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## **APPENDICES**

## **APPENDIX A**

### **CARBONIZATION PROCESS OF NATIVE STARCH AND MODIFIED STARCH (PRELIMINARY RESULTS)**

## A.1 Introduction

According to carbonization process in Chapter 5, we carried out the carbonization process on carbon microspheres from hydrothermal of native corn starch and modified starch (HI-CAP®100). In this appendix, other types of native starch (native tapioca starch, native rice starch, native sticky rice starch, and native wheat starch) and modified starch (CAPSUL®) were used to synthesize carbon microspheres with initial concentration of 10wt% at 180°C for 24 hours. After hydrothermal process, the as-prepared CMS particles were carbonized under nitrogen atmospheres with the same condition as in Chapter 5. After carbonization process, obtained porous CMS particles were characterized by various techniques in order to reveal their specific properties.

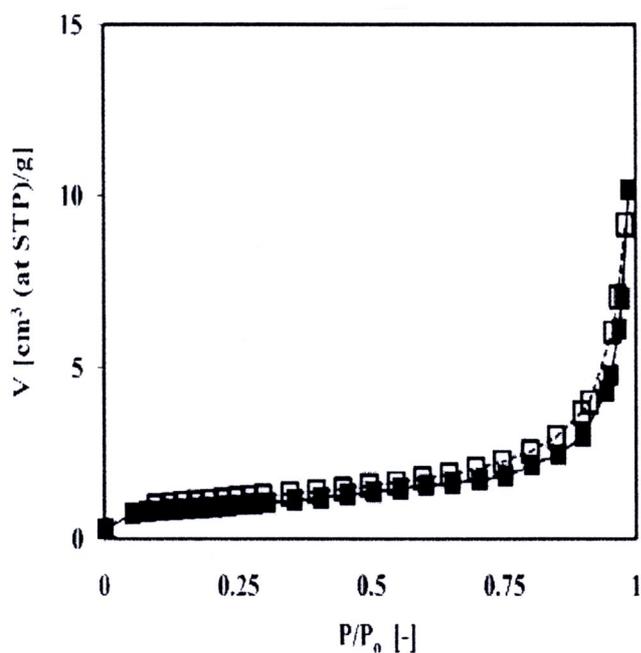
## A.2 Carbonization process of carbon microspheres

The obtained powders will be carbonized in a tube furnace under N<sub>2</sub> atmosphere. The N<sub>2</sub> flow rate, final temperature, heating rate of the furnace, and holding time will be 100 ml/min, 600°C, 1°C/min, and 3 h, respectively. Effects of carbonization process were revealed by many analysis techniques in order to understand particular properties of carbon microspheres.

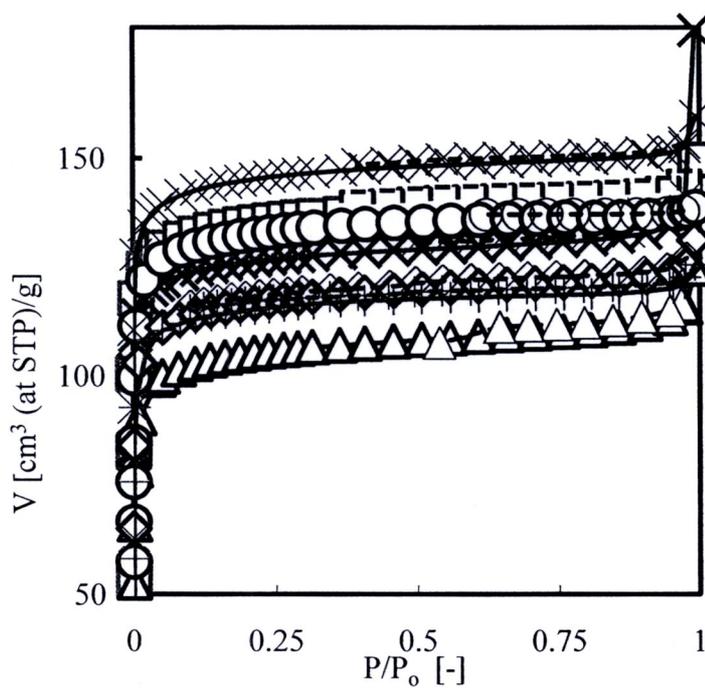
### A.2.1 Porosity of porous carbon microspheres

In the carbonization process, carbon microsphere particles were developed porous structure by losing some C, H, and O in gaseous products. The porosity of porous carbon microspheres was determined by adsorption-desorption of nitrogen gas at -196°C. Typical isotherms of adsorption-desorption of porous carbon microspheres in different types of native starch were demonstrated in Figure. All isotherm is type I isotherm which indicates micropore structure of the samples (as shown in Figure A.1).





**Figure A.1** N<sub>2</sub> adsorption-desorption isotherm of CAPSUL<sup>®</sup>-CMSs before carbonization process



**Figure A.2** N<sub>2</sub> adsorption-desorption isotherm of CMSs after carbonization which are (\* ) HI-CAP<sup>®</sup>100, (×) CAPSUL, (□) Tapioca, (○) Corn, (◇) Rice, (+) Wheat, (△) Sticky rice

An BET equation was used to calculate surface area of porous carbon microspheres after carbonization. Specific surface area of porous carbon microspheres in different type of native starch were shown in Table. All samples have the same range of surface area between 400-500 m<sup>2</sup>/g (as shown in Table 5.5). These results demonstrate that the carbonization process gave the same porous structure of carbon microspheres from different types of native starch.

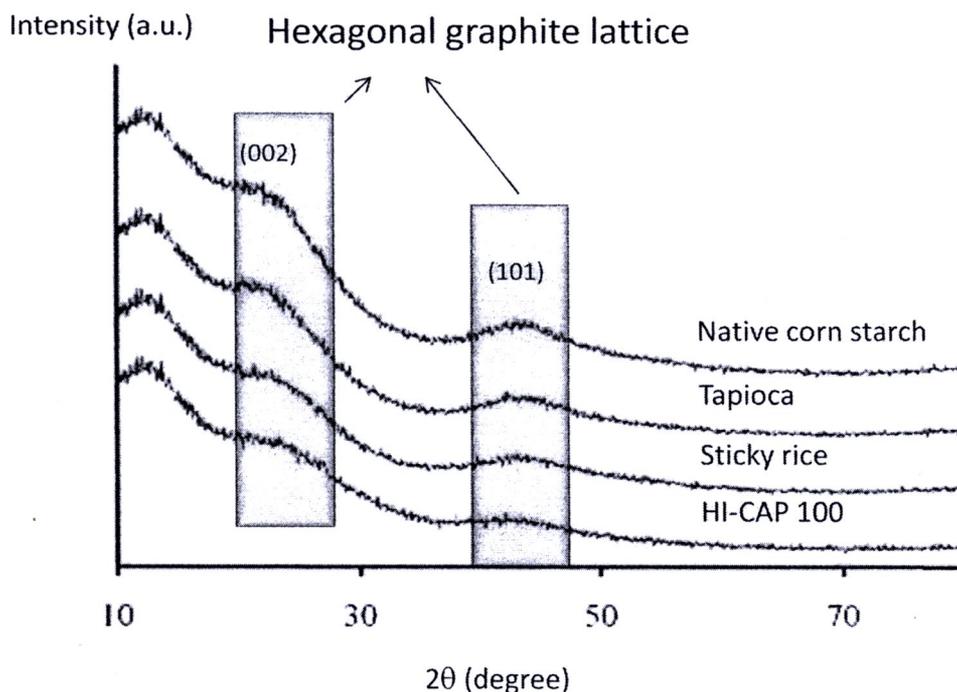
**Table A.1** Specific BET surface area of the porous CMS particles

Starch	Specific BET surface area, $S_{\text{BET}}$ [m <sup>2</sup> /g]	
	Before carbonization	After carbonization
HI-CAP®100	4.32	560
CAPSUL®	3.41	530
Tapioca	3.23	546
Corn	3.57	520
Rice	2.89	457
Wheat	1.23	444
Sticky rice	3.12	415

Brunauer–Emmett–Teller (BET) surface areas of CMSs before and after carbonization are also summarized in Table 2. The CMSs surface areas were dramatically increased after carbonization. The release of H, O and C during carbonization process gives rise to large quantities of micropores throughout the bulk of the samples[43].

### A.2.2 Crystallinity of carbon microspheres

In addition, the XRD patterns of some CMSs after carbonization are shown in Figure A.3. There are the presences of two broad peaks at  $2\theta = 24.8$  and  $43.5$  which are reflections from the (002) plane and the (101) plane, respectively [45]. The peaks can be indexed to a hexagonal graphite lattice. The broadening of the peaks suggests the presence of an amorphous carbon phase within the CMSs [1].



**Figure A.3** XRD patterns of carbon microspheres after carbonization process of various starch

### A.2.3 Elemental components of carbon microspheres

The energy-dispersive X-ray (EDX) analysis (as shown in Table 5.6.) on CMSs after carbonization shows that carbon is the main component of the CMSs [26]. The oxygen component may mainly come from the absorbed water molecules. The carbonization process mainly removed an oxygen and hydrogen components which contained in through carbon microspheres structure [50]. Porous carbon microspheres was increased their carbon content in the structure which was particularly properties [49]. The properties were inert materials which were suitable for catalyst support application. Although each samples was obtained from different types of starch, they have the same carbon content as shown in Table A.2. All carbohydrates have different structure and composition but they were hydrolyzed to yield glucose products [12]. The glucose product subsequently dehydrated to form intermediates. These behaviors were the same which caused the same structure of carbon microspheres [51].

**Table A.2** The elemental components of porous CMSs from energy dispersive X-ray

Starch	Carbon (%)	Oxygen (%)
Native corn starch	66.67	33.33
Native Tapioca starch	69.11	30.89
Native Rice starch	68.44	31.56
Native Wheat starch	67.72	32.28
Native Sticky rice starch	69.01	30.99
HI-CAP®100	71.08	28.92
CAPSUL®	68.15	31.85

**APPENDIX B**

**KINETIC MODEL OF HYDROTHERMAL OF NATIVE  
CORN STARCH**

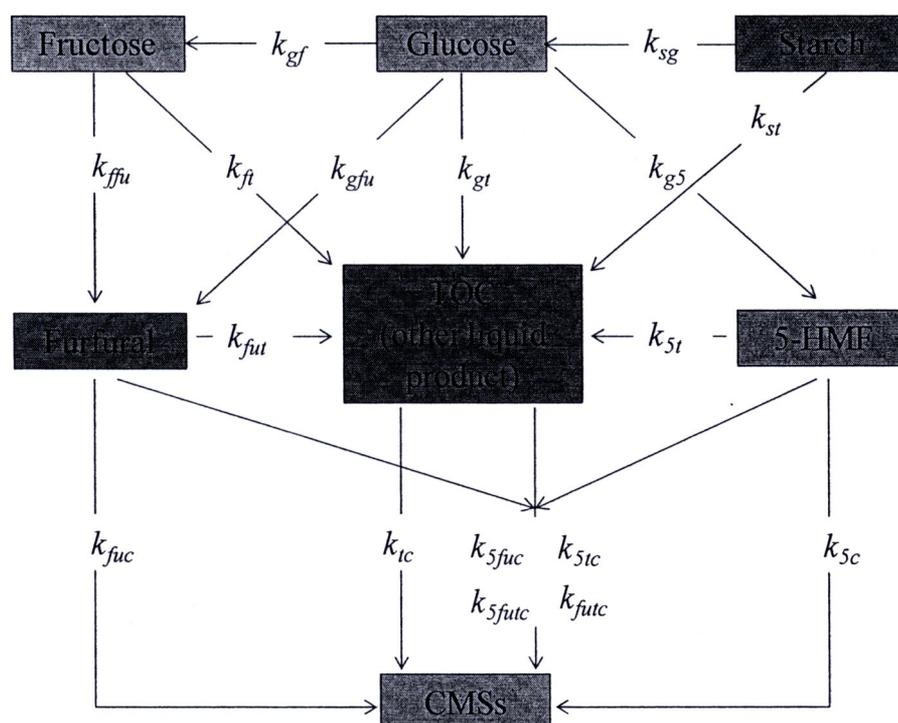
## B.1 Introduction

According to kinetic model fitting for hydrothermal process of glucose in Chapter 8, this section will discuss modified reaction pathway of carbon microsphere formation from native corn starch. The rate equations then were proposed to calculated rate constants of the reactions. First order reaction assumption was also used as the model. We used various types of starch in these experiments including native corn starch, Hi-CAP®100, amylopectin and amylose.

## B.2 Results and discussion

### B.2.1 Modified reaction pathway for hydrothermal process of native corn starch

For using native starch as carbon precursor for CMS formation, the reaction pathway of glucose could be modified to propose reaction pathway of CMS formation from native starch as shown in Figure B.1. In this pathway, native starch can be hydrolyzed to yield both of glucose and TOC compounds. Reaction rate constants ( $k_{sg}$  and  $k_{st}$ ) were introduced to describe hydrolysis reaction of native starch.

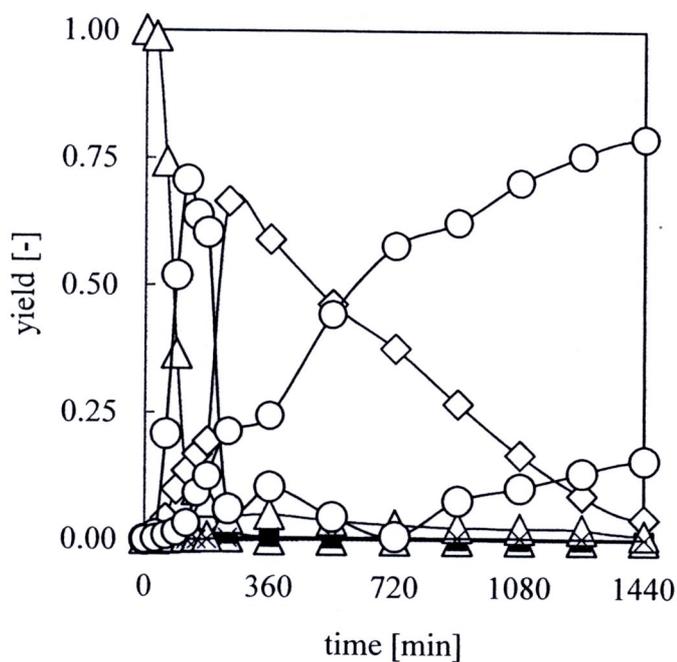


**Figure B.1** Reaction pathway of CMS formation from starch

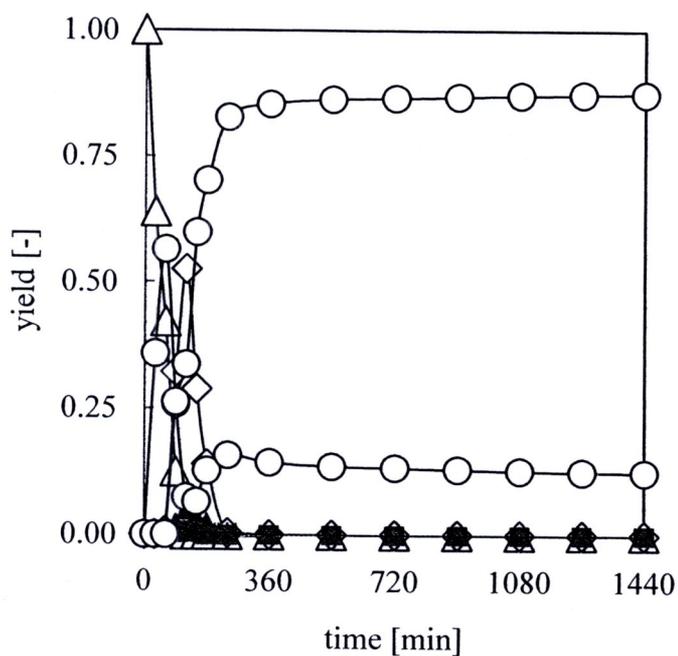
### **B.2.2 Effects of reaction time and temperature on product yield rates**

According to glucose decomposition behavior (in Chapter 7), native corn starch could be inferred that it also resists decomposition at low temperature (under 160°C) as well as glucose decomposition. Therefore, native corn starch experiments were carried out over reaction temperature of 160°C as same as the glucose experiment. In contrast to glucose decomposition (chapter 5), native corn starch was firstly hydrolyzed to form TOC compound before continuously hydrolyzed to produce glucose as shown in Figure B.2.

Although starch was used to substitute of glucose, CMSs generation rate is similar to the CMSs generation rate from glucose experiment. This result demonstrates that corn starch could be immediately hydrolyzed to form intermediate compounds for CMS formation. After 6h of reaction, the reaction was complete which provide constant of CMS formation and TOC compound. Figure B.3 shows that the CMS generation rates obtained from starch decomposition reactions, was strongly affected by temperature when the water the temperature rose. A temperature increases the concentration of free radical intermediates necessary for CMSs formation reaction (hydrolysis, dehydration, polymerization reaction). For this reason, the relative CMSs generation rate in our experiment at 220°C was dramatically higher than the rates in our experiments conducted at lower temperatures as well as the glucose experiment in Chapter 7.



**Figure B.2** Product yield rates from hydrothermal process of native corn starch with initial concentration of 10wt% at temperatures of 180°C, and reaction times from 0 to 1440 min



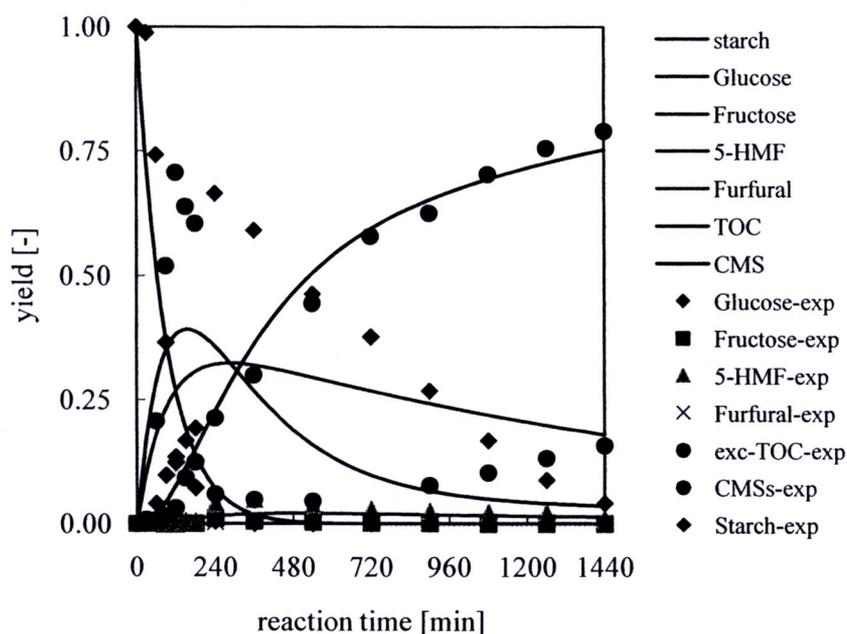
**Figure B.3** Product yield rates from hydrothermal process of native corn starch with initial concentration of 10wt% at temperatures of 220°C, and reaction times from 0 to 1440 min

### B.2.3 First-order kinetic modeling and its deficiency

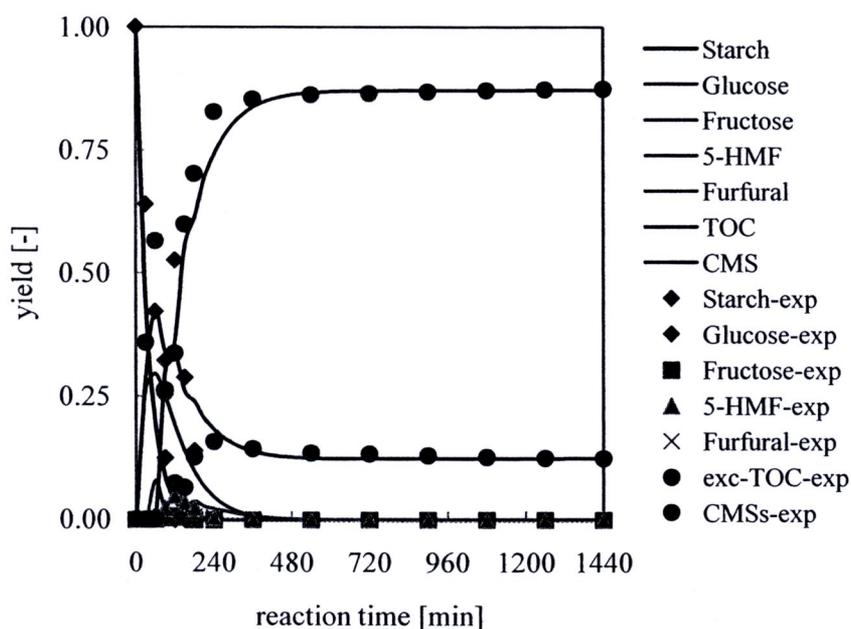
In paralleling to the glucose decomposition reaction, the rate equation and rate constants were proposed and determined. The rate equations, hence, can be written as follows:

$$\begin{aligned}
 r_{starch} &= -(k_{st} + k_{sg})[starch] \\
 r_{glucose} &= k_{sg}[starch] - (k_{gf} + k_{gfu} + k_{gt} + k_{gs})[glucose] \\
 r_{fructose} &= k_{gf}[glucose] - (k_{fs} + k_{ffu} + k_{ft})[fructose] \\
 r_{5-HMF} &= k_{gs}[glucose] + k_{fs}[fructose] - k_{st}[5-HMF] \\
 &\quad - k_{sc}[5-HMF]^{\alpha_{sc}} - k_{sfuc}[5-HMF][furfural][TOC] \\
 &\quad - k_{sfuc}[5-HMF][furfural] - k_{stc}[5-HMF][TOC] \\
 r_{furfural} &= k_{gfu}[glucose] + k_{ffu}[fructose] - (k_{fut} + k_{fuc})[furfural] \\
 &\quad - k_{sfuc}[5-HMF][furfural][TOC] - k_{sfuc}[5-HMF][furfural] \\
 &\quad - k_{fuc}[furfural][TOC] \\
 r_{TOC} &= k_{st}[starch] + k_{gt}[glucose] + k_{ft}[fructose] + k_{st}[5-HMF] + k_{fut}[furfural] \\
 &\quad - k_{tc}[TOC]^{\alpha_{tc}} - k_{tg}[TOC] - k_{sfuc}[5-HMF][furfural][TOC] \\
 &\quad - k_{stc}[5-HMF][TOC] - k_{fuc}[furfural][TOC] \\
 r_{CMSs} &= k_{fuc}[furfural] + k_{sc}[5-HMF]^{\alpha_{sc}} + k_{tc}[TOC]^{\alpha_{tc}} \\
 &\quad + 3k_{sfuc}[5-HMF][furfural][TOC] + 2k_{sfuc}[5-HMF][furfural] \\
 &\quad + 2k_{stc}[5-HMF][TOC] + 2k_{fuc}[furfural][TOC]
 \end{aligned}$$

- where,  $[starch]$  = starch concentration (mol-C/L)
- $[glucose]$  = glucose concentration (mol-C/L),
- $[fructose]$  = fructose concentration (mol-C/L),
- $[5-HMF]$  = 5-HMF concentration (mol-C/L),
- $[furfural]$  = furfural concentration (mol-C/L),
- $[TOC]$  = lumped carbon concentration of the other liquid products (mol-C/L),
- $[CMSs]$  = carbon microspheres concentration (mol-C/L),
- $k_{ij}$  = rate constant ((mol-C/L)<sup>1- $\alpha_{ij}$</sup>  · min<sup>-1</sup>),
- $t$  = reaction time (min).



**Figure B.4** Product yields based on carbon content, hydrothermal process of native corn starch with initial concentration of 10wt% at temperatures of 180°C and reaction time from 0 to 1440 min (symbols, experimental data; lines, model predictions)



**Figure B.5** Product yields based on carbon content, hydrothermal process of native corn starch with initial concentration of 10wt% at temperatures of 220°C and reaction time from 0 to 1440 min (symbols, experimental data; lines, model predictions)

**Table B.1** Reaction and kinetic parameters from hydrothermal process of native corn starch with initial concentration of 10wt% at 220°C

Kinetic parameters	Type of reaction	$k_{ij}$ (mol-C/L)min <sup>-1</sup>	$\alpha$ (-)
$k_{sg}$	hydrolysis	$8.89 \times 10^{-3}$	1
$k_{st}$	hydrolysis	$9.65 \times 10^{-3}$	1
$k_{gf}$	isomerization	0	-
$k_{gfu}$	dehydration	$1.50 \times 10^{-4}$	1
$k_{gt}$	decomposition (many reaction)	$8.70 \times 10^{-4}$	1
$k_{g5}$	dehydration	$1.00 \times 10^{-2}$	1
$k_{f5}$	dehydration	$9.62 \times 10^{-5}$	1
$k_{ffu}$	dehydration	$1.45 \times 10^{-4}$	1
$k_{ft}$	decomposition (many reaction)	$4.26 \times 10^{-4}$	1
$k_{5t}$	decomposition (many reaction)	0	-
$k_{5c}$	polymerization	$1.00 \times 10^{-5}$	1
$k_{fut}$	decomposition (many reaction)	$7.04 \times 10^{-4}$	1
$k_{fuc}$	polymerization	$3.00 \times 10^{-8}$	1
$k_{tc}$	polymerization	$1.00 \times 10^{-5}$	1
$k_g$	total reaction	0	-
$k_{5futc}$	polymerization	$3.52 \times 10^{-2}$	1
$k_{5tc}$	polymerization	$3.21 \times 10^{-2}$	1
$k_{5fuc}$	polymerization	$4.23 \times 10^{-6}$	1
$k_{fuc}$	polymerization	0	-

The iteration procedure and assumption were the same procedure as in Chapter 8 (equation 8.7). Figure B.5 shows the model could not be fitted with the experimental data from reaction at 180°C. These results can be described by the different structure of native starch from glucose. The hydrolysis reaction rate played an important role in the whole reaction. In concluding, it was found that the hydrothermal carbonization of native starch was not the first order reaction at low temperature. In higher temperature, the reaction tended to obey first order model which was discussed as follows.

Nevertheless, the model could be fitted fairly well with the experimental data in the experiment at 220°C. In higher temperature may accelerate reaction which make they follow first-order kinetic model. The kinetic parameters were determined as listed in Table B.4. Although the fitting seems reasonable in general, the limitations of the first-order model have been stated in many publications. This limitation caused from the effect of concentration of reactant played a vital role in the rate of reaction.

## BIOGRAPHY

Mr. Sakhon Ratchahat was born on March 5, 1983 in Sakhon Nakhon, Thailand. He studied in a primary and secondary education at Sakhon Nakhon province. In 2007, he received the Bachelor Degree of Science (Chemical Technology) from Chulalongkorn University. After that, he gained admission to Graduate School of Chulalongkorn University and he graduated in 2010 with the thesis entitled “Synthesis of carbon microspheres by hydrothermal process of native starch”.



