CHAPTER VII

CARBON MICROSPHERES FORMATION FROM GLUCOSE

7.1 Introduction

Synthesis of carbon microspheres (CMSs) by hydrothermal process of native starch, native corn starch was employed as a model compound of native starch (described in Chapter 5). In order to deeply understand mechanisms of CMSs formation from native starch, other carbohydrates [i.e. glucose (GC), amylopectin (AP), amylose (AL), and modified starch (HICAP®100)] were also used in this work to compare reaction rates, morphology and particle size distributions of as-prepared CMS particles. In this two main study was focused and discussed in details. Firstly, effects of reaction time and reaction temperature on the CMS morphology and particle size distribution were revealed by SEM and laser scattering technique, respectively. Second step concentrated on kinetic of hydrothermal reaction of glucose. In generally, carbohydrates in hydrothermal process are firstly hydrolyzed to produce glucose before glucose product is subsequently dehydrated to form many compounds: 5-HMF, furan compounds, and small acid [31]. Finally, these intermediates are then polymerized to form CMS particles. These intermediates are mainly glucose, fructose, 5-hydroxymethylfurfural (5-HMF), furfural, and total organic carbon (TOC, excluding glucose, fructose, 5-HMF, and furfural) [33]. Nevertheless, these intermediate compounds are not yet quantitatively identified. Therefore, this study attempted to identify these compounds to reveal reaction rate and reaction pathway. Moreover, to confirm that native corn starch firstly hydrolyzed to yield glucose and subsequently followed the same reaction pathway, this chapter is, therefore, contributed to investigate CMS formation from glucose in hydrothermal process.

The compound 5-hydroxymethylfurfural (5-HMF) is thought to be an intermediate for the formation of carbon microspheres in hydrothermal of glucose [31]. It is the known product of the acid-catalyzed dehydration of the glucose, which is the one of the main components of starch [33]. Due to its unsaturated and low-

Table 6.1 Compositions of native starch

Types of native starch	amylopectin (wt%)	amylose(wt%)
corn	73	27
wheat	77	23
tapioca	82	18
rice	83	17

6.2 Experimental procedures

In brief, pure amylopectin or pure amylose was suspended in de-mineralized water and subsequently filled into the autoclave reactor. The autoclave reactor was kept in an oven at reaction temperature (180, 220°C). After reached desired reaction time, the reactor was removed from an oven to cool down naturally. The liquid product was collected by syringe sampling with 0.45 μm polyvinylidene fluoride (PVDF) membrane. The product was filtered with 0.45 μm PVDF membrane and/or was centrifuged to obtain solid product (CMSs).

The glucose and fructose in the liquid product were quantified by high-performance liquid chromatography (HPLC) using a sugar KS-802 column (Shimadzu LC-3A, LDC 4100). The 5-HMF and furfural in the liquid product were quantified by high-performance liquid chromatography (HPLC) using an RSpak DE-413 L column (Shodex). The liquid product was analyzed by a total organic carbon analyzer or TOC analyzer to check the amounts of carbon in the liquid product (non-purgeable organic carbon or NPOC) and in the dissolved gas product (inorganic carbon or IC).

A size distribution of CMSs was determined by laser particle size distribution analyzer (MALVERN, Mastersizer 2000). Mean size and monodisperse of CMSs were determined by geometric mean and (d_g) geometric coefficient of variance (CV_g), respectively. Morphology of CMSs was imaged by scanning electron microscopy (JEOL, JSM-5410LV).

6.3 Experimental conditions

The amylopectin or amylose suspension was used as a carbon precursor to synthesize carbon microspheres by hydrothermal process. The experimental conditions were shown in Table 6.2. However, carbonization process was not carried out in this experiment. From the previous section, they showed that the carbonization process made the porous CMS structure. Therefore, the same porous structure might be obtained from the carbonization process. The carbonization process was be neglected.

Table 6.2 Experimental conditions for the amylopectin and amylose experiments

Temperature (°C)	180 and 220
Pressure	autogenously
Pure amylopectin or amylose concentration (wt%)	10
Fill rate in reactor (%v/v)	80
Reaction time (min)	30, 60, 120, 150, 180, 240, 360, 540, 720, 900, 1080, 1260 and 1440

6.4 Results and discussion

6.4.1 Effects of hydrothermal reaction temperature of native corn starch, amylopectin and amylose on their CMS yield rates and CMS morphology

Hydrothermal process of native corn starch, amylopectin and amylose were carried out to reveal their CMS yield rates and CMS morphology. To investigate their CMS yield rates, the hydrolyzed rates (glucose yield rates) were determined to reveal their effects on CMS yield rates and CMS morphology. At 180°C of hydrothermal process, the hydrolyzed rates of native corn starch, amylopectin and amylose were shown in Figure 6.2. The hydrolyzed rates (glucose yield rates) of various types of starch demonstrated the ability to be hydrolyzed of the starch which strongly affected on CMS yield rates. Amylopectin is a one of components of native corn starch (~ 73wt%). The amylopectin have a $\alpha(1\rightarrow4)$ and $\alpha(1\rightarrow6)$ glycosidic bond structure which can be easily hydrolyzed by water at moderate reaction temperature. Therefore, the amylopectin can yield glucose in the short reaction time as shown in Figure 6.2 (symbol : ■). On the other hand, amylose have a $\alpha(1\rightarrow4)$ glycosidic bond structure which seem to cellulose structure [63]. The amylose therefore was difficult to be hydrolyzed than amylopectin [64]. The hydrolyzed rate of amylose at 180°C was lower than others as shown in Figure 6.2 (symbol : ▲). For the controlled carbon precursor, native corn starch was a mixture of 73wt% of amylopectin and 27wt% of amylose which were hydrolyzed faster than pure amylose but lower than pure amylopectin as shown in Figure 6.2(symbol : ◆). At 220°C, the hydrolyzed rates of native corn starch, amylopection and amylose also were the same patterns as the reaction temperature at 180°C (as shown in Figure 6.3). In the beginning of reaction, the glucose yield rate of amylopectin was faster than others because its structure was easy to be hydrolyzed by water. Nevertheless, the glucose yield rate of amylopectin was then decreased than others when the reaction time increased over 2 hours.

According to the glucose yield rates of various types of starch, the hydrolyzed rates which strongly also affected on the CMS yield rates. The CMS yield rates of various types of starch were shown in Figure 6.5. The CMS yield rate of hydrothermal of amylopectin was fatser than others because its hydrolyzed rate was also faster than others. At 220°C, this behavior can be still observed as shown Figure 6.5.
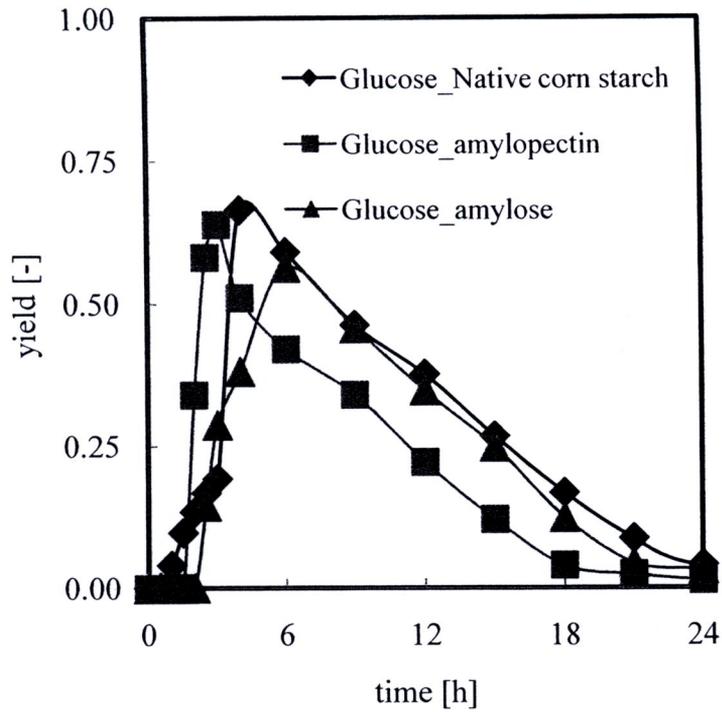
Figure 6.2 Glucose yield rates of hydrothermal process of native corn starch, amylopectin and amylose with initial concentration of 10wt% at 180°C
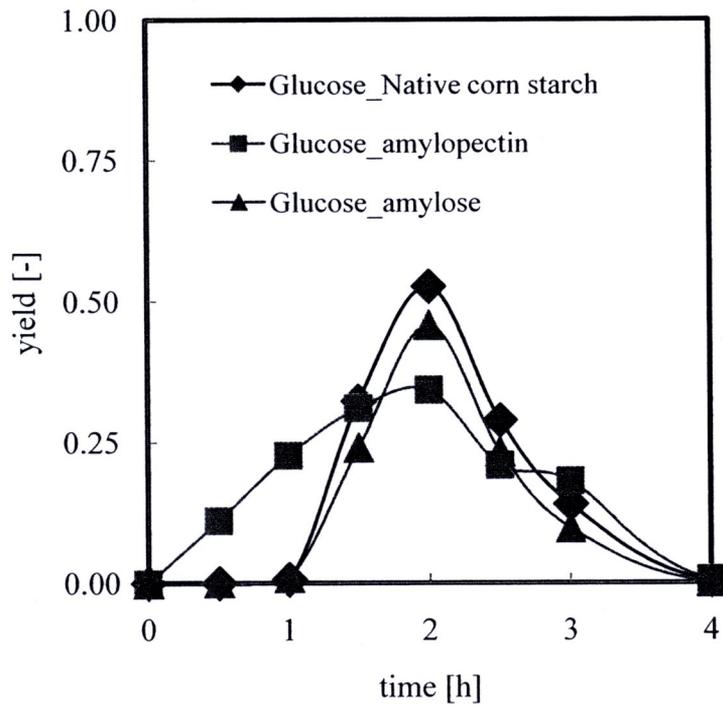

Figure 6.3 Glucose yield rates of hydrothermal process of native corn starch, amylopectin and amylose with initial concentration of 10wt% at 220°C
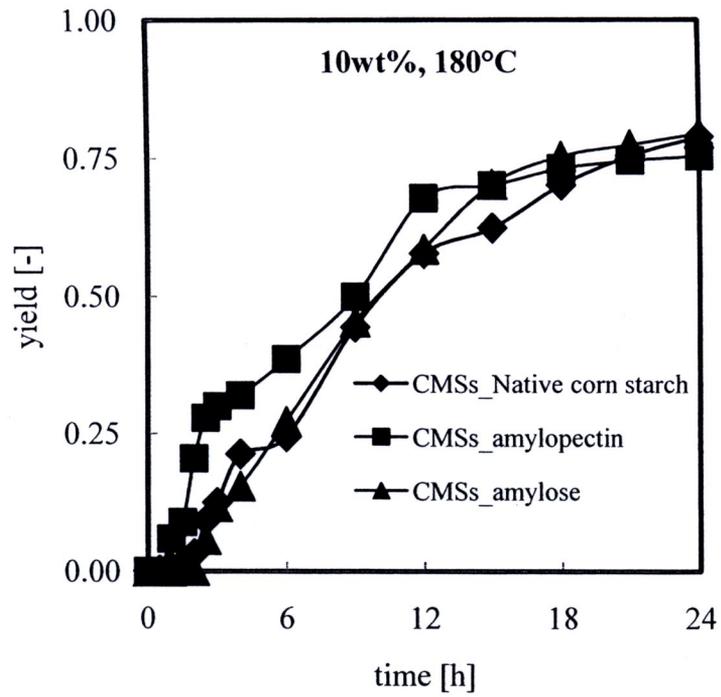
Figure 6.4 The yield rates of CMS formation from hydrothermal process of native corn starch, amylopectin and amylose with initial concentration of 10wt% at 180°C
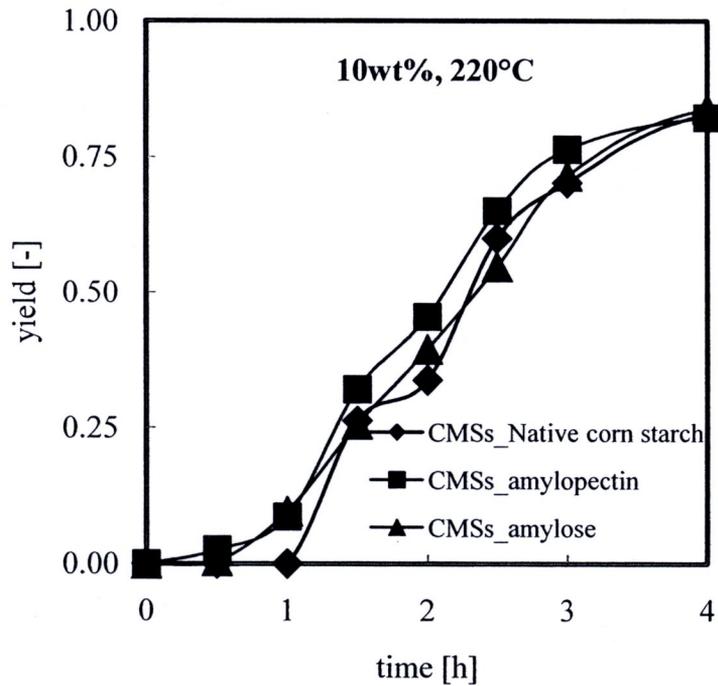

Figure 6.5 The yield rates of CMS formation from hydrothermal process of native corn starch, amylopectin and amylose with initial concentration of 10wt% at 220°C

6.4.2 Effects of reaction time on CMS morphology and particle size distributions from hydrothermal process of amylopectin and amylose

Figure 6.6(a)-(f) shows SEM images of as-prepared CMSs from hydrothermal process of amylopectin with initial concentration of 10wt% at 180°C for various points of reaction time. The CMS particles could be observed after 3 hours as same as the hydrothermal process of native corn starch in Chapter 5.
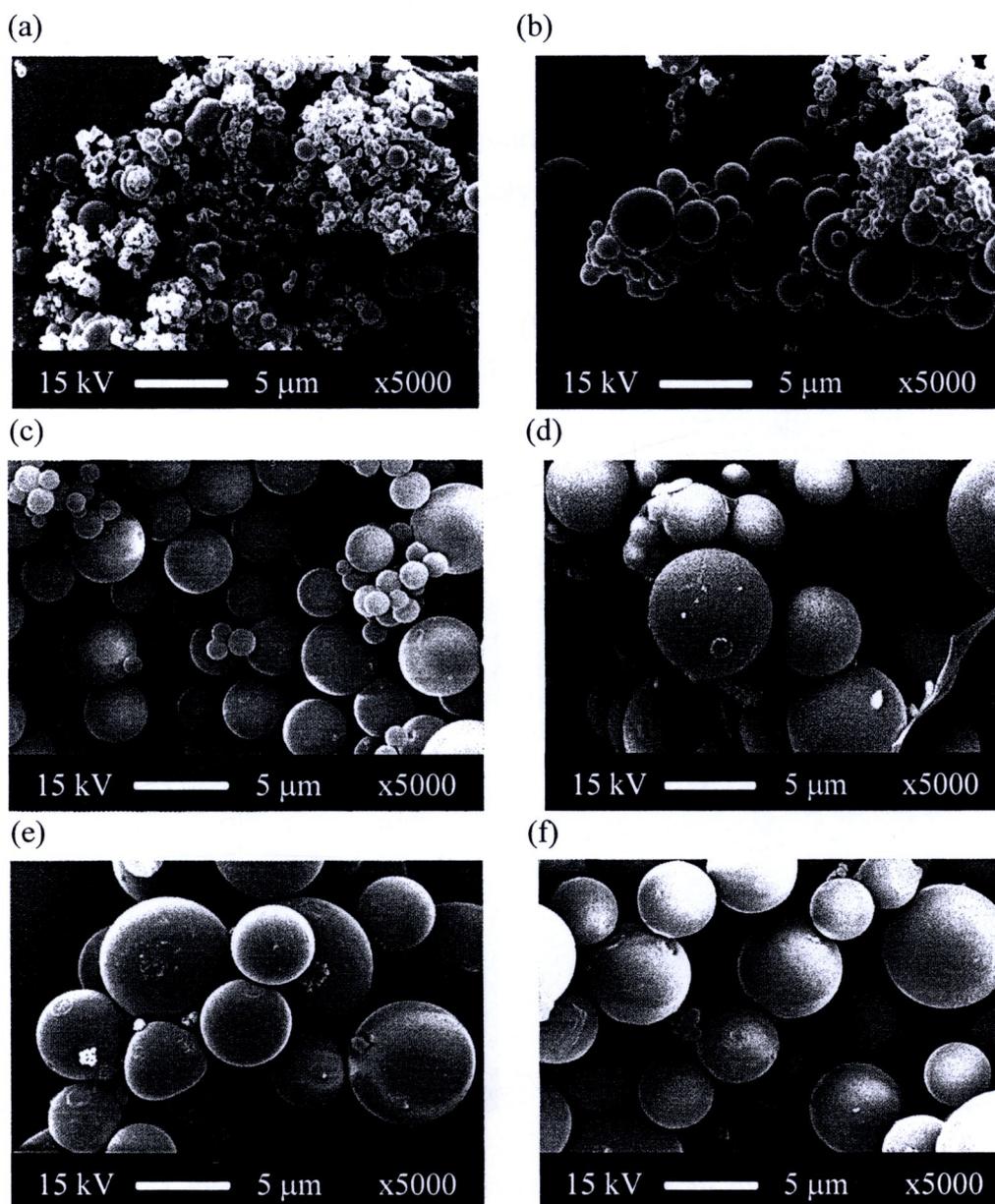
(a)

(b)

(c)

(d)

(e)

(f)

Figure 6.6 SEM micrographs of synthesized CMSs from hydrothermal process of amylopectin with initial concentration of 10wt% at 180°C for reaction time of (a) 3h, (b) 4h, (c) 6h, (d) 9h, (e) 12h, and (f) 24h, respectively

At 180°C, the morphology of CMSs was irregular shape at short reaction time subsequently became uniform and larger size as reaction time increased. Although the CMS size increased with the reaction time increased, the particle size became constant in size in the long reaction time (see Figure 6.6c) since the intermediates was continuously used to form solid product until nearly complete reaction [65]. This results completely agreed with the results from native corn starch experiment in Chapter 5. For high reaction temperature (at 220°C), the as-prepared CMSs were likely to small primary particles, but the aggregated behavior was still observed as same as hydrothermal process of native corn starch in Chapter 5. When it comes to obtained particle size from SEM after 9 hours, the CMS particle were likely to small primary particles since the particles slightly shrank to more dense particles in the longer reaction time.
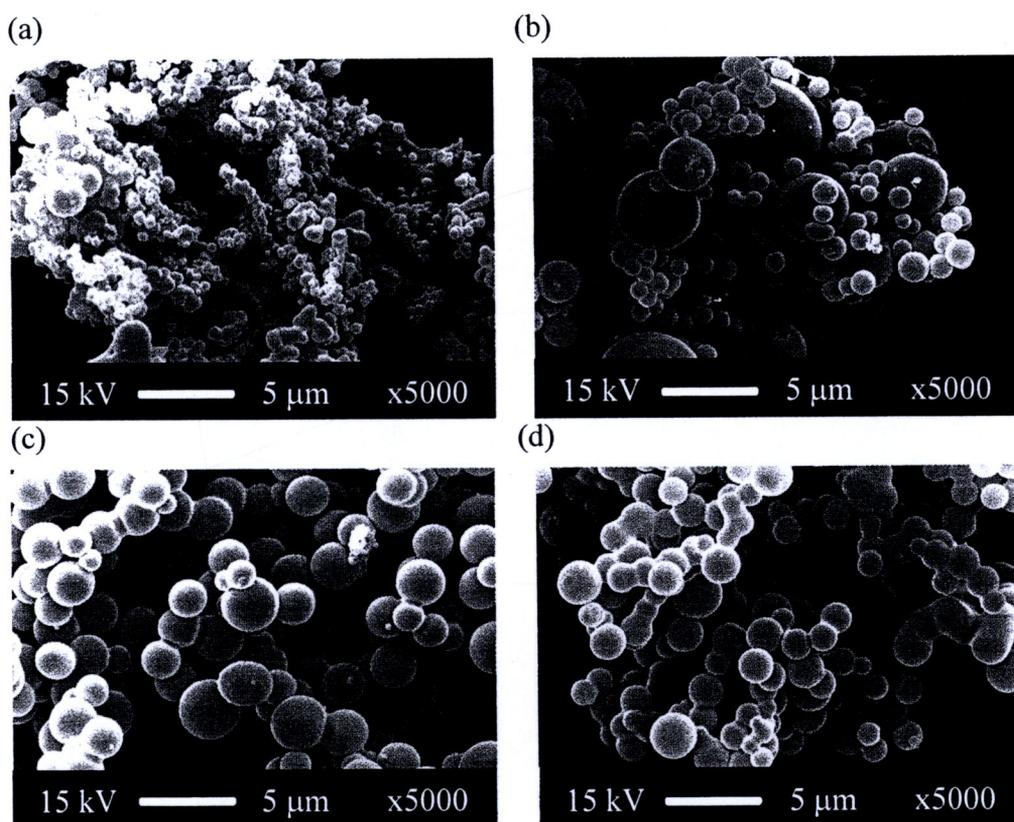
(a)   (b)

Figure 6.7 SEM micrographs of synthesized CMSs from hydrothermal process of amylopectin with initial concentration of 10wt% at 220°C for reaction time of (a) 1 h 30 min, (b) 3h, (c) 6h, and (d) 9h, respectively

Unexpectedly, the solid product from hydrothermal process of amylose at short reaction time (3 hours) and low reaction temperature (180°C), the morphology

was irregular shape as shown in Figure 6.8(a). These results were different from the result of hydrothermal process of glucose, native corn starch, and amylopectin. This behavior was described by its crystalline structure of amylose. The linear chemical structure of amylose is likely a structure of cellulose which is difficult to be hydrolyzed [25]. Therefore, the solid product from short reaction time could be a mixture of linear polymer chain.
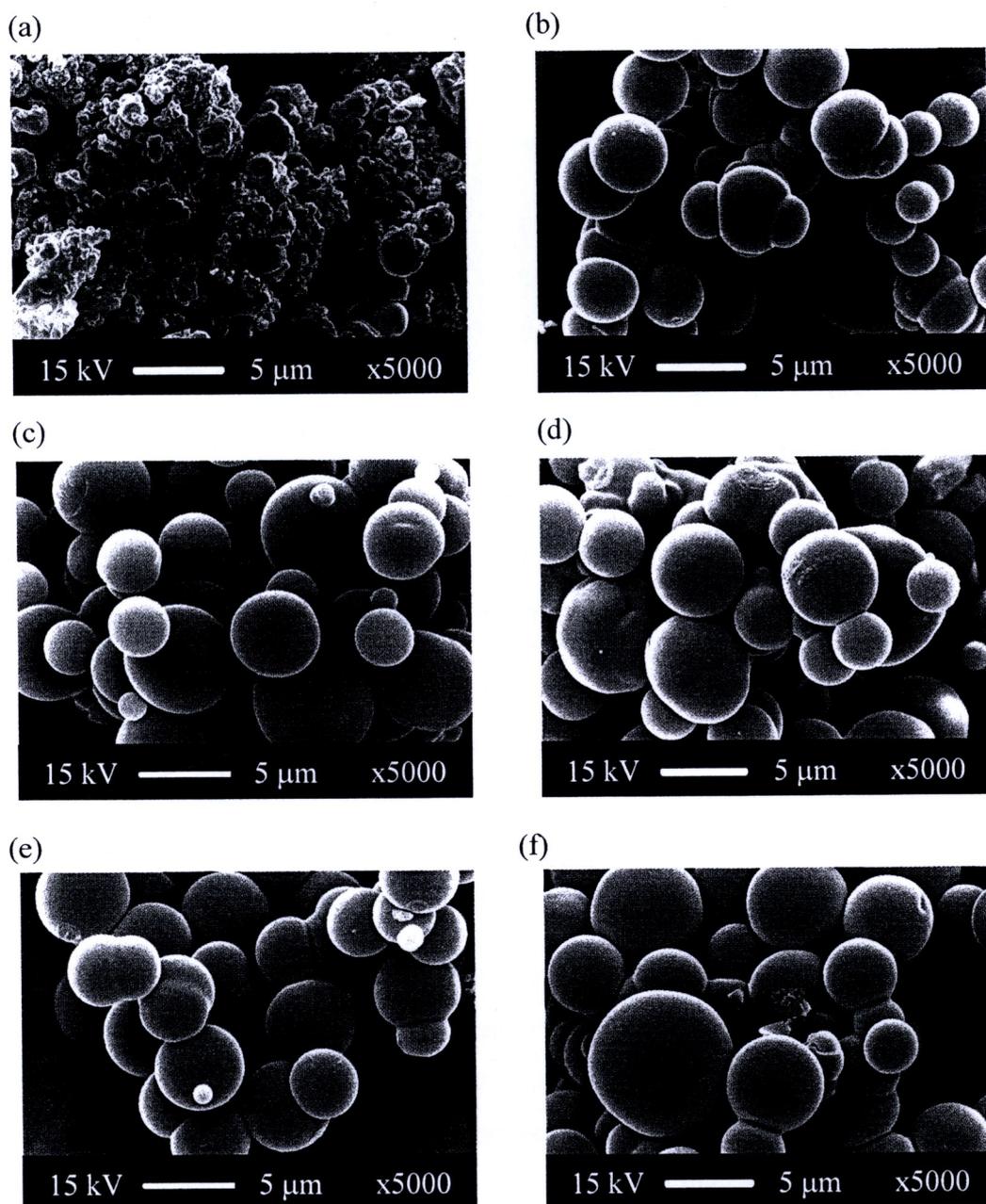
(a)

(b)

(c)

(d)

(e)

(f)

Figure 6.8 SEM micrographs of synthesized CMSs from hydrothermal process of amylose with initial concentration of 10wt% at 180°C for reaction time of (a) 3h, (b) 4h, (c) 6h, (d) 9h, (e) 12h, and (f) 24h, respectively
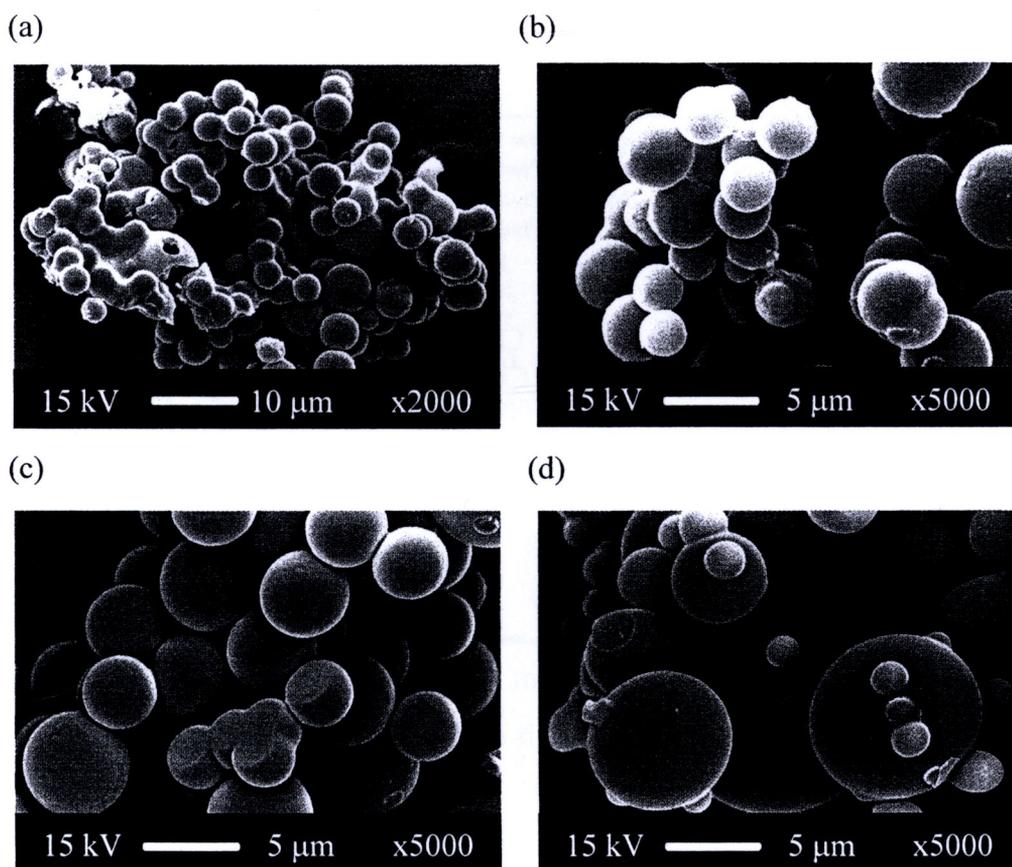
(a) (b)

(c) (d)

Figure 6.9 SEM micrographs of synthesized CMSs from hydrothermal process of amylose with initial concentration of 10wt% at 220°C for reaction time of (a) 3h, (b) 4h, (c) 6h, and (d) 9h, respectively

Nevertheless, the CMS particles became large size and aggregated together as shown in Figure 6.9(b)-(d). This result caused from the carbon microspheres growth when the reaction time increased. The morphology of CMSs from amylose was fusible particles.

At high reaction temperature (at 220°C), the CMS particles were small size than the CMS particles from the hydrothermal process at 180°C. However, the CMS particles also became large size when the reaction time increased. This ressult was absolutely different from the other carbon precursor such as glucose, native corn starch, and amylopectin. The particles was not aggregated niether high temperature or long reaction time. In concluding, we can infer this result caused from their chemical structure of amylose which was difficult to be hydrolized by water.
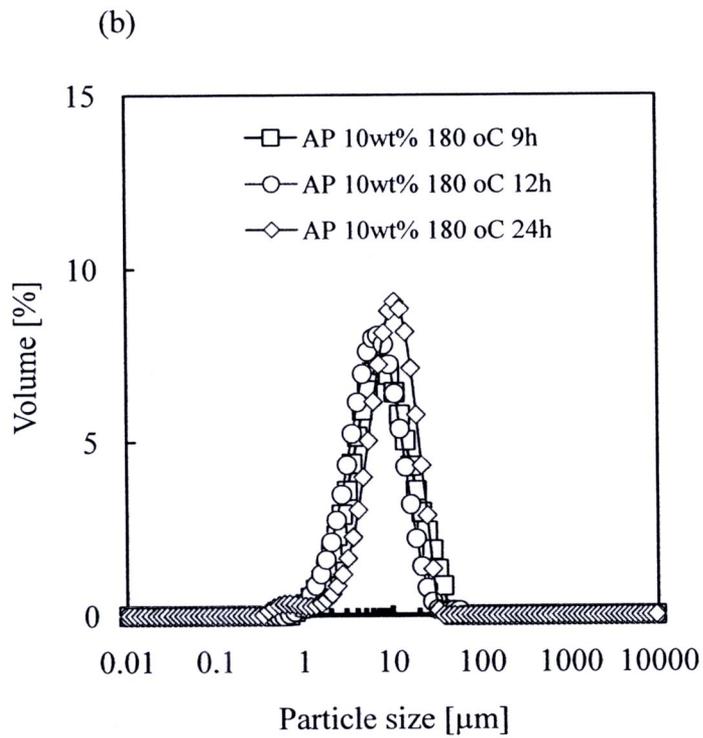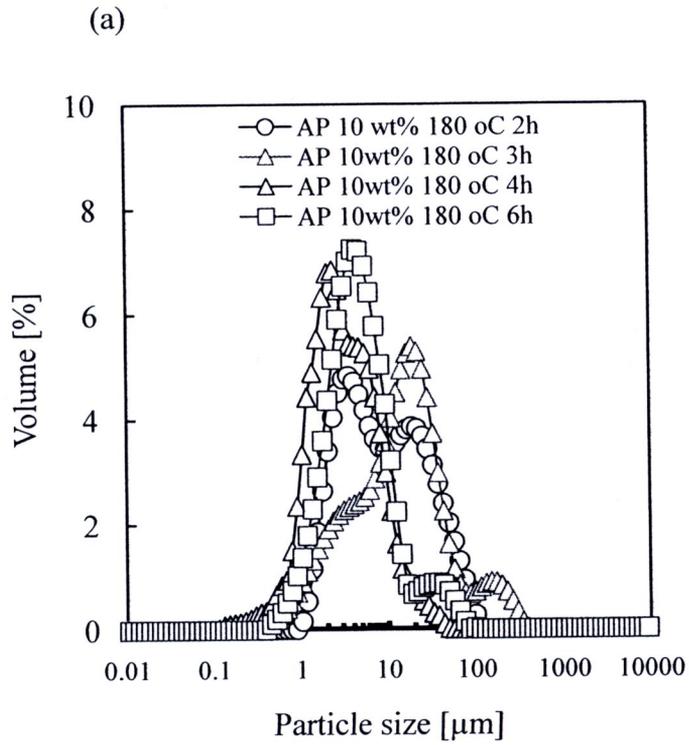
(a)

(b)

Figure 6.10 Particle size distributions of sythesized CMSs from hydrothermal process of amylopectin with initial concentration of 10wt% at 180 °C in each points of reaction time
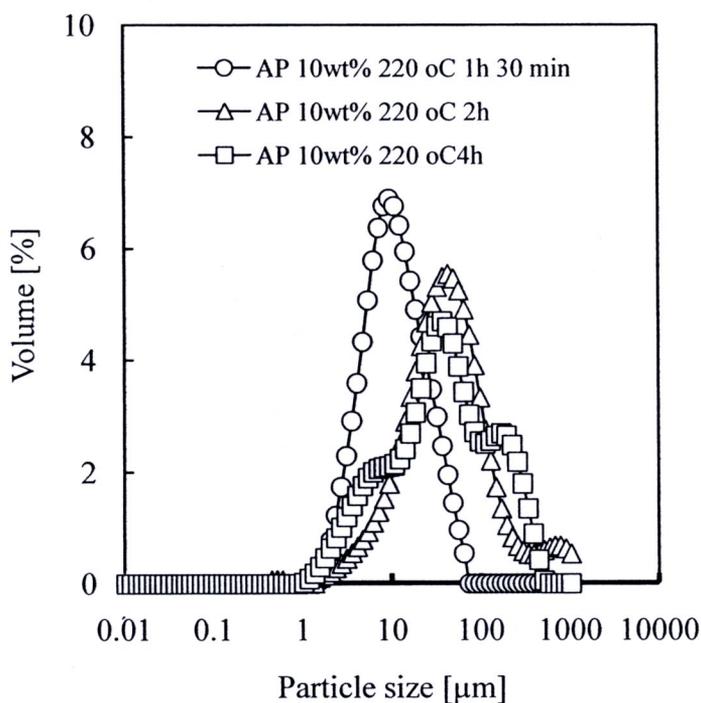
Figure 6.11 Particle size distributions of sythesized CMSs from hydrothermal process of amylopectin with initial concentration of 10wt% at 220 °C in each points of reaction time

Particle size distributions of obtained solid products were determined as shown in Figure 6.8-6.9. In the experiment at low temperature, the solid particles had a wide size distribution which agreed with the obtained size from SEM image. Nevertheless, the particle size distribution became narrow when the reaction time increased as shown in Figure 6.8-6.9.
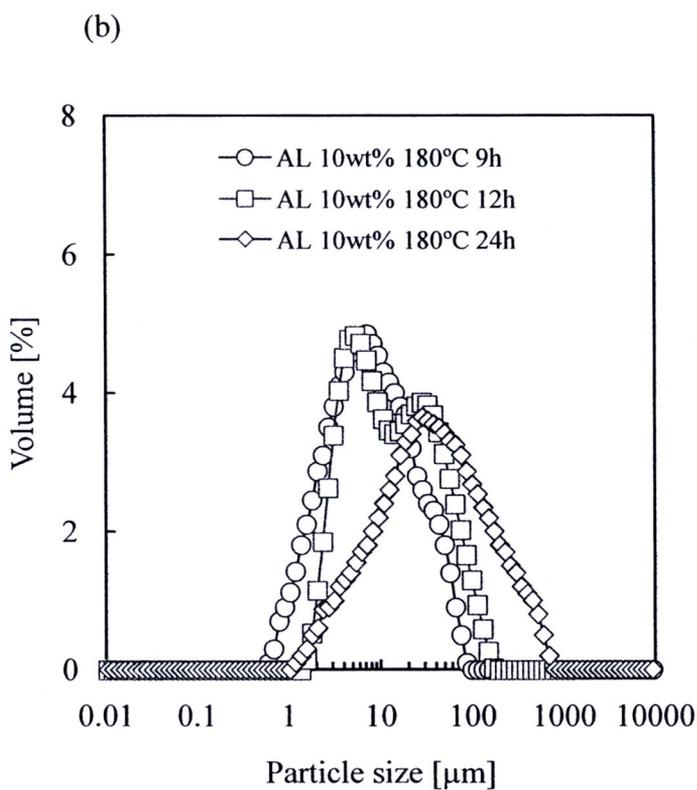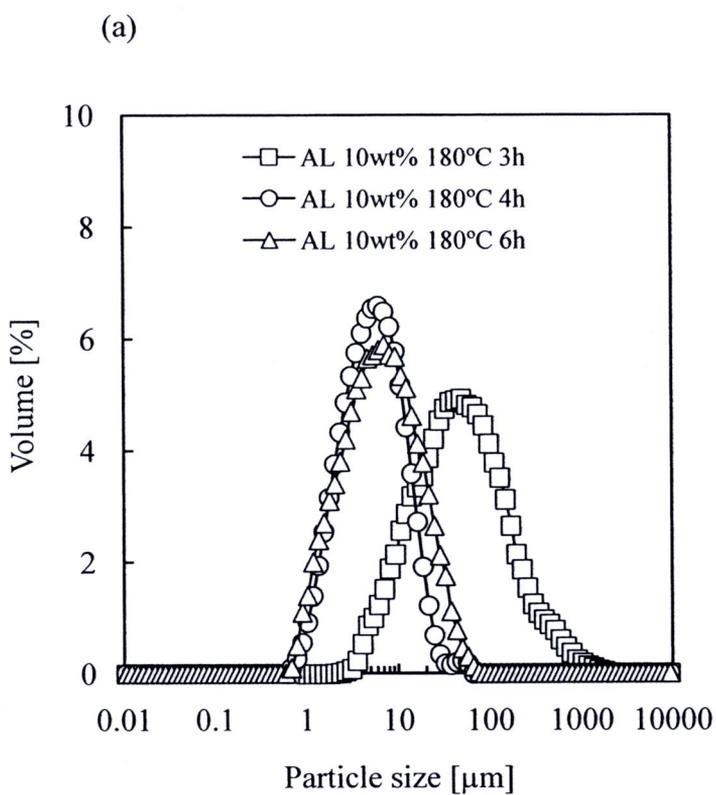
(a)

(b)

Figure 6.12 Particle size distributions of sythesized CMSs from hydrothermal process of amylose with initial concentration of 10wt% at 180 °C in each points of reaction time
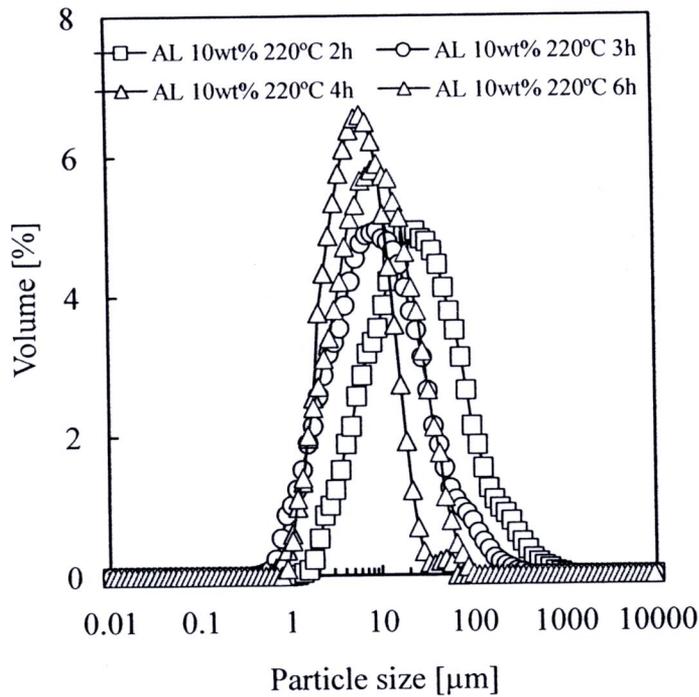
Figure 6.13 Particle size distributions of sythesized CMSs from hydrothermal process of amylose with initial concentration of 10wt% at 220 °C in each points of reaction time

Particle size distributions of the obtained CMS particles from hydrothermal process of amylose was shown in Figure 6.10-6.11 Morphology, geometric mean particle size (d_g), geometric coefficient of variance of size distribution (CV_g), and yield (based on carbon yield) of carbon microspheres from hydrothermal process of amylopectin and amylose with initial concentration of 10wt% at 180°C and 220°C in each points of reaction time was listed in Table 6.3-6.6.

Table 6.3 Summary of morphology, geometric mean particle size (d_g), geometric coefficient of variance of size distribution (CV_g), and yield (based on carbon yield) of carbon microspheres from hydrothermal process of amylopectin with initial concentration of 10wt% at 180°C in each points of reaction time

Samples	Morphology	d_g [μm]	CV_g [-]	yield [-]
AP 10 wt%, 180°C, 2h	irregular	8.67	74.02	20.5
AP 10 wt%, 180°C, 3h	aggregated spherical	11.67	1730.10	30.0
AP 10 wt%, 180°C, 4h	spherical	3.18	23.54	32.0
AP 10 wt%, 180°C, 6h	spherical	4.70	19.60	38.6
AP 10 wt%, 180°C, 9h	spherical	7.33	9.56	50.0
AP 10 wt%, 180°C, 12h	spherical	6.22	7.28	67.9
AP 10 wt%, 180°C, 24h	spherical	8.77	8.00	75.5

From Table 6.3, the particle had an irregular shape in a short reaction time and became aggregated spherical morphology when the reaction time increased.

Table 6.4 Summary of morphology, geometric mean particle size (d_g), geometric coefficient of variance of size distribution (CV_g), and yield (based on carbon yield) of carbon microspheres from hydrothermal process of amylopectin with initial concentration of 10wt% at 220°C in each points of reaction time

Samples	Morphology	d_g [μm]	CV [-]	yield [-]
AP 10 wt%, 220°C, 1h 30 min	irregular	10.66	10.55	16.4
AP 10 wt%, 220°C, 2h	aggregated spherical	41.40	283.54	45.4
AP 10 wt%, 220°C, 4h	aggregated spherical	34.16	1108.78	82.2

Table 6.5 Summary of morphology, geometric mean particle size (d_g), geometric coefficient of variance of size distribution (CV_g), and yield (based on carbon yield) of carbon microspheres from hydrothermal process of amylose with initial concentration of 10wt% at 180°C in each points of reaction time

Samples	Morphology	d_g [μm]	CV [-]	yield [-]
AL 10 wt%, 180°C, 3h	aggregated spherical	59.55	277.82	11.7
AL 10 wt%, 180°C, 4h	spherical	5.21	10.71	15.5
AL 10 wt%, 180°C, 6h	spherical	7.42	40.68	27.3
AL 10 wt%, 180°C, 9h	spherical	7.64	71.38	45.4
AL 10 wt%, 180°C, 12h	spherical	13.13	74.12	58.7
AL 10 wt%, 180°C, 24h	spherical	25.92	1310.52	79.7

Table 6.6 Summary of morphology, geometric mean particle size (d_g), geometric coefficient of variance of size distribution (CV_g), and yield (based on carbon yield) of carbon microspheres from hydrothermal process of amylose with initial concentration of 10wt% at 220°C in each points of reaction time

Samples	Morphology	d_g [μm]	CV [-]	yield [-]
AL 10 wt%, 220°C, 2h	irregular	28.66	255.89	39.5
AL 10 wt%, 220°C, 3h	aggregated spherical	10.30	234.56	71.5
AL 10 wt%, 220°C, 4h	spherical	5.17	9.24	83.9
AL 10 wt%, 220°C, 6h	aggregated spherical	10.05	42.41	86.6

6.5 Conclusions

In the hydrothermal process of amylopectin, hydrolyzed rate of amylopectin to yield glucose was faster than those of native corn starch and amylose. The rapid hydrolyzed rate of amylopectin also gave fast CMS yield rate. Hydrolyzed rate of amylose was lower than others because amylose had 1,4 glycosidic bond structure. This structure is likely to the structure of cellulose which was difficult to be hydrolyzed by water. Therefore, the hydrolyzed rate of amylose were slow than others

consequently the CMS yield rate from amylose also were slow. The CMS morphology from hydrothermal process of amylopectin seemed to the CMS morphology from hydrothermal process of native corn starch. They had spherical shape and primary particle size about 5-8 μm. In concluding, the obtained CMS particles from hydrothermal process of amylopectin were similar in size to the obtained CMS particles from native corn starch. These findings provided the information about reaction pathway of native starch. Amylose shows resistance behavior to be hydrolyzed in hydrothermal process. The CMS morphology from hydrothermal process of amylose was large size than others because they gradually grew from the continuous intermediates in the system. This behavior caused from the structure of amylose which was difficult to be hydrolyzed.