity [29].

2.1.4 Adsorption

An adsorption is a phenomenon of solid material which captures a contacted liquid, gas or vapor on its surface or its pore [30]. Generally, porous solid materials are called adsorbent and those captured molecules are called adsorbate. Figure 8 presents an adsorption process.

Mostly, an adsorption is classified into 2 types includes physical adsorption and chemical adsorption.

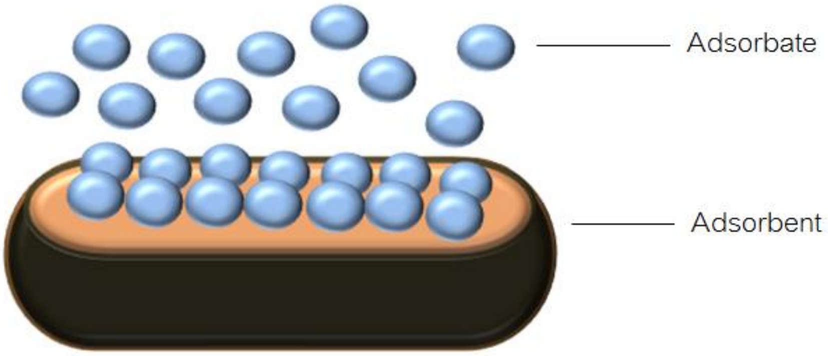


Figure 8 Adsorption process

2.1.4.1 Classification of adsorption

A) Physical adsorption (Physisorption)

For this type of adsorption, adsorbent and adsorbate are bonded with very weak forces includes Van der Waals force and hydrogen bond. A process occurs when forces between adsorbate and adsorbent are larger than forces between adsorbate and adsorbate. There are no activation energy and there are not limited by available surface area. Moreover, adsorbates appear on surface of adsorbent in multilayer form which shown as figure 9 [31, 32].

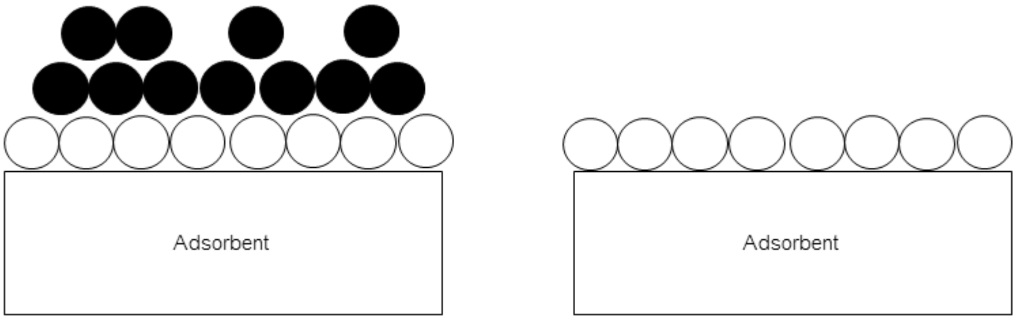


Figure 9 Multilayer and monolayer adsorption

B) Chemical adsorption (Chemisorption)

This type of adsorption occurs when chemical reaction takes place between adsorbent and adsorbent. There are an electron sharing, electron donating or electron exchanging between adsorbent and adsorbate. So, adsorbent and adsorbate are bonded with strong force as covalent bond. However, adsorbate of this adsorption type appear on surface of adsorbent in monolayer form which shown as figure 9 [31, 32].

For more detail, this below table shown differences between physical and chemical adsorption.

Table 6 Comparison between physisorption and chemisorption [31]

Physisorption	Chemisorption
Low heat of adsorption	High heat of adsorption
Non specific	Highly specific
Monolayer or multilayer	Monolayer only
No dissociation of adsorbed species	May involve dissociation
Rapid and reversible	May be slow and irreversible
No electron transfer	Electron transfer leading to bond formation between adsorbate and surface
Only significant at low temperature	Possible over a wide range of temperature

2.1.4.2 Adsorption isotherm

An adsorption isotherm is a relationship between adsorbate which adsorbed on surface of adsorbent and equilibrium concentration at constant temperature. There are many models of adsorption isotherm but there are 2 popular models includes Langmuir isotherm and Freundlich isotherm [33].

A.) Langmuir isotherm

Langmuir isotherm is a very common model which suggested by Irving Langmuir in 1916 A.D. This model are based on assumptions as following:

- Monolayer adsorption
- Homogeneous adsorption surface
- All adsorption sites are similar
- Each site adsorbs only one molecule of adsorbate
- All sites are independent from adsorption capacity

An expression of Langmuir isotherm model in nonlinear form shown in equation (8). Then, this equation is adjusted to be in linear form which shown as equation (7). A linear form of Langmuir is used for determining constants.

Nonlinear form :

$$q_e = q_m K_L \frac{C_e}{1+K_L C_e} \tag{7}$$

Linear form :

$$\frac{1}{q_e} = [\frac{1}{q_m K_L}]\frac{1}{C_e} + \frac{1}{q_m} \tag{8}$$

When :

	C_e	is adsorbate concentration at equilibrium (ppm)
	q_e	is adsorption capacity (mg adsorbate/ mg adsorbent)
	q_m	is maximum monolayer coverage capacity
	K_L	is Langmuir isotherm constant

2 constants in equation can be determined by plotting $1/q_e$ and $1/C_e$. Afterward, constants q_m and K_L are found from intercept and slope of those relation [34-36].

B.) Freundlich isotherm

Freundlich isotherm is the most widely used model which is discovered by Herbet Freundlich in1909 A.D. An assumptions of Freundlich isotherm are included :

- Heterogeneous adsorption surface
- Multilayer adsorption
- Adsorption sites are different
- Reversible adsorption

An original equation is nonlinear form which shown as equation (9). However, this equation is developed to be in linear form that represents as equation (10). So, K_F and 1/n parameters can be determined from intercept and slope of relation between ln q_e and ln C_e in linear form.

Nonlinear form : $$q_e = K_F C_e^{1/n} \quad (9)$$

Linear form : $$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (10)$$

When : C_e is adsorbate concentration at equilibrium (ppm)

q_e is adsorption capacity (mg adsorbate/ mg adsorbent)

n is adsorption intensity

K_F is Freundlich isotherm constant

K_F and 1/n are parameters which describe characteristics of adsorbent-adsorbate system. Normal adsorption generally occurs when 1/n is lower than 1. Meanwhile, K_F indicates adsorption capacity [34, 36, 37].

2.1.5 VOCs

Volatile organic compounds or VOCs are chemical compounds which compositions can be volatized at atmospheric conditions of temperature and pressure [38]. In more details, VOCs are any chemical compounds based on carbon chains or rings with a vapor pressure greater than 2 mmHg at 25 ˚C excluding methane [39]. In general, VOCs are classified into 3 types include very volatile organic compound (VVOC), volatile organic compound (VOC) and semi volatile organic compound (SVOC) by using boiling point [38]. Ranges of boiling point and example for each type are shown in table 7.

Table 7 Classification of VOCs by WHO [38]

Types	Boiling point (˚C)	Example compounds
Very volatile organic compound (VVOC)	0 to 50-100	Propane, Butane, Methyl chloride
Volatile organic compound (VOC)	50-100 to 240-260	Formaldehyde, Toluene, Hexanol
Semi volatile organic compound (SVOC)	240-260 to 380-400	Pesticides, Fire retardants

There are 2 main sources that emitted VOCs to atmosphere include man-made source and natural source [40]. An example of each source shown as table 8.

Table 8 Source of VOCs [40, 41]

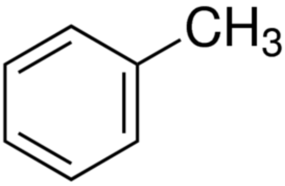
Man-made sources	Natural sources
Motor vehicle exhaust	Fossil fuel
Paints and thinners	Volcanoes
Adhesives	Plants
Nail polish	Bacteria

Because of its properties, a mainly harmful of VOCs is a health effect in human as carcinogen. There are many levels of effect which range from no effect to highly toxic effect. However, influential levels depend on 3 parameters include nature of VOCs, level of exposure to VOCs and duration of exposure to VOCs [40]. In this situation, an exposure means 3 major pathways that chemical compounds enter human body include breathing, touching and swallowing [41]. In addition, age, health condition and gender also make different effects. Furthermore, VOCs also effect on environment as pollutant. For example, sensitive vegetation are damaged during growing season [41]. So, VOCs level in atmosphere are limited in many countries. For instance, level of toluene limited at 375 and 750 mg/m^3 in Japan and USA respectively [42, 43].

2.1.5.1 Toluene

Toluene is a colorless liquid which naturally occurs from crude oil [44]. Toluene is a component of many products such as aromatic mixture, paints and coating solvents. In each year, toluene usually releases to atmosphere by production, automobile exhaust gases, processing and transportation [41].

Table 9 Properties of Toluene [45]

Name	Toluene ($C_6H_5CH_3$)
Synonym	Methylbenzene, Methacide, Phenylmethane
Structure	
Appearance	Colorless
Molecular weight (g/mol)	92.056
Boiling point (˚C)	110.6
Vapor pressure at 30 ˚C (mmHg)	36.7
Autoignition temperature (˚C)	422
Solubility	Insoluble

2.2 Literature review

Resorcinol-Formaldehyde gel was firstly prepared by R.W. Pekala which had 4 components includes resorcinol(R), formaldehyde(F), distilled water(W) and catalyst(C). There were varied amount of catalyst which found that a surface area of RF-gel was decreased with a lower catalyst [12].

T. Horikawa et al. (2004) prepared RF-gel solution by setting resorcinol to formaldehyde ratio(R/F) 0.25, resorcinol to water ratio(R/W) 0.037 and varying resorcinol to catalyst ratio(R/C) at 50, 200 and 1000. The affecting of R/C ratio, mesoporosity increased with increasing of catalyst quantity and there were no significantly effect on microporosity. Moreover, gelation time decreased with catalyst quantity increasing [46].

In addition, One of factors that effected to porosity was types of catalyst. RF-gel that was prepared with different catalyst includes Potassium carbonate (K_2CO_3), Potassium hydrogen carbonate ($KHCO_3$), Sodium carbonate (Na_2CO_3) and Sodium hydrogen carbonate ($NaHCO_3$) were carbonized at 800 ˚C and then, porosity of carbon product were investigated. Microporosity had a small difference for each catalyst species, but mesoporosity had a greatly difference. As following, a mesoporosity were 0.79, 0.7, 0.53 and 0.42 cm^3/g by using $NaHCO_3$, Na_2CO_3, K_2CO_3 and $KHCO_3$ as a catalyst respectively [46].

AH. Moreno et al. (2016) investigated effects of carbonization temperature and heating rate on the carbon porosity which was received after carbonization of RF-gel with pH 6.5 and particle size ±212 μm. A porosity of carbon product at any temperatures in range 700 to 950 ˚C were analyzed by N_2 adsorption. A hysteresis loop was found similarly which mean that all carbon product had both microporous and mesoporous. Especially at 850 °C, At this temperature gave highest adsorbed volume. For a study of heating rate, there were no significantly changed in carbon product porosity ,but a carbonization time was decreased from 2.77 to 0.3 hours because of an increasing of heating rate [47].

RF-gel that was carbonized usually activated for an increasing of surface area and getting narrow micropore distribution [48].

K. Ananthaprayoon and V. Pavarajarn (2015) studied carbon fiber production via needle-less electrospinnig. An appropriate ratio of RF-gel solution were R/F 0.5, R/W ∞ and R/C 500. Then, a solution was kept in a box which was controlled humidity by silica gel. After 24 to 40 hours, RF-gel was ready to spin by twisted-wire electrospinning. Conditions which gave the highest productivity included 12 cm of distance between twisted-wire and collector, 30 kV of applied high voltage, 45-50% of humidity and 20 ml/h of feed flow rate. After that, RF-gel fibers were carbonized at 250 ˚C and 750 ˚C for 2 and 4 hours respectively. There was 53.02 % weight loss from carbonization. Finally, carbon fibers were investigated by N_2 adsorption which shown a slightly hysteresis loop [21].

Chapter III

Experimental

In this chapter, details of all experimental were explained. There were 3 parts included chemicals list, equipment, experimental procedures and characterizations.

3.1 Chemicals

There were 5 chemicals that used in this experiment. A detail of each chemical shown as table 10.

Table 10 List of chemicals

Chemical name	Manufacture and grade
Resorcinol ($C_6H_4(OH)_2$)	Sigma Aldrich, 99%
Formaldehyde (HCHO)	UNIVAC, 37% w/v
Sodium hydrogen carbonate (Na_2HCO_3)	Suksapanpanit
Toluene ($C_6H_5CH_3$)	Fisher chemical, 99.99%
Distilled water (H_2O)	

3.2 Equipment

3.2.1 Magnetic stirrer

For resorcinol-formaldehyde gel (RF-gel) preparation, a magnetic stirrer model Plus AI S/N made a homogeneous RF-gel solution.

3.2.2 High voltage power supply

An applied voltage in needle-less electrospinning generated from high voltage power supply model ES50P-20W.

3.2.3 Syringe and silicone tube

In fiber production step, 10-ml TERUMO® syringe which filled with RF-gel solution was connected to 45-cm silicone tube and wrapped with insulation tape at joint.

3.2.4 Syringe pump

A steady flowing rate of polymeric solution controlled by syringe pump model KDS-100.

3.2.5 Spinneret

A twisted metal wire which has 3-mm diameter and 30-cm length used as spinneret in needle-less electrospinning.

Figure 10 Twisted metal wire

3.2.6 Collector

A plate collector which made from polypropylene sheet and wrapped with aluminium foil had dimension 25 cm x 7 cm x 35 cm.

Figure 11 Plate collector

3.2.7 Wood stand and tools

A twisted metal wire was held in vertical by 3 pieces of tools includes 2 pieces of metal tools and 1 piece of acrylic tool shown as figure 12. Finally, All tools were attached to wood stand with insulation tape.

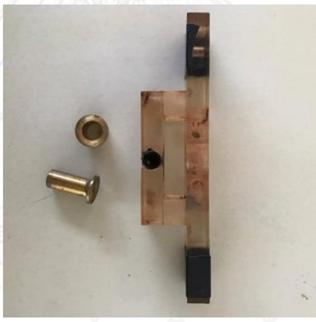


Figure 12 Tools

3.2.8 Plastic cup

A plastic cup that has 7-mm diameter and 10-cm height was placed in the bottom of twisted metal wire for collecting non-electrospun solution.

Figure 13 Plastic cup

3.2.9 Headspace vial and PTFE/silicone aluminium seal

27-ml headspace vials which contained adsorbent and toluene were crimped with 20-mm PTFE/silicone aluminium seal.

Figure 14 Headspace vial and aluminium seal

3.2.10 Water bath

A selected temperature of adsorption isotherm were controlled by M-LAB water bath.

3.3 Experimental procedures

3.3.1 Resorcinol-Formaldehyde gel preparation

Resorcinol-formaldehyde gel (RF-gel) was prepared from a polycondensation reaction between resorcinol and formaldehyde under alkali condition. Resorcinol (R) which is a white solid was dissolved in formaldehyde (F) by using electromagnetic stirrer. Then, An alkali solution that prepared by 0.1 g of sodium hydrogen carbonate ($NaHCO_3$) in 10 ml of distilled water was added and stirred for 15 minutes. Finally, A homogeneous solution was kept in a humid-controlled box for 24-48 hours. A solution texture changed from yellow clear liquid to orange gel solution.

3.3.2 Fiber production via needle-less electrospinning

The diagram of twisted wire needle-less electrospinning shown as figure 15. RF-gel was sucked with 10-ml syringe. Then, silicone tube was connected to syringe and wrapped with insulation tape at joint. For process combination, twisted metal wire was held in vertical by tools and wood stand. RF-gel was fed to system by connecting silicone tube and acrylic tool. A plate collector that wrapped with aluminium foil located on the left side of twisted metal wire for 12 cm. When 30-kV of voltage were applied to system, RF-gel fibers occurred on collector and non-electrospun solution dropped into plastic cup. This process was controlled humidity about 45-50% by nitrogen gas.

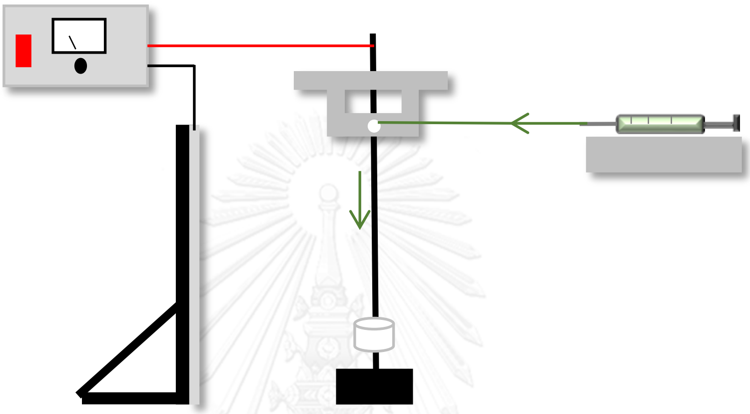


Figure 15 Twisted wire needle-less electrospinning

3.3.3 Carbonization of RF-gel

Carbonization process occurred in horizontal tubular furnace. RF-gel fibers were contained in ceramic container. Then, a container was put into furnace and 40 ml/min of nitrogen was fed into a system respectively. After 20 minutes, system was heated up by pressing the start button. There were 2 steps of carbonization. First, holding temperature at 250 ˚C for 2 hours and following by 650-850 ˚C for 4 hours. After process ended, nitrogen still fed into a system until temperature was under 200 ˚C.

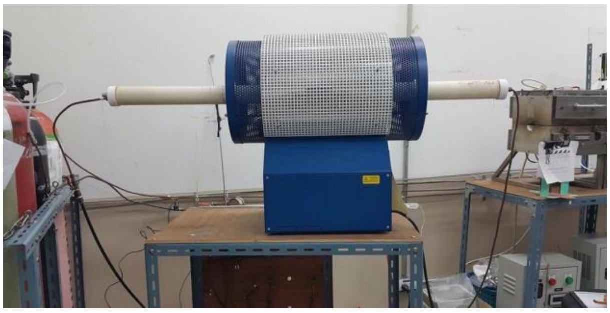


Figure 16 Horizontal tubular furnace

3.3.4 Activation of carbon fiber

Activation process occurred in horizontal tubular furnace. Carbon fibers were contained in ceramic container. Then, a container was put into furnace and 100 ml/min of nitrogen was fed into a system respectively. After 20 minutes, system was heated up by pressing the start button. Erlenmeyer flask that filled with distillation water was heated by magnetic stirrer at 20 minutes before the temperature rose to activation temperature that was set at 700-900 °C. At final temperature, steam was fed instead of nitrogen for 30 minutes. At the outlet, there was a cooling flask for water trapping. When process ended, nitrogen was fed instead of steam into a system until temperature was under 200 °C.

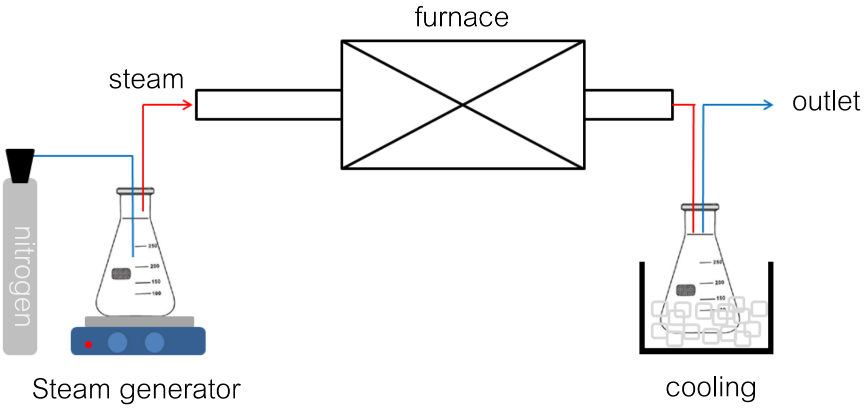


Figure 17 Activation system

3.3.5 Adsorption behavior

Adsorption behavior studied by adsorption isotherm. 4-mg of adsorbent and toluene were filled in 27-ml headspace vial. Then, vial crimped immediately with a crimper and all vials were kept in water bath at controlled temperature.

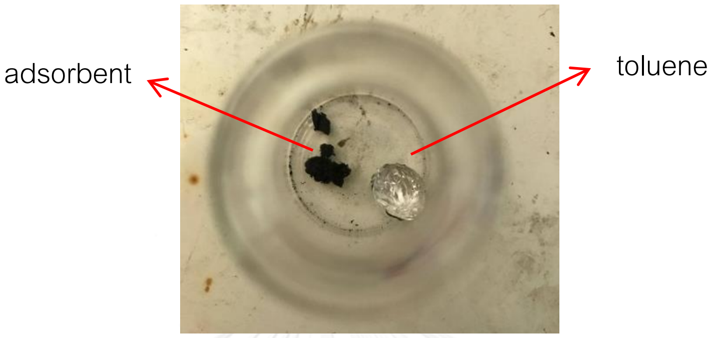


Figure 18 adsorbent and toluene in headspace vial

3.4 Characterizations

3.4.1 Scanning electron microscope (SEM)

Morphology of fibers were investigated by using SEM JSM-6610LV at Scientific and Technological Research Equipment Centre (STREC), Chulalongkorn university.

3.4.2 Total organic carbon analyzer (TOC)

Total organic carbon of 1-octanol were investigated by using total organic carbon analyzer (TOC-VCPH, Shimadzu) at Center of Excellence in Particle Technology (CEPT), Chulalongkorn university.

Chapter IV

Results and discussions

In this chapter, all experiment results were discussed. There are 7 parts of results and discussion includes needle-less electrospinning of resorcinol-formaldehyde fiber, carbonization of resorcinol-formaldehyde gel fiber, steam activation of carbon fiber, toluene adsorption isotherm, toluene adsorption isotherm, 1-octanol adsorption, N_2 adsorption of particle and pore structure of carbon fiber.

4.1 Needle-less electrospinning of resorcinol-formaldehyde gel

At the beginning, experiments were repeated from a previous thesis[21]. All ratios of RF-gel preparation, type of catalyst and conditions of electrospinning were used in experiment. The highest continuous fiber quantity produced from ratios of resorcinol to formaldehyde (R/F), resorcinol to water (R/W) and resorcinol to catalyst (R/C) equaled to 0.5, ∞ and 500 respectively. Sodium carbonate (Na_2CO_3) was used as catalyst. Then, needle-less electrospinning of RF-gel were occurred at 12 cm of distance between twisted wire and collector, 30 kV of applied voltage, 20 ml/h of feed flowing rate and 45-50% of relative humidity. Nevertheless, electrospraying occurred instead of fibers. So, many possible causes were investigated. First, difference between former thesis and repeated experiment was room temperature. The formation of RF-gel fibers were sensitively with room temperature and those temperatures were difficult to controlling. Afterward, distance between twisted wire and collector was increased to 15 cm. Spraying of RF-gel still appeared on collector. Similarly, lower productivity and electrospraying can be occurred with other ratios of RF-gel. However, there was reported from previous research about effect of catalyst type on quantity and porosity of fiber. So, types of catalyst were considered. Sodium hydrogen carbonate ($NaHCO_3$) was used as new catalyst. Then, there was RF-gel fibers which greatly deposited on plate collector instead of electrospraying. Accordingly, $NaHCO_3$ was used as a catalyst for all RF-gel fiber production in this research.

Resorcinol-formaldehyde gel (RF-gel) was selected as a carbon precursor. RF-gel solution was prepared by defining ratios of resorcinol to formaldehyde(R/F), resorcinol to water(R/W) and resorcinol to catalyst(R/C) which equaled to 0.5, ∞ and 500 respectively. For solution preparing step, resorcinol was firstly dissolved with formaldehyde and followed by mixing with catalyst. This solution was kept in closed-system which controlled percentage of humidity by silica gel. A solution occurred polycondensation reaction which made solution texture changed to gel texture in 24 to 48 hours. Then, RF-gel was ready for electrospinning process. Parameters of needle-less electrospinning were specified includes twisted wire spinneret for guiding simultaneously rotation of RF-gel by the twist in a wire which fibers were ejected from self-formed multiple Taylor cones at the same time, 12 cm of distance between twisted wire and collector, 30 kV of applied voltage, 20 ml/h of feed flowing rate and 45-50% of relative humidity.[15, 21]

RF-gel fibers were generated repeatedly for great product. Although a needle-less electrospinning was used, quantity of RF-gel fibers in each batch was not enough. Table 11 is shown sample of product weight for needle-less electrospinning in each time.

Table 11 Product weight from needle-less electrospinning

Time	Product weight (g)
1	2.65
2	2.17
3	2.43
4	1.78
5	2.05

In each time, 10 ml of RF-gel can produce RF-gel fiber 1 g to 3 g which gave production rate 5.34 to 7.95 g per hour. Moreover, the important thing was morphology and size of RF-gel fiber. In early, RF-gel fibers had no long line. It was short, broken and various size fibers which resulted from solution viscosity. Subsequently, an appropriate RF-gel viscosity can be determined from stirring RF-gel with needle tip. RF-gel should have enough viscosity that cannot see a droplet of RF-gel at needle tip.

Figure 19 is shown SEM images and size distributions of RF-gel fiber which harvested from needle-less electrospinning. Each SEM image was RF-gel fiber which produced from 1 batch of electrospinning. And all needle-less electrospinning were occurred at 45-50 % of relative humidity.

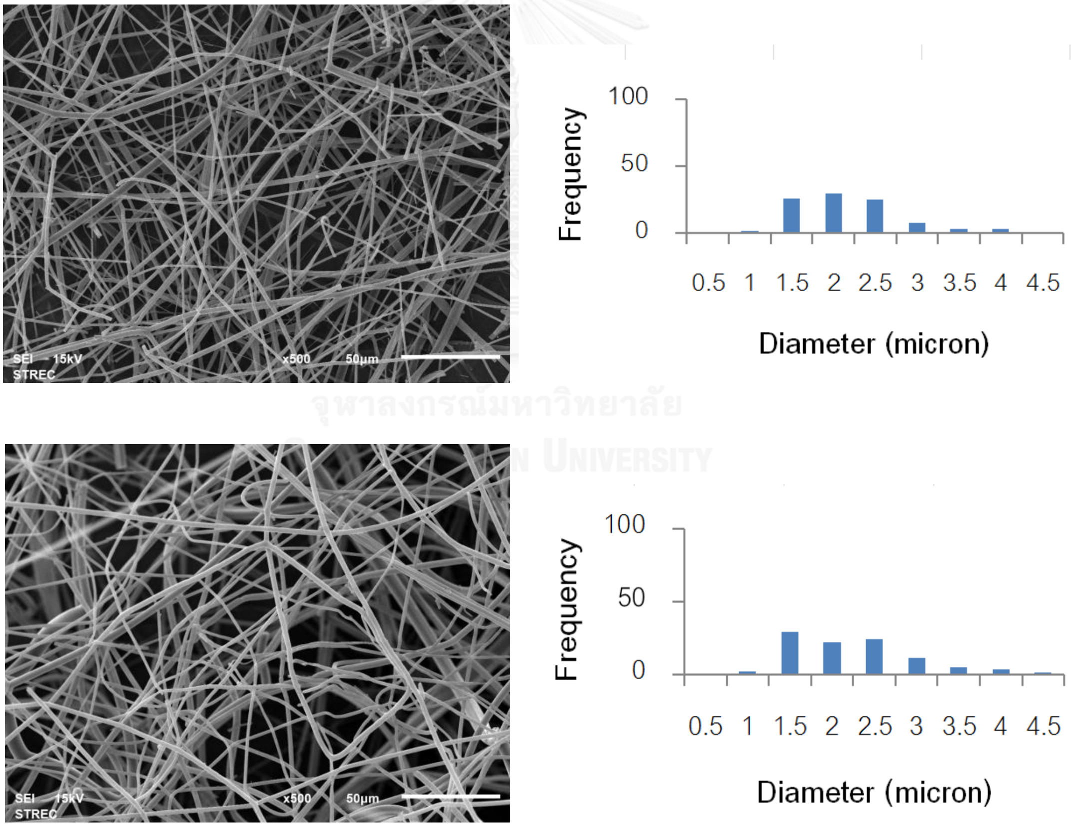


Figure 19 SEM images and size distribution of RF-gel fibers from each batch of needle-less electrospinning

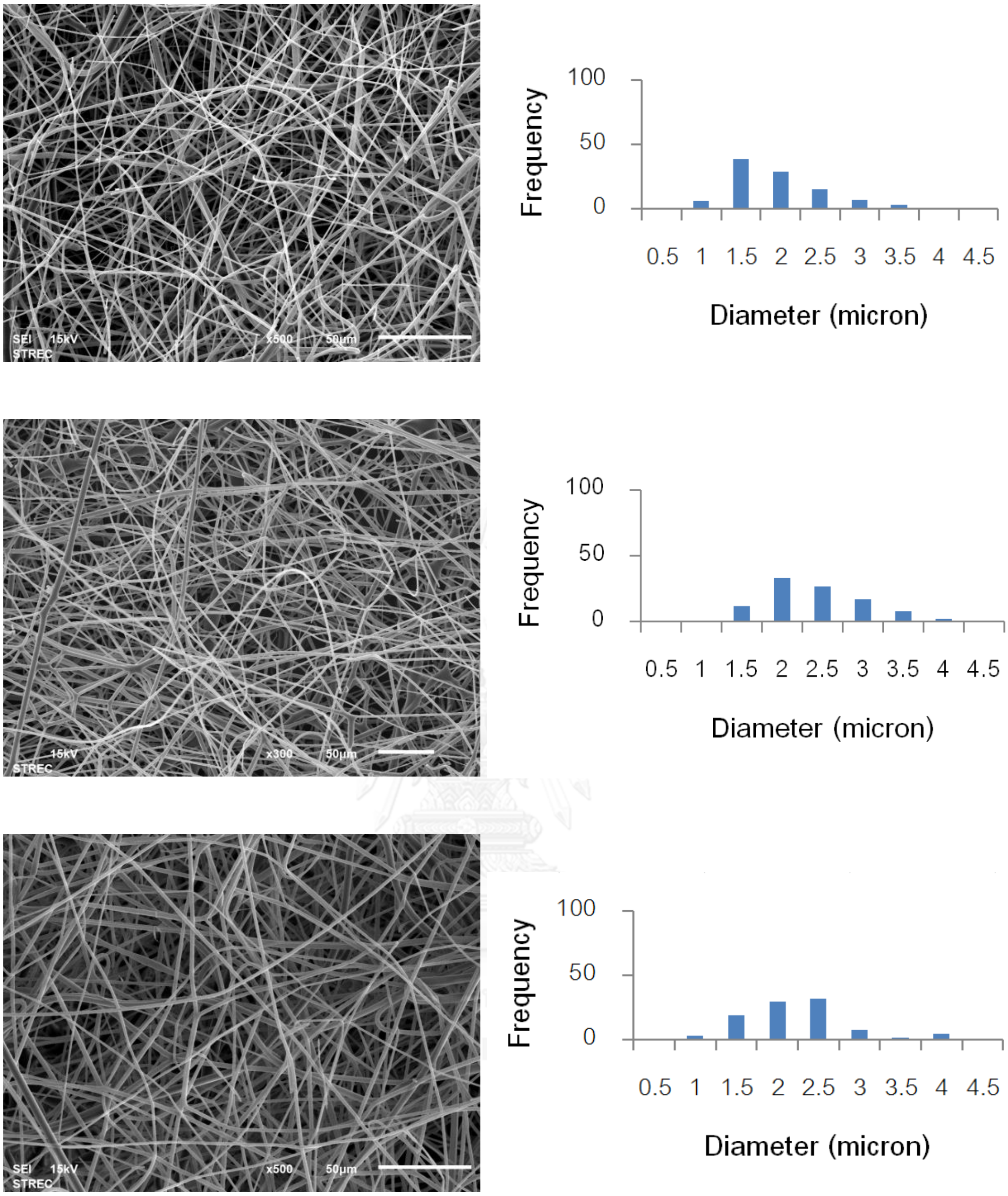


Figure 19 (cont.) SEM images and size distribution of RF-gel fibers from each batch of needle-less electrospinning

Needle-less electrospinning produced RF-gel fiber which had uniform morphology and size. Diameter of RF-gel fiber was mostly in range 1.5 to 2.5 microns and partly in range 3 to 4 microns.

As a previous thesis, all parameters have important roles on RF-gel fiber properties. If percentage of humidity is too low or high, solvent of RF-gel is evaporated too fast or too slow and there are a short time or long time for stretching by voltage force which mean that small quantity or large diameter of RF-gel fibers occurred respectively. In addition, distance between spinneret and collector must be balanced because solvent of RF-gel needs an appropriate distance for evaporation before deposition on collector. Finally, fiber can be generated when an applied voltage is higher than tension of polymer jet. But, if an applied voltage are too high, fiber diameter are increased or fiber have network morphology[21].

4.2 Carbonization of resorcinol-formaldehyde gel fiber

RF-gel fibers were carbonized at high temperature in inert condition. Fixed conditions of carbonization are shown as following:

- Horizontal tubular furnace was used.
- N_2 was selected as inert gas and flowing of N_2 was fixed at 40 ml/min.
- The first step was carbonized at 250 ˚C for 2 hours and the second step was carbonized at any temperatures for 4 hours.
- Fibers were put in oval ceramic container.
- Product was harvested after temperature decreased to room temperature.

There were 2 parameters which investigated in this section included heating rate and final temperature.

4.2.1 Effect of carbonization heating rate on morphology

Heating rates of carbonization were studied at 1, 5 and 10 ˚C/min which final temperature was determined at 750 ˚C [21]. Comparison of morphology between RF-gel fiber and carbon fiber which carbonized with different heating rate shown as figure 20.

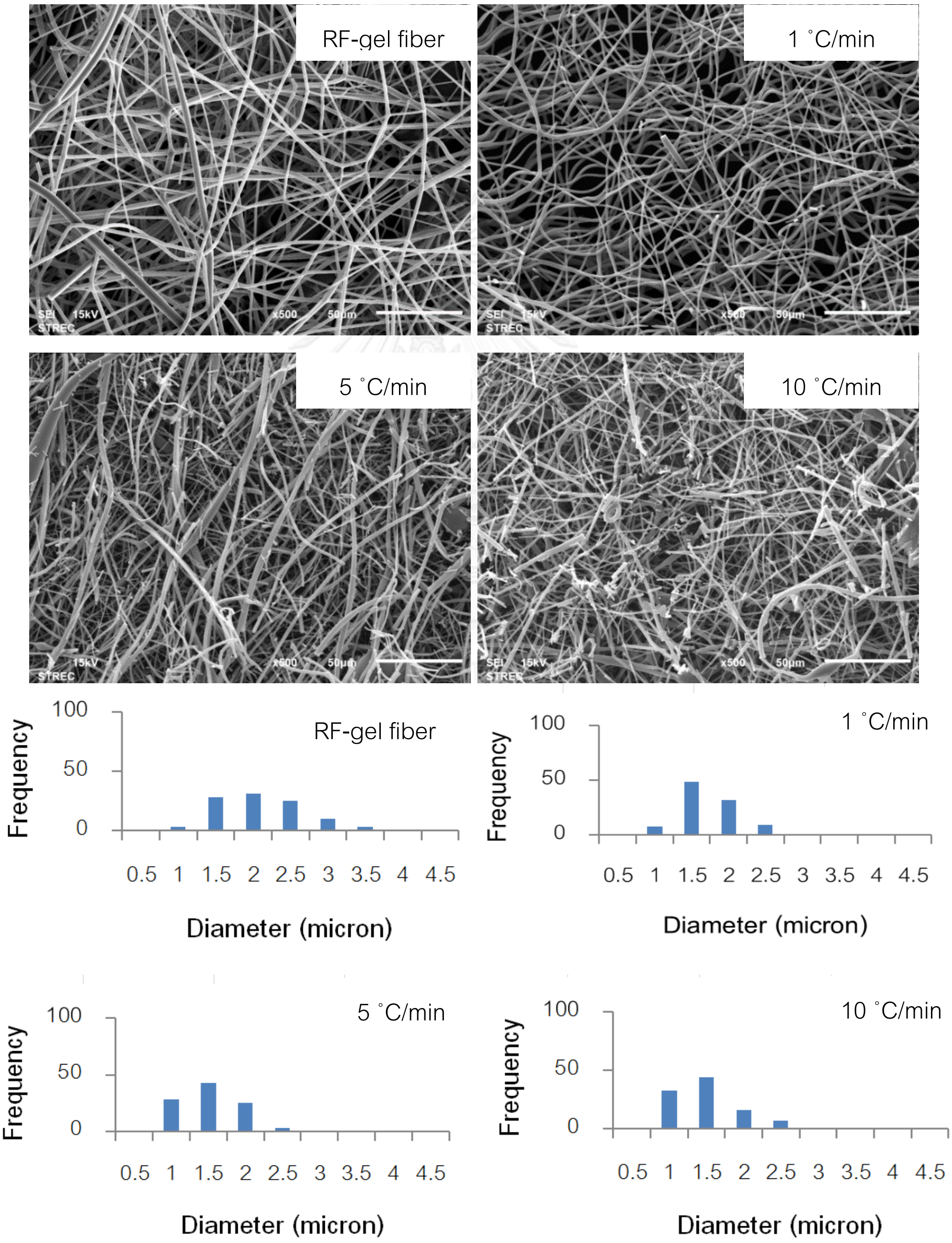


Figure 20 SEM images and size distributions of RF-gel fiber and carbon fiber which

carbonized at 750 ˚C

As a result, there were decreasing of diameter of carbon fiber. Because of elimination of non-carbon elements which included hydrogen, nitrogen and oxygen. All carbon fiber which carbonized at different heating rate had diameter size mostly in range 1 to 1.5 microns. However, there were some differences between them. Carbon fibers with 1 ˚C/min had smooth, long and unbroken filaments. On the other hand, carbon fiber with 5 and 10 ˚C/min had various structures included short and broken filaments. This means that those heating rate were too fast and non-carbon elements were rapidly eliminated.

Nonetheless, the duration of carbonization with heating rate 1˚C/min was too long. Hence, heating rate 5 and 10 ˚C/min were considered for all experiments. Carbon fibers which carbonized with 5 and 10˚C/min had slightly different. Carbonization with heating rate 10˚C/min gave shorter and more crack carbon fiber although duration was shorter. So, heating rate 5˚C/min was selected for all experiments.

Moreover, effect of heating rate on adsorption capacity was studied in the beginning of experiment. Figure 36 (in appendix A) was shown adsorption capacity of 3 different heating rate carbon fiber. Carbon fiber with 5 ˚C/min gave the highest adsorption capacity while carbon fiber with 1 and 10 ˚C/min had closely adsorption capacity.

Generally, weight of fiber was decreased after carbonization occurred. Table 12 is shown percentage of weight loss at different heating rate. There were no significant in weight loss [47].

Table 12 Weight loss of carbon fiber at different heating rate

Heating rate (˚C/min)	% weight loss
1	45.32
5	46.14
10	43.57

4.2.2 Effect of carbonization temperature on morphology

Final temperature were studied at 650, 750 and 850 ˚C with heating rate 5 ˚C/min. Comparisons of carbon fiber morphology which carbonized with different final temperature shown as figure 21.

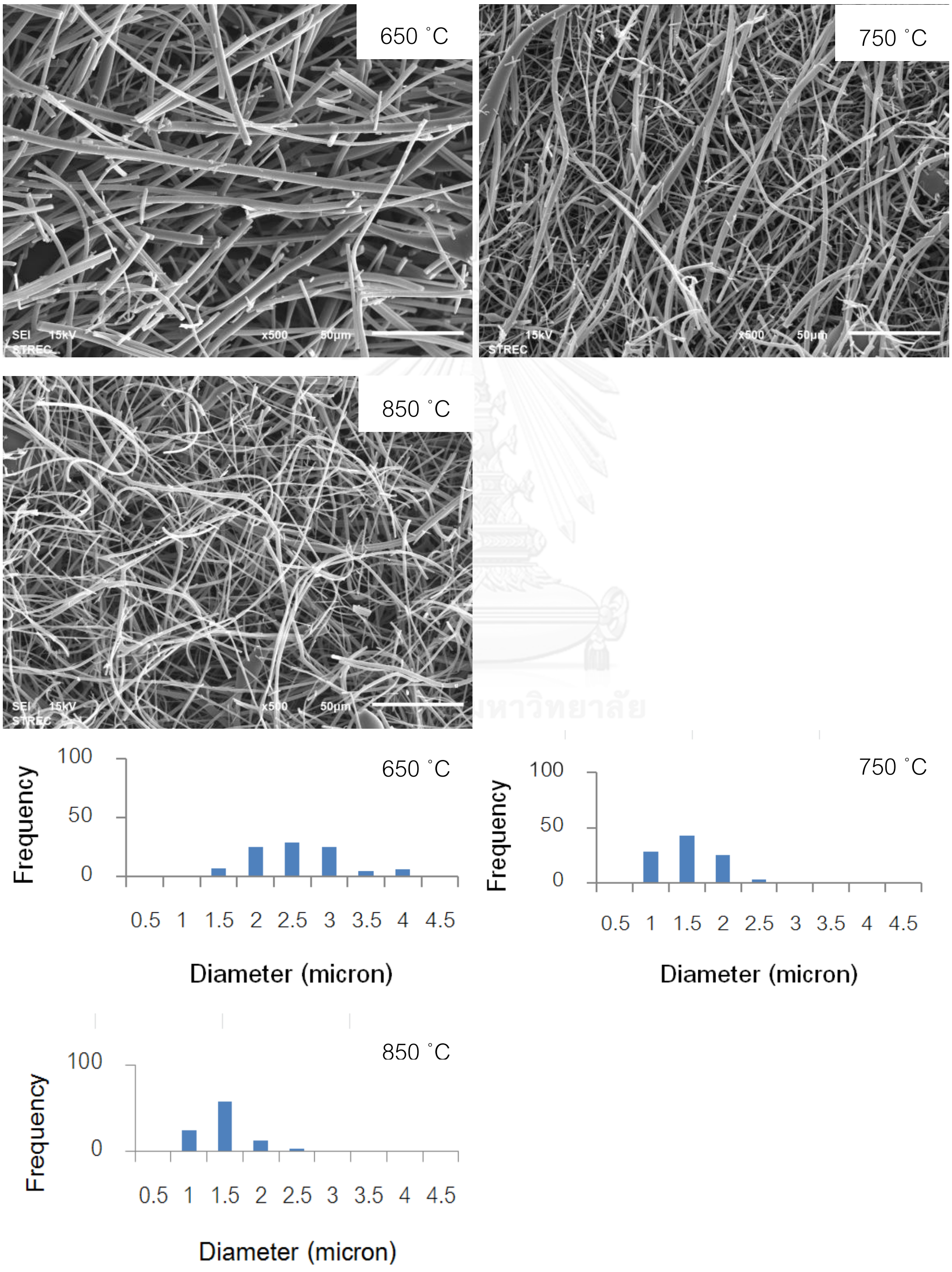


Figure 21 SEM images and size distributions of carbon fiber with heating rate 5 ˚C/min

In the first step of carbonization, adsorbed water was eliminated at 250 ˚C by endothermic reaction. Then, the others components were released at second step.[13] Carbon fibers from carbonization at 650 ˚C had larger diameter than carbon fiber which pyrolyzed at 750 and 850 ˚C. Its diameter was mostly 2 to 3 microns while the others were mostly 1 to 1.5 microns. Moreover, morphology of carbon fiber over the studied temperature range had no uniform structure. Due to carbon fiber had broken, shorter line and various size.

However, a relation between final temperature and percent weight loss is shown in table 13. At higher temperature made higher weight loss from 45.36% to 48.74 % because there were strong elimination of non-carbon elements at higher temperature [49].

Table 13 Weight loss of carbon fiber at different final temperature

Final temperature ˚C	% weight loss
650	45.36
750	46.14
850	48.74

4.3 Steam activation of carbon fiber

From previous topic, there was studied about parameters in carbonization process. After carbonization process, carbon fibers generally have many blocked pores. So, an activation is needed. Carbon fibers were activated at high temperature in inert conditions. Fixed parameters of activation are shown as following:

- Carbon fibers were prepared from carbonization of RF-gel fibers at final temperature 750 ˚C with heating rate 5 ˚C/min.
- Horizontal tubular furnace was used.

- N_2 was selected as inert gas and flowing of N_2 was fixed at 135 ml/min.
- Activation with heating rate 5 ˚C/min.
- An activation time was fixed at 30 minutes.
- Carbon fibers were put in oval ceramic container.
- Product was harvested after temperature decreased to room temperature.

There was only one parameter which was investigated in this section. Activation temperatures were varied from 700, 800 and 900 ˚C

4.3.1 Comparison of carbon fiber and activated carbon fiber

Morphology of carbon fiber and activated carbon fiber were compared. Figure 22 shows SEM images and size distributions. There were no difference in both diameter size and morphology. Carbon fibers and activated carbon fibers had diameter size in range 1 to 2 microns. Moreover, both fibers had totally same structure. Short, broken and long fibers were mixed together. These results were only quantitative. There were more results about adsorption isotherm in next topic.

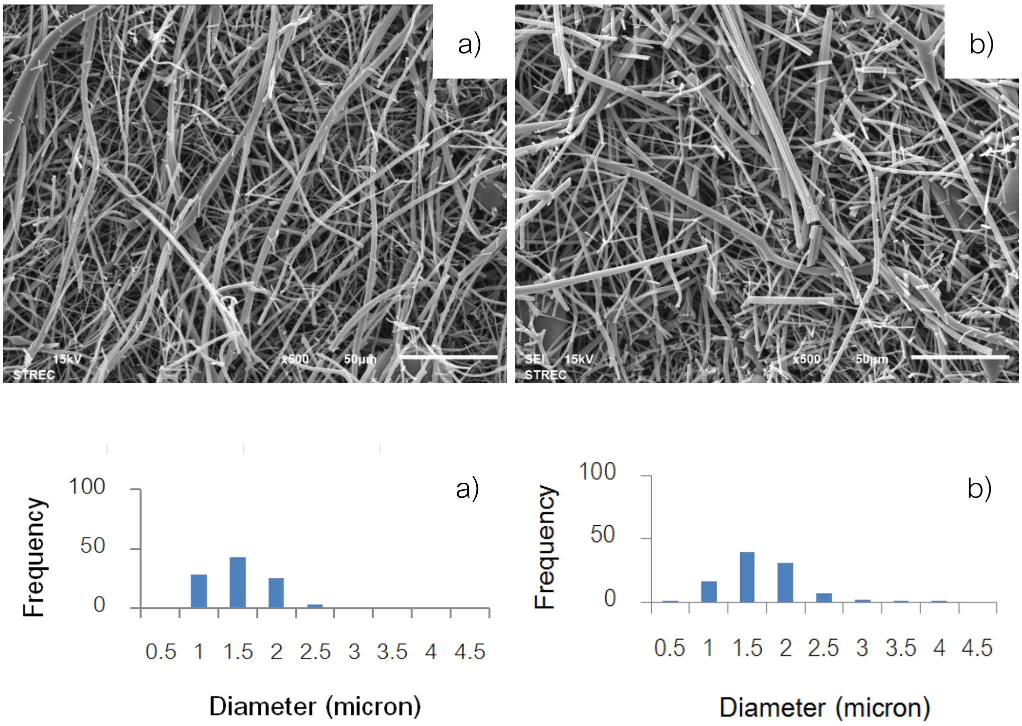


Figure 22 SEM images and size distributions of (a) carbon fiber and (b) carbon fiber which activated by steam at 800 ˚C

4.3.2 Effect of activation temperature on morphology

Activation temperatures were investigated at 700, 800 and 900 ˚C. Comparison of carbon fiber morphology which activated with different activation temperature shown as figure 23.

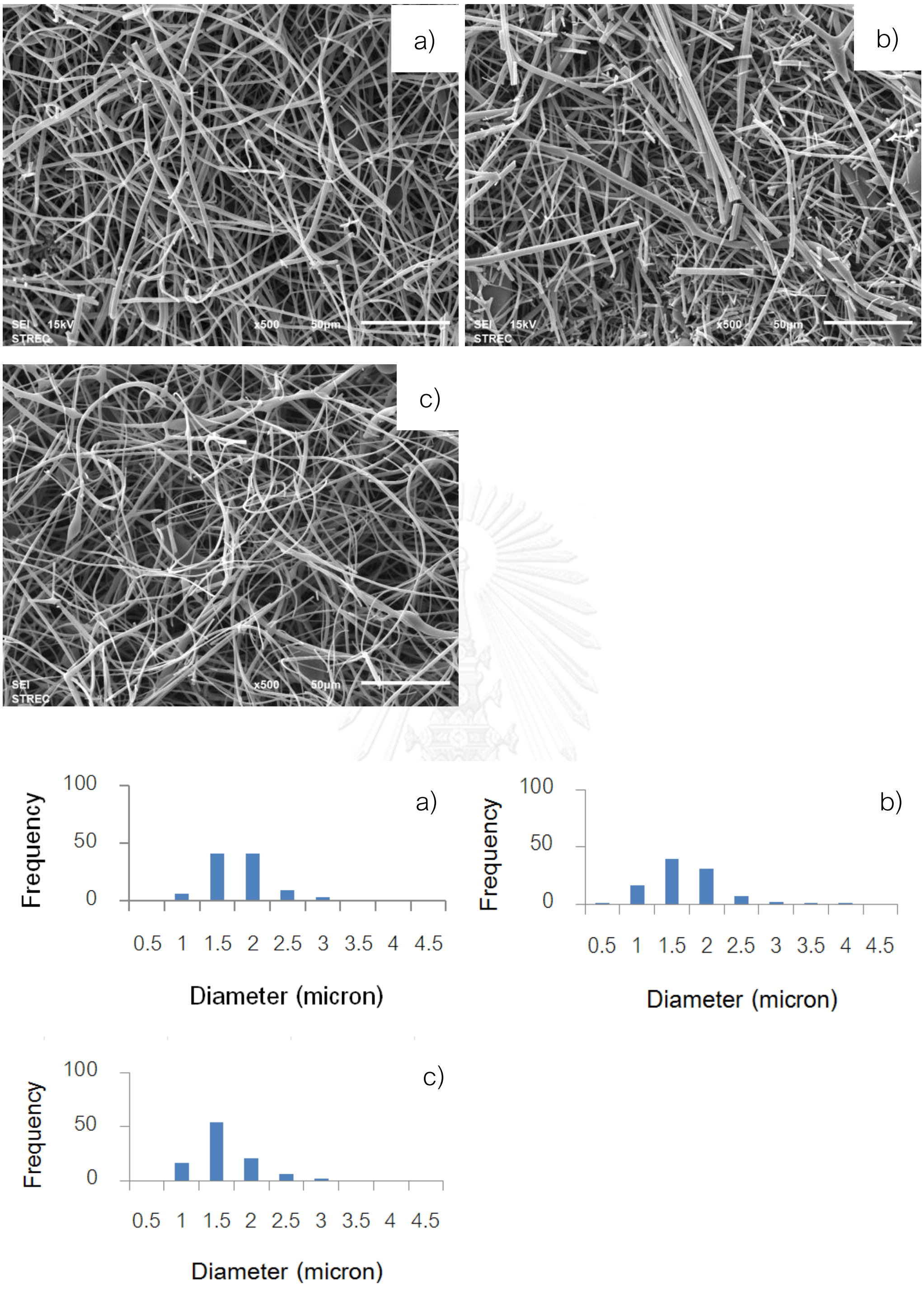


Figure 23 SEM images and size distributions of carbon fiber with different activation temperatures (a) 700 ˚C b) 800 ˚C and (c) 900 ˚C by using steam

As a result, activation with steam at various temperatures gave no different morphology on carbon fibers. All activated carbon fibers had mostly diameter size in range 1 to 2 microns. Its appearances were similar. Short, broken, long and smooth lines were noticed. However, activation temperature affected on percent weight loss which shown as table 14. Higher temperature gave burning off of fiber.

Moreover, functional groups on surface of activated carbon fiber were confirmed by FTIR spectra in next topic.

Table 14 Weight loss of activated carbon fiber at different activation temperature

Activation temperature ˚C	% weight loss
700	7.06
800	10.23
900	12.59

4.4 Toluene adsorption isotherm

Apart from previous topic, adsorption behavior of each adsorbent was studied. Firstly, adsorption equilibrium was investigated by sampling vapor in vial which contained adsorbent and adsorbate for 7 days. Concentration in each day was shown as table 18 in appendix D. Concentrations of first three days were closely which can be concluded that adsorbent-adsorbate reached equilibrium since first three days. Afterward, there were fixed parameters for adsorption isotherm experiment as following:

- 4 mg of carbon fiber for each bottle
- Adsorption for 3 days
- Volume of toluene sucked by GC syringe.

In this experiment, toluene was used as adsorbate which had molecule dimensions shown as figure 24. Toluene molecular size had 8.252 Å x 6.625 Å that can entered to micropore of adsorbent which had pore size under 2 nm. This section has 3 studied parameters include effect of carbonization temperature, effect of activation temperature and effect of adsorption temperature on adsorption capacity.

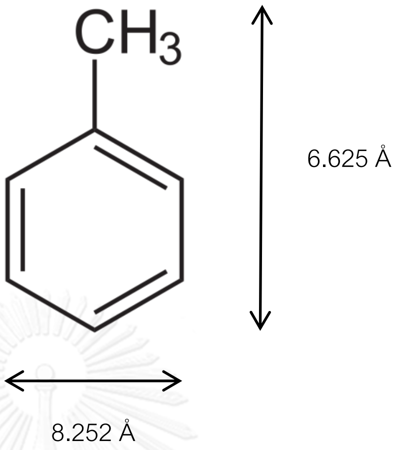


Figure 24 Shape and molecular size of toluene[50]

At the beginning, experimental data were investigated from gas chromatography (GC) and Thermo gravimetric analysis (TGA) for equilibrium concentration (C_e, mg/ml) and adsorption capacity (q_e, mg/mg adsorbent) respectively. Many problems occurred in this step. First, capacity of adsorbed toluene which measured by TGA gave too much quantity (see figure 37 in appendix A). Because toluene and adsorbed moisture had closely boiling point which cannot identify substance by TGA slope at low temperature. Therefore, GC was used for measurement both C_e and q_e instead of TGA. q_e was found from difference between initial concentration (vapor toluene in vial without adsorbent) and equilibrium concentration (vapor toluene in vial with adsorbent at equilibrium). However, some problems still occurred. Experimental data cannot fit with Langmuir and Freundlich model or some experimental data can fit with those models with few points. There were many ways to solve this problem included repeating experiment, GC examining and vial-leaked checking but, scattering of experimental data was still occurred. Finally, microliter-GC syringe was used instead of micro-pipette for toluene volume measurement. All experimental data had more accuracy and no scattering of data point.

After that, experimental data of toluene adsorption was fitted with both Langmuir and Freundlich model. Figure 25 shows data fitting with 2 models. R^2 value of Freundlich and Langmuir model were 0.9942 and 0.9296 respectively. It means that RF-gel carbon fiber had adsorption behavior which can describe under Freundlich's assumptions. Generally, assumptions of Freundlich isotherm were multilayer adsorption and there were difference in each adsorption site. So, Freundlich model was used for all adsorption data in this research because R^2 value of Freundlich model was higher than Langmuir model.

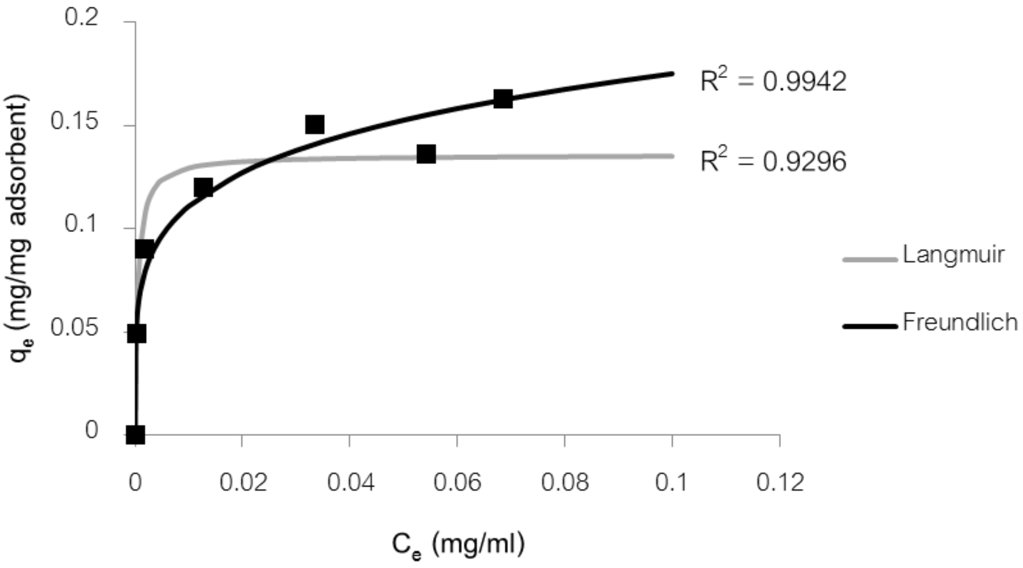


Figure 25 Comparison between Langmuir and Freundlich model

After that, all adsorption data were fitted with Freundlich model which shown as equation (9) and (10). As Freundlich model, adsorption mechanism related to multilayer adsorption and reversible process [51].

Nonlinear form : $$q_e = K_F C_e^{1/n} \qquad (9)$$

Linear form : $$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \qquad (10)$$

4.4.1 Effect of carbonization temperature

Carbon fibers which carbonized at different temperature 650, 750 and 850 ˚C were used as an adsorbent in this experiment. An adsorption was performed at fixed temperature 30 ˚C.

At equilibrium, figure 26 shown adsorption isotherm of 3 adsorbents. An isotherm presented type II [36]. This concave indicated that an adsorbent has wide pore size distribution. Multi-layer adsorption can be formed after monolayer adsorption was completed [52]. Moreover, each curve had no strict plateau which means that this adsorbent does not show obviously limitation adsorption capacity in studied range.

As a result, carbon fiber adsorbed toluene only in first layer because there was no appearance of the second inflexion point. Carbon fiber which carbonized at final temperature 850 ˚C gave higher adsorption capacity up to 0.2 mg toluene/mg adsorbent than 650 and 750 ˚C which similarly reported by A.H. Morino et al. The adsorption capacity was higher because more microporosity was created at appropriated carbonization temperature. In the other hand, those carbons gave type IV isotherm which mean that an adsorbent had both micro and mesoporosity. But, there were no confirmation about it in this experiment.

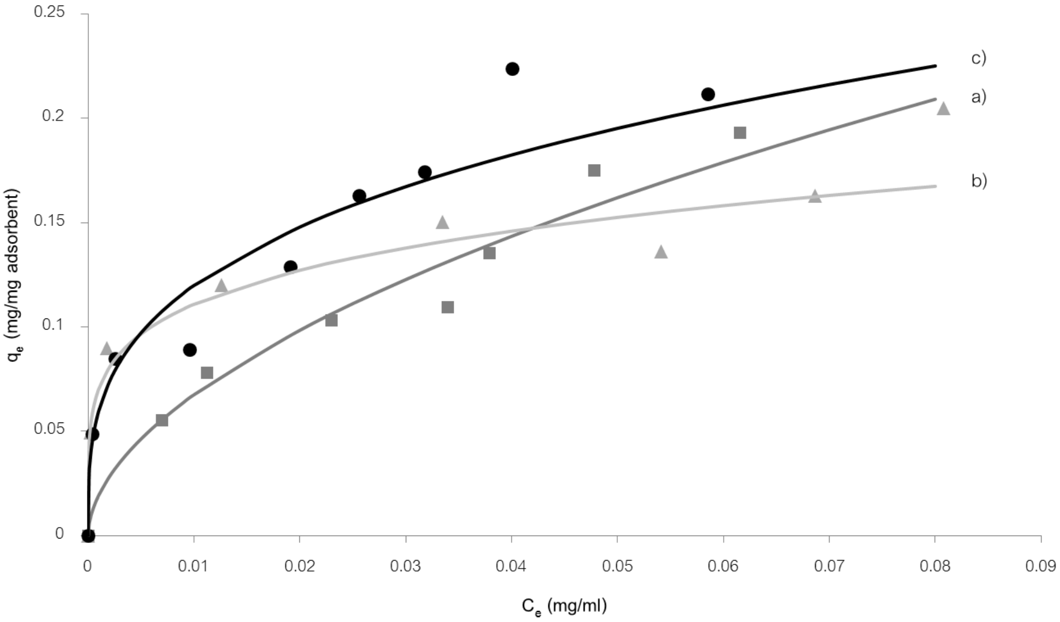


Figure 26 Adsorption isotherm of carbon fibers with different carbonization (a) 650 ˚C (b) 750 ˚C and (c) 850 ˚C at temperature at 30 ˚C

4.4.2 Effect of activation temperature

Carbon fibers which carbonized at final temperature 750 ˚C were activated at different temperature 700, 800 and 900 ˚C. There were 3 adsorbents in this experiment. An adsorption was performed at fixed temperature 30 ˚C. Figure 27 shown adsorption isotherm of 3 adsorbents.

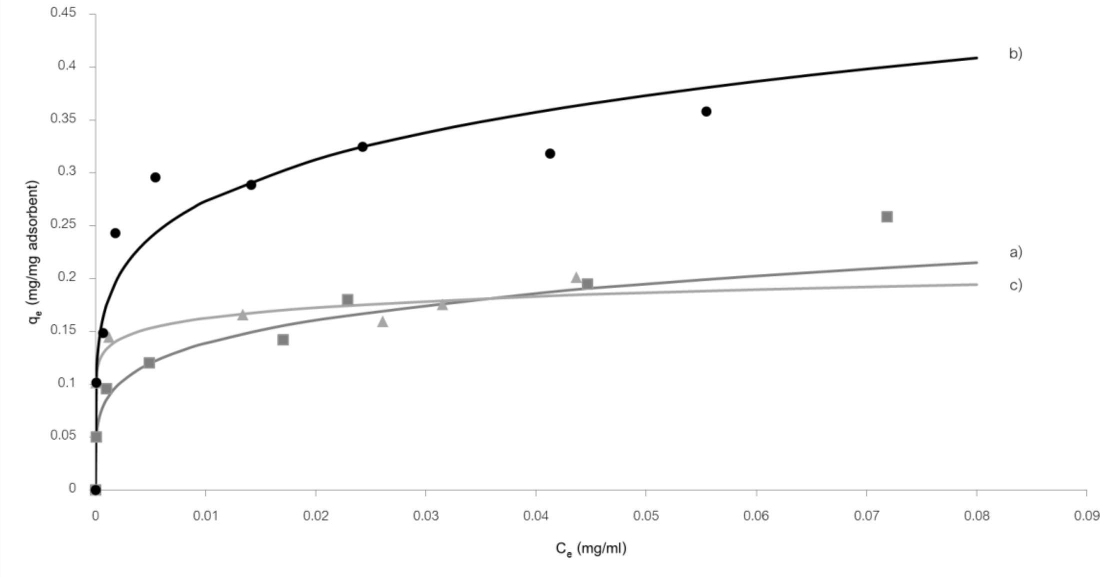


Figure 27 Adsorption isotherm of carbon fibers with different activation temperature (a) 700 ˚C (b) 800 ˚C and (c) 900 ˚C at 30 ˚C

As previous topic, carbon fiber adsorbed toluene up to 0.2 mg toluene/ mg adsorbent. When carbon fiber was activated, adsorption capacities were increased. There were significantly changed in capacity at activation temperature 900 ˚C. Because higher temperature can eliminate more disorganized carbon. For 700 and 800 ˚C, effect of activation temperature cannot see clearly because carbon fiber was not reactive with steam at those temperatures. Activation process can be increased capacity because of disorganized carbon elimination.

However, there were reported about influence of activation temperature by S. Park and K. Kim [53]. At higher temperature gave higher adsorption capacity but, there were limitation of temperature. If activation temperature up to 1000 ˚C, adsorption capacity was decreased.

4.4.3 Effect of adsorption temperature

Carbon fibers which carbonized at 750 ˚C with heating rate 5 ˚C/min were used as an adsorbent in this experiment. An adsorption was performed at various temperature 30, 45 and 80 ˚C. Figure 28 shown adsorption isotherm at different temperature.

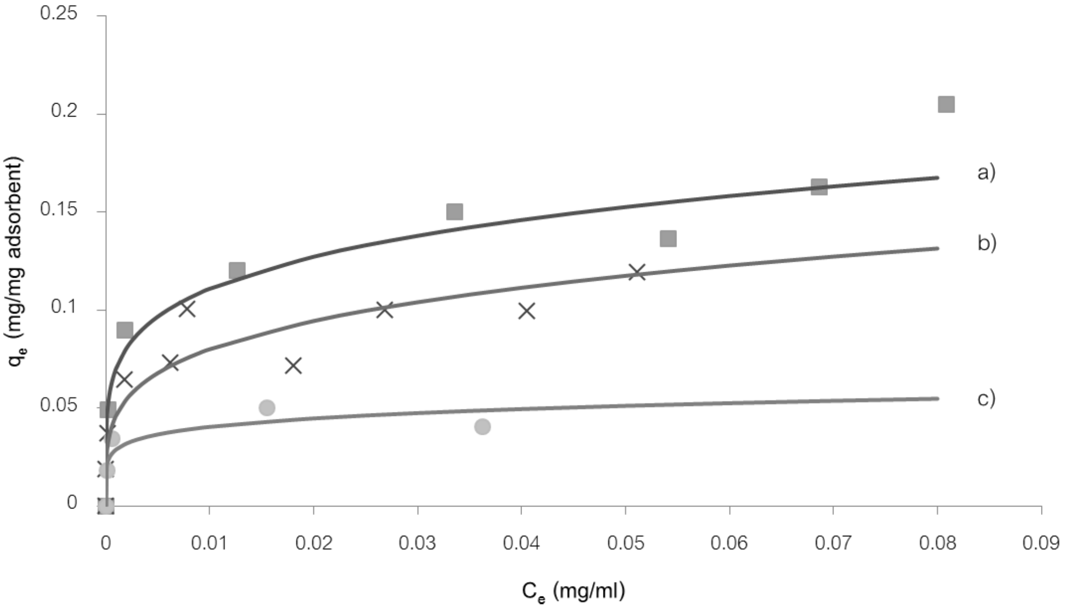


Figure 28 Adsorption isotherm of carbon fibers at temperature (a) 30 ˚C (b) 45 ˚C and (c) 80 ˚C

Adsorption capacity of carbon fiber was significantly decreased at higher temperature which indicated that adsorption reaction of this adsorbent is an exothermic reaction.

Lastly, there was an investigation about porosity of all adsorbents. Because all adsorbents can be adsorbed toluene which dimension of toluene molecule was shown as figure 24, This means that porosity of adsorbents probably had both big and small porosity. So, 1-octanol was used for clearly investigation on pore structure.

4.5 1-Octanol adsorption

Liquid phase adsorption was studied for more details of porosity behavior. 6 Adsorbents were used in this experiment. There were various ratios between resorcinol and water or catalyst of 5 adsorbents which formed in particle type. And there was 1 adsorbent which formed in fiber type. All formulas of each adsorbent were shown in table 16. All adsorbents were carbonized at final temperature 750 ˚C with heating rate 5 ˚C/min. In addition, 1-octanol was selected as an adsorbate because of higher molecular weight than toluene. There were fixed parameters for liquid phase adsorption experiment as following:

- Initial concentration of 1-octanol solution was 171.9 ppm
- 4 mg of adsorbent per 25 ml of 1-octanol solution
- Adsorption at 30 ˚C
- Adsorption for 3 days

In this studied, there were 2 parts of adsorption included effect of RF-gel formulas on adsorption capacity and effect of adsorbent shape on adsorption capacity.

Table 15 Types of adsorbent

	Adsorbent 1	Adsorbent 2	Adsorbent 3	Adsorbent 4	Adsorbent 5	Adsorbent 6
R/F	0.5	0.5	0.5	0.5	0.5	0.5
R/W	∞	∞	0.25	0.5	∞	∞
R/C	200	1000	500	500	500	500
Type	particle	particle	particle	particle	particle	fiber

4.5.1 Effect of RF-gel formulas on adsorption capacity

As a previous research, effect of RF-gel formulas in RF-gel preparation on needle-less electrospinning process were studied. There was the best formula which can be fabricated RF-gel fiber. This formula was consisted 0.5 of R/F, 500 of R/C and ∞ of R/W. For more investigation, effect of RF-gel formulas on porosity was considered by varying ratios of RF-gel preparation. However, there were investigated in particle form because of those formulas cannot be fabricated. Particle form was produced from solidifying and smashing of RF-gel. No. 1 to 5 were noticed as 5 adsorbent which had different formulas. Afterward, comparison between initial concentration and final concentration of 1-octanol is shown as figure 29.

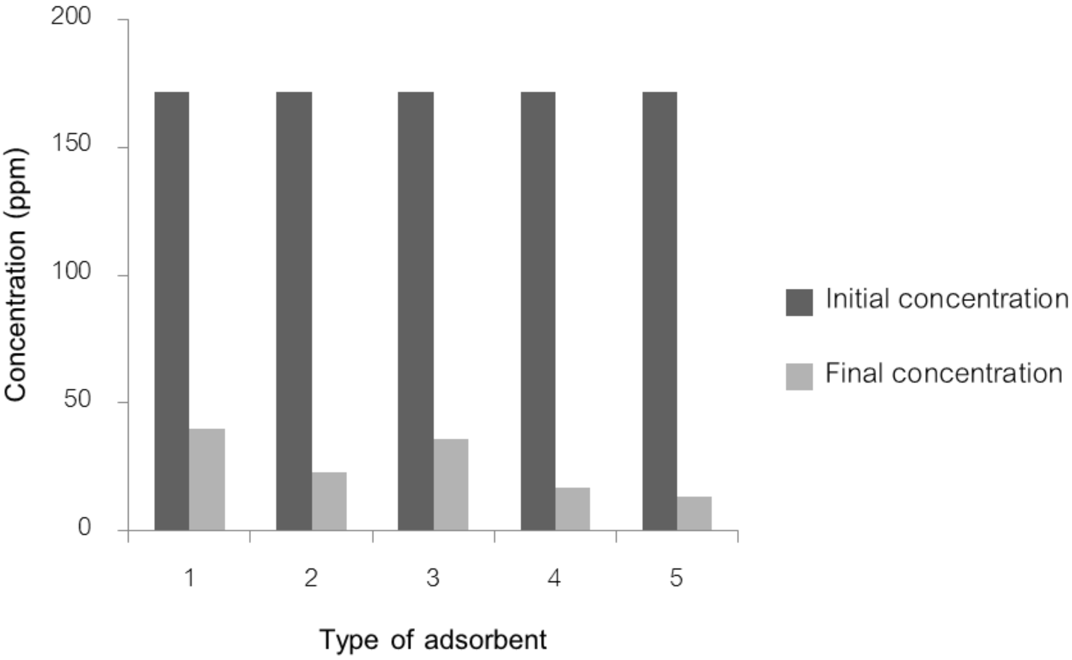


Figure 29 1-octanol adsorption with 5 different RF-gel formulas carbon particle

At equilibrium, there were different in adsorption capacity of 1-octanol. Adsorbent no.5 had highest adsorption capacity. And adsorbent no.4, 2, 1 and 3 had lower adsorption capacity respectively. As a result, formulas of RF-gel affected on adsorption capacity which mean that each formula gave different pore structure. Pore structure is an important property which affected on adsorption capacity. Effect of ratio between formaldehyde and catalyst on surface area had no significant trend. But, there was reported that gelation time of RF-gel was decreased at higher R/C [13]. Moreover, ratio of resorcinol to water was considered. At lower R/W, pore structure was poly-dispersed structure and gelation time was also decreased [13].

Moreover, pore size of adsorbent can find approximately from bond lengths of octanol structure. Octanol plane structure consists of 7 bonds of C-C, 1 bond of C-H, 1 bond of C-O and 1 bond of O-H. And octanol width can calculate from 2 bonds of C-H. Table 16 shows bond lengths which octanol molecule length can calculate approximately.

Table 16 Bond lengths

Bond	Length (Å)
C-C	15.4
C-H	10.9
C-O	14.3
O-H	0.96

Octanol length = (7*15.4) + (1*10.9) + (1*14.3) + (1*0.96)
= 133.96 Å
Octanol width = (2*10.9)
= 21.8 Å

So, octanol molecule has approximate dimension which show as figure 30.

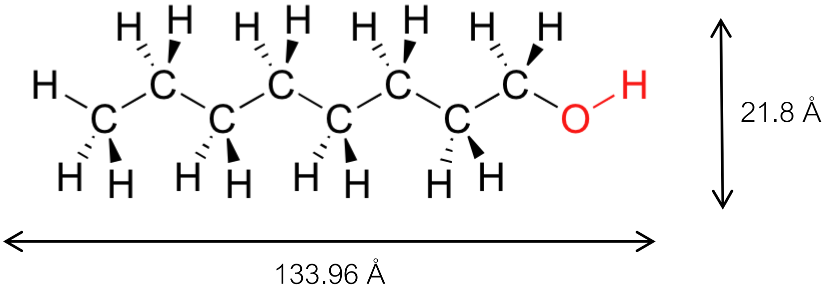


Figure 30 Octanol structure

Octanol molecule size makes more clearly investigation about pore size of all adsorbent. This was confirmed that different of RF-gel formulas gave different pore structure.

4.5.2 Effect of adsorbent shape on adsorption capacity

From the previous topic, there were studied an effect of formulas on adsorption capacity. In this topic, configuration of adsorbent was investigated. A formula of adsorbent no.5 which gave an outstanding pore structure was used. There were 2 configurations of adsorbent included particle and fiber which noticed as no.5 and no.6 respectively. Adsorption capacity of each adsorbent was presented in figure 31.

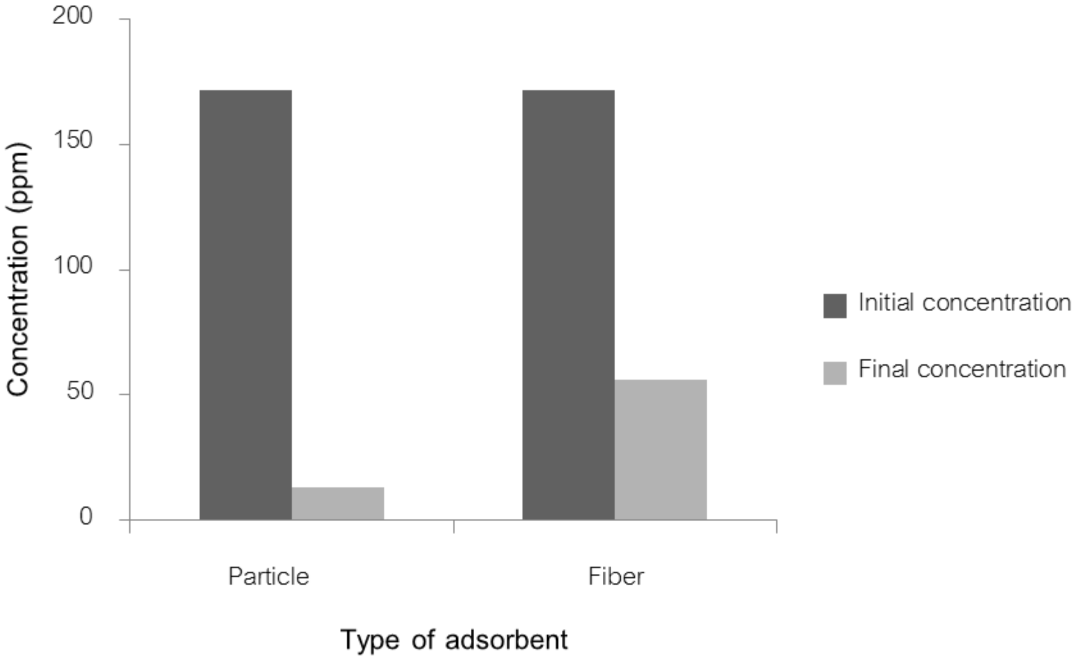


Figure 31 1-octanol adsorption on different shape adsorbents

At equilibrium, adsorption capacity was clearly seen difference. Fiber form can adsorb 115.96 ppm of 1-octanol and particle form can adsorb 158.78 ppm of 1-octanol. This means that fiber production process made changing on pore structure. In the same way, resorcinol-formaldehyde gel is carbon precursor which generally gives a mesoporous carbon [13]. But, there were reported that adsorbent no.6 had no occurrence of mesoporosity which confirmed that electrospinning affected on carbon porous structure [21].

As mentioned before, there was adsorption of toluene with carbon fiber. Adsorption of bigger molecule was investigated in this topic. 1-Ocatanol has length which 16 times larger than toluene molecule approximately. This means that carbon fibers also have bigger pore size instead of microporous because 1-octanol molecule cannot enter micropore. Meanwhile, types of large pore size cannot verify. Those pore size can be both mesoporous or macroporous.

Although fiber adsorbed lower quantity of 1-octanol, but this was not meant that its structure had lower surface area. Because carbon fiber may have much more small porosity than carbon particle which 1-octanol molecule cannot enter.

4.6 N_2 adsorption of particle

Surface area and porosity of each adsorbent were investigated by N_2 adsorption. Table 17 was shown a repeated experiment of N_2 adsorption.

Table 17 N_2 adsorption of adsorbent

Type	Result	Operating time (h)
Carbon particle (1st time)	Desorption line was not met adsorption line after measurement ended which caused by lower temperature in degas stage (100 °C).	24
Carbon particle (2nd time)	Adsorption and desorption line were overlapped that caused by higher degas temperature (250 °C).	24
Carbon particle (3rd time)	Irregular adsorption isotherm	24
Carbon fiber	1st data point still measured and there was cancellation of measurement after operating hour	72

For 3rd time of carbon particle measurement, an irregular adsorption isotherm of carbon particle was shown as figure 32.

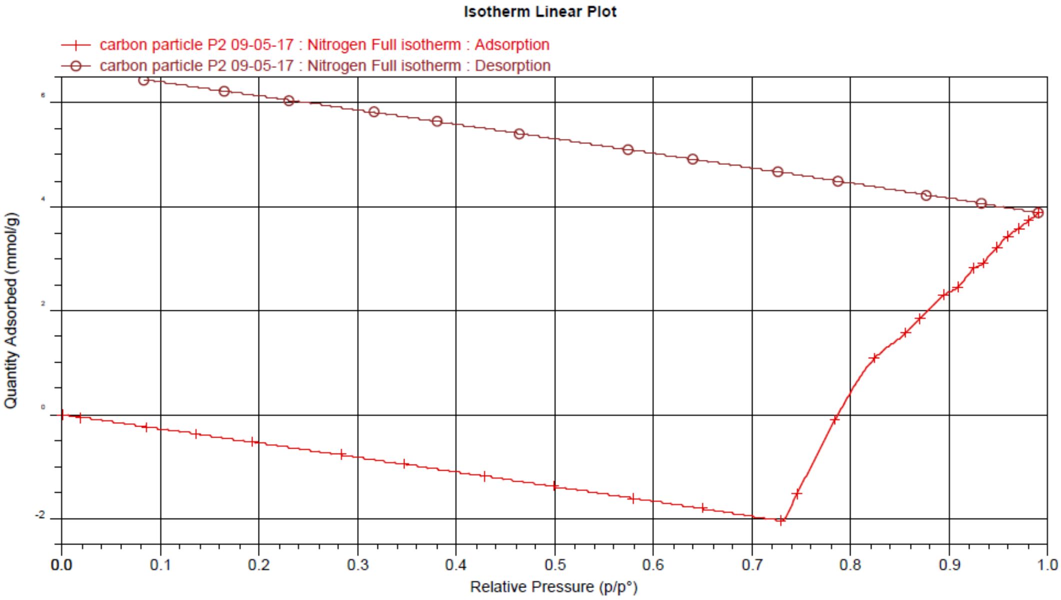


Figure 32 N_2 adsorption of carbon particle

In the low relative pressure range, adsorbed nitrogen decreased instead of increasing which mean that something wrong was happened. Firstly, the main reason probably came from instrument error. But, there had a maintenance and standard operating which result as regular adsorption isotherm. So, there were discussed about this again. It can be resulted from an adsorbent could be have a complex pore structure included occurrence of small porosity such as microporous, super-microporous or ultra-microporus. This complex pore structure could be trapped N_2 that made system cannot reach an equilibrium and data point cannot collect.

However, data point of carbon fiber cannot collect in duration 72 hours. Carbon fiber consisted of much more small porosity.

4.7 Pore structure of carbon fiber

Although carbon fiber cannot measure surface area and adsorption/desorption isotherm by N_2 adsorption, its pore structure can predict from overall experimental data included;

- Long line fiber which had shallow pore structure
- Ability to adsorb toluene molecule
- Ability to adsorb 1-octanol molecule
- N_2 trapped in N_2 adsorption

Because 1-octanol molecule cannot entered to microporosity which mean that this molecule may be adsorbed by bigger porosity such as macroporosity or microporosity. Moreover, microporosity was surely appeared on carbon fiber from N_2 trapped. Nevertheless, it cannot conclude that toluene molecule adsorbed by microporous because toluene molecule was small and it can be entered both big and small pore. Finally, pore structure prediction of carbon fiber was shown as figure 33.

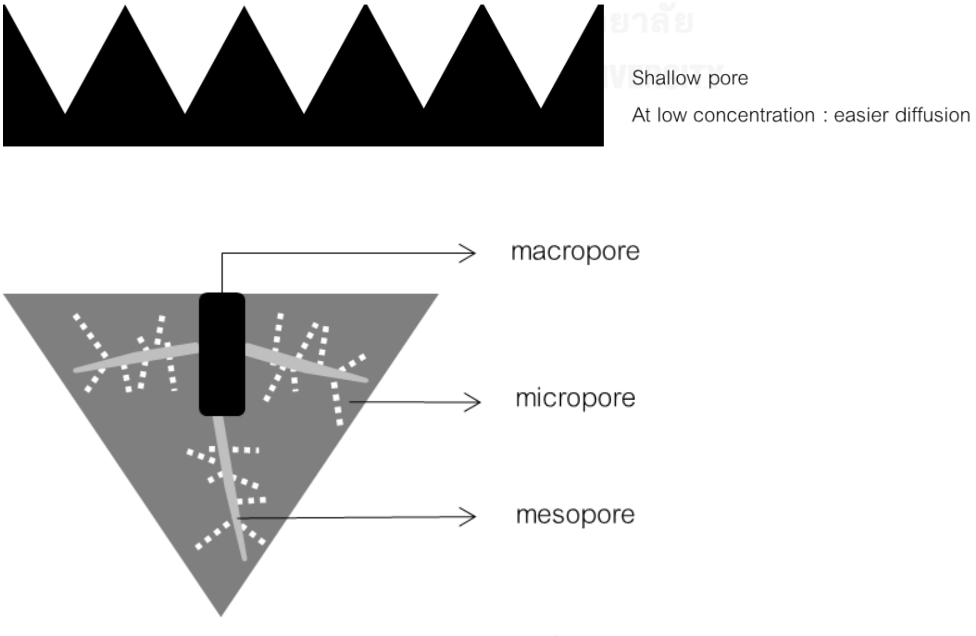


Figure 33 carbon fiber pore structure

Chapter V

Conclusions and recommendations

5.1 Conclusions

5.1.1 Heating rate in carbonization affected only on carbon fiber morphology.

5.1.2 Carbonization temperature made different porosity of carbon fiber. Highest toluene adsorption capacity was came from carbon fiber which carbonized at 850 ˚C

5.1.3 Activation temperature significantly developed porosity of carbon fiber at 900 ˚C.

5.1.4 Higher adsorption temperature gave lower adsorption capacity.

5.2 Recommendations

5.2.1 Size of bottle in adsorption experiment can be increased for wide range of concentration.

5.2.2 Complex structure of carbon fiber should be investigated.

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APPENDIX

Appendix A

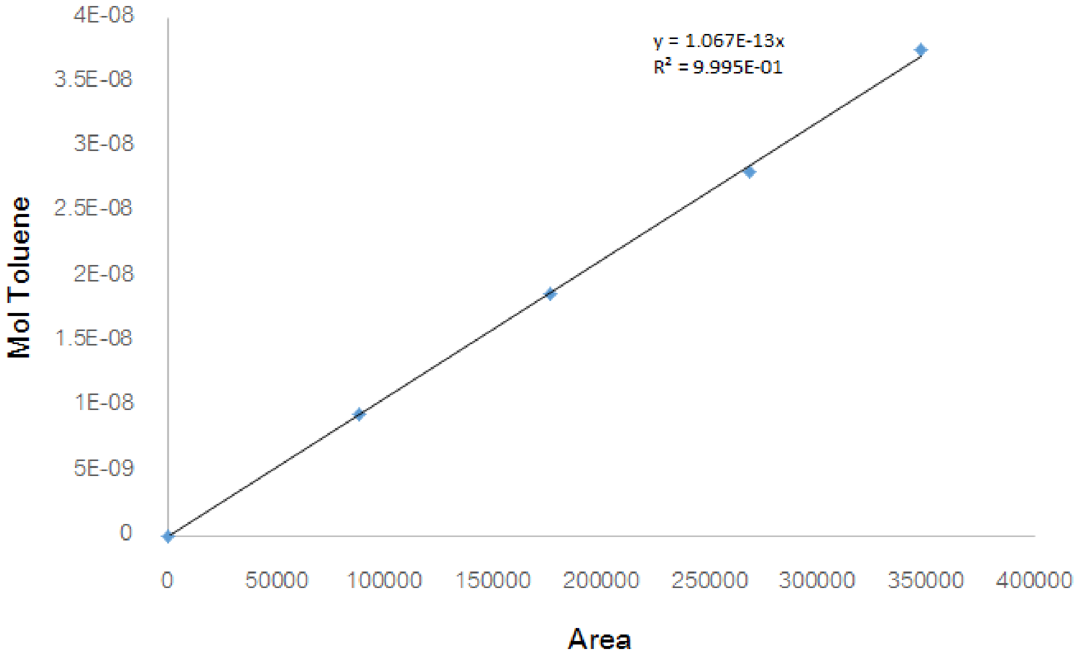

Figure 34 Toluene calibration curve

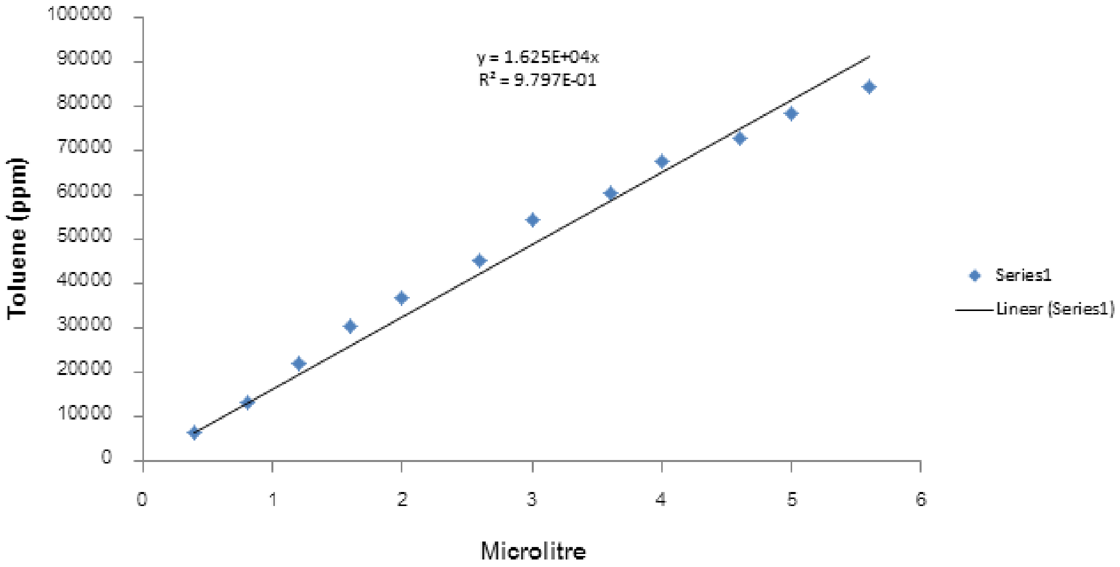

Figure 35 Initial concentration of toluene

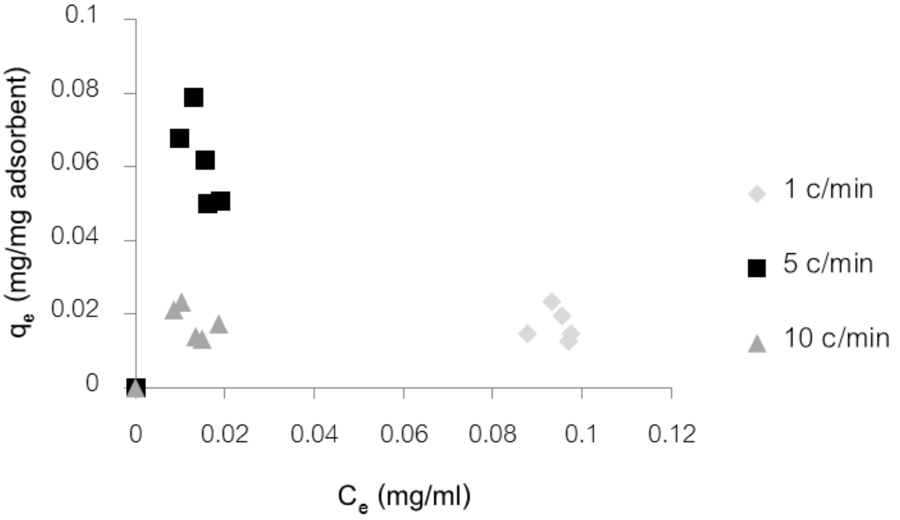

Figure 36 Adsorption experiment data of 3 different heating rates

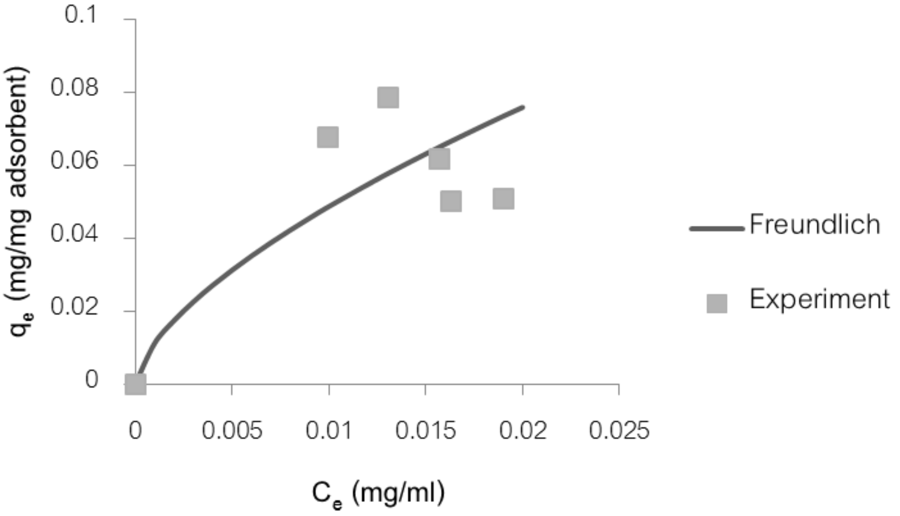

Figure 37 example of wrong isotherm in the beginning experiment

Appendix B

Calculations of RF-gel preparation

Resorcinol molecular weight = 110.11 g/mol

Formaldehyde molecular weight = 30.03 g/mol

Sodium hydrogen carbonate molecular weight = 84.007 g/mol

Density of formaldehyde = 1.08 g/cm^3

Formaldehyde concentration = 37.25%

Resorcinol was fixed at 15 g = 0.1362 mol

Ratios of R/F, R/W and R/C were fixed in this experiment included:

R/F = 0.5

R/W = ∞

R/C = 500

- Formaldehyde Volume

R/F = 0.5

F = R/0.5

$$F = \frac{0.1362 mol}{(0.5)} = 0.2724 \text{ mol} = 8.1826 \text{ g}$$

$$F = \frac{(8.1826 g) * (100)}{(37.25)} = 21.9666 \text{ g}$$

F = 20.1529 ml

- Catalyst volume

Catalyst solution preparation by 10 ml of water and 0.1 g of Sodium hydrogen carbonate.

R/C = 500

C = R/500

$$C = \frac{0.1362\,mol}{500} = 0.00027 \text{ mol} = 0.0227 \text{ g}$$

$$C = 0.0227 * \frac{10}{0.1} = 2.27 \text{ ml of solution}$$

Appendix C

Calculation for maximum toluene volume

At 30 ˚C

P^{sat} = 4.8885 kPa = 0.0482 atm

Density of toluene = 0.858 g/ml

Toluene molecular weight = 92.14 g/mol

From PV = nRT

$$n = \frac{PV}{RT} = \frac{(0.0482\,atm)(27\,ml)}{(82.06\,\frac{cm^3 atm}{mol.K})(303K)} = 5.234x10^{-5} \text{ mol}$$

From D = m/V

$$V = \frac{(5.234x10^{-5})(92.14\,\frac{g}{mol})}{(0.858\,\frac{g}{ml})} = 5.6208\,\mu L$$

Appendix D

Adsorption duration

An adsorption of carbon fiber which carbonized at final temperature 750 ˚C was used as an adsorbent. Toluene was used as adsorbate. Adsorption performed at 30 ˚C

Table 18 Toluene are of each day

Day	Concentration (ppm)
1	28798.05
2	27918.68
3	25968.92
4	27777.90
5	28602.27

Appendix E

Percent weight loss after carbonization

1 molecule of resorcinol-formaldehyde gel was shown in figure 38.

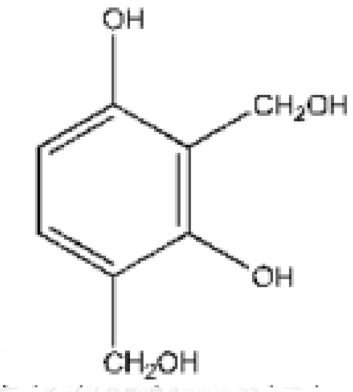

Figure 38 resorcinol-formaldehyde

1 molecule of resorcinol-formaldehyde gel includes 8 atoms of C, 10 atoms of hydrogen and 4 atoms of hydrogen which molecular weight were shown as following;

C = 8*(12 g/mol) = 96 g/mol
H = 10*(1 g/mol) = 10 g/mol
O = 4*(16 g/mol) = 64 g/mol
Total = 96+10+64 = 170 g/mol

After carbonization process, hydrogen and oxygen atoms were eliminated. So, percent weight loss can be calculated

$$\%\text{weight loss} = 100 * \frac{74}{170} = 43.53\ \%$$

List of publication

1. Asamaphorn Pudindarn and Varong Pavarajarn. “ผลของการเผาและการกระตุ้นต่อประสิทธิภาพในการดูดซับโทลูอีนของเส้นใยถ่านกัมมันต์ซึ่งได้มาจากเรโซซินอลฟอร์มาลดีไฮด์เจล”. Proceeding of The 26th National Thai Institute of Chemical Engineering and Applied Science Conference 2016, Bangkok, Thailand, October 26th-28, 2016.

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