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 lowaromaticity nature, 5-HMF is likely to polymerize to form carbon microsphere particles in hydrothermal process [32]. In the previous work, 5-HMF and carbon microspheres are usually detected at the higher yields in the subcritical condition than in the supercritical condition, due to the catalytic effect of the high ionic product of the subcritical water [66].

High temperature and long reaction time are needed for the significant glucose decomposition and carbon microspheres polymerization to observe [33]. The carbon microspheres polymerization pathway is found to be strongly dependent on temperature and reaction time. In this chapter, the hydrothermal process of pure glucose at high initial concentration of 10wt% under hot compressed water was described and discussed. This high concentration was used here so that the carbon microspheres formation could be clearly revealed.

7.2 Experimental procedures

Full details of the batch reactor (Teflon-lined autoclave) and the experimental procedures used in this experiment have been described in Chapter 4. In brief, glucose was dissolved in de-mineralized water and subsequently filled into the autoclave. The autoclave was kept in an oven at reaction temperature (180, 220°C). After reached reaction time, the autoclave reactor was removed from an oven to cool down naturally. The liquid product was collected by syringe sampling with 0.45 μm polyvinylidene fluoride membranes (PVDF). The product was filtered with 0.45 μm PVDF membrane and/or was centrifuged to obtain solid product (CMS particles). The gas product was neglected in all experiments because of low gas product formation in this subcritical water (180-220°C).

The sugar, glucose remaining and fructose in the liquid product, were quantified by high-performance liquid chromatography (HPLC) using a Lichrocart amino-NH_2 250x4 mm ID, packing 5 μm (Shimadzu LC-3A, LDC 4100) with a condition; 89% acetonitrile and 11% H_2O, 1.5 mL/min, 25°C of detector 20 μL sampling. 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 Analyzer or TOC analyzer (TOC-VCPH, Shimadzu) 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). The TOC (TC-IC) was determined using 680°C catalytically-aided combustion oxidation/non-dispersive infrared detection (NDIR).

A size distribution of CMSs was determined by laser particle size distribution analyzer (MALVERN, Mastersizer 2000). Mean particle size and monodispersity of CMSs were determined by geometric mean particle size (d_g) and geometric coefficient of variance (CV_g), respectively. Morphology of CMSs was determined by scanning electron microscopy (JEOL, JSM-5410LV). Functional group and chemical structure were characterized by Fourier Transform Infrared Spectroscopy (PerkinElmer). Elemental analysis of CMSs was analyzed by CHNS/O analyzer (Perkin Elmer PE2400 Series II). Gaseous products freed by pyrolysis in high-purity oxygen and were chromatographically separated by frontal analysis with quantitatively detected by thermal conductivity detector. Core/shell structure of CMSs was revealed by transmission electron microscopy (JEOL, JEM-2100). For FT-IR and elemental analysis results have been separately discussed in chapter 8.

7.3 Experimental conditions

The glucose aqueous solution was used as a carbon precursor in the experiments. The experimental conditions are shown in Table 7.1.

Table 7.1 Experimental conditions for hydrothermal process of glucose

Temperature (°C)	180 and 220
Pressure	autogenously
Glucose initial concentration (wt%)	10
Fill rate in reactor (%v/v)	80
Reaction time (min)	0, 30, 60, 120, 150, 180, 240, 360, 540, 720, 900, 1080, 1260 and 1440

7.4 Results and discussion

7.4.1 Effects of reaction time and temperature on CMS morphology and particle size distributions

The obtained product was separately characterized (solid and liquid product) and yield was then calculated. The yield was calculated based on the carbon content in glucose reactant (see equation (7.1)):

$$\text{product yield}(-)=\frac{\text{carbon content in product}(\text{mol - C/L})}{\text{carbon content in initial glucose }(\text{mol - C/L})} \tag{7.1}$$

Carbon microspheres, solid product, were characterized to reveal morphology by SEM. Figure 7.1(a)-(d) shows typical SEM micrographs of as-prepared CMSs from glucose hydrothermal at 180°C revealed their spherical shape. By varying reaction time, the particles were observed after 4 hours of reaction time with the geometric mean size of 0.12 μm (see Figure 7.1(a) and Table 7.2, respectively). The CMS particles became larger in size as the reaction time increased to 6 hours since the soluble carbon compounds in liquid phase were more converted to solid particles as shown in Figure 7.1(b) [45]. This result can be inferred from decreasing of TOC compounds during the progress of reaction [67]. Due to its decreasing, the consequence increased in solid yield. Nonetheless, at the reaction time of 9 hours, it was found that CMS particles began to aggregate with their neighboring. This fusible behavior was described by nucleation growth mechanism which was nearly completed [38]. Therefore, the aggregation mechanism plays an important role in the reaction. During the particles collision, the reactive shell of particles was then partially polymerized to form a solid bridge [68]. In addition, solid bridges were observed to be formed at the contact points of the adjacent CMS particles because of the collision and the deposition of the carbonaceous nuclei as shown in Figure 7.1(c) (details of this mechanism have been separately discussed in Chapter 8). Clearly observed in effects of reaction time on aggregation of the particles after 12 hours, solid product was finally fused to form large irregular shapes as shown in Figure 7.1(d).

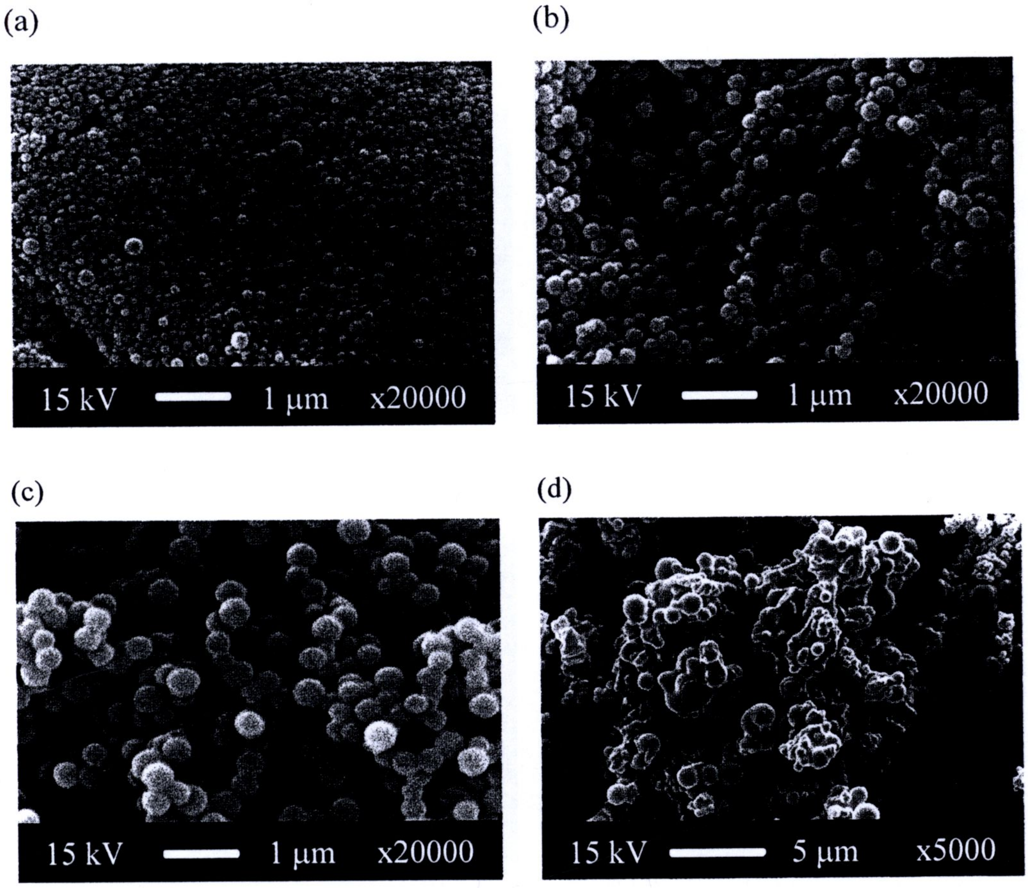

Figure 7.1 SEM micrographs of synthesized CMSs from hydrothermal process of glucose with initial concentration of 10wt% at 180°C for reaction time of (a) 4h, (b) 6h, and (c) 12h, respectively

Increasing in temperature to 220°C, CMS particles were firstly observed in very short reaction time (1 hour and 30 minutes) with the smallest primary particle size of about 0.15 μm as shown in Figure 7.2(a). The solid product yield was dramatically increased when the reaction time increased after 30 minutes (from 1 hour and 30 minutes to 2 hours) as shown in Table 7.3. Similarly to carbon microsphere formation behaviors with the reaction temoerature at 180°C, the particle size of carbon microspheres became larger when reaction time increased from 1 hour and 30 minutes to 2 hours (see Figure 7.2(b)). The growth mechanism was described by dramatic decreasing in TOC compounds to be converted to solid products. In other word, intermediates gradually polymerized on surface of carbon microspheres when reaction time increased [69]. The primary particle of carbon microspheres after 2 hours of reactin time was about 0.5 μm.

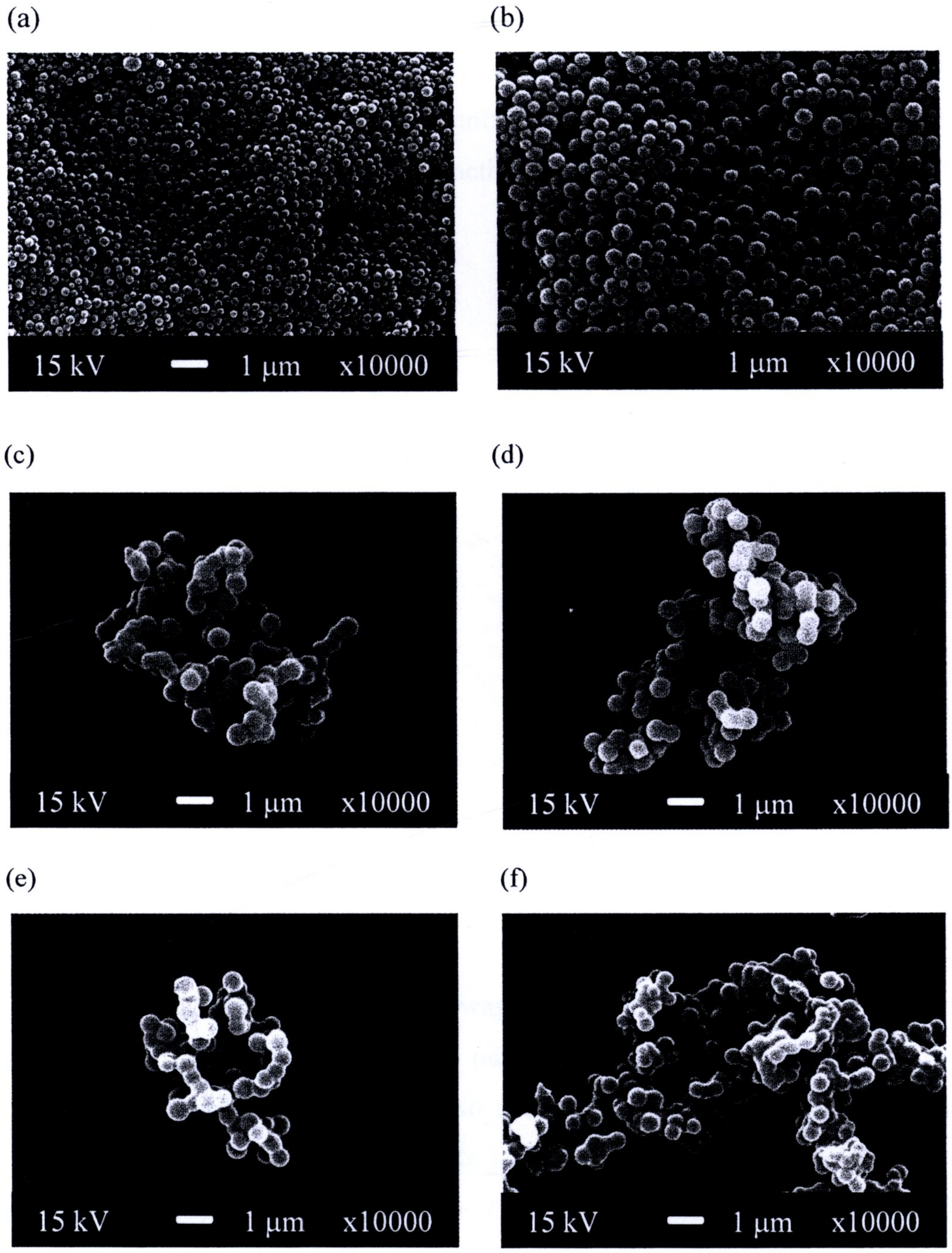

Figure 7.2 SEM micrographs of synthesized CMSs from hydrothermal process of glucose with initial concentration of 10wt% at 220°C for reaction time of (a) 1h 30 min, (b) 2h, (c) 3h, (d) 4h, (e) 6h, (f) 9h, and (g) 12h, respectively

The dramatic decrease of glucose in the system was resulted from high temperature condition since this condition has a high energy to accelerate the reaction [70]. Fusible particles was observed after 3 hours of reaction time which was still fused structure until 9 hours as shown in Figure 7.2(c)-(d). However, this fused structure was more irregular shape (see Figure 7.2(f)). Simulatenousely, yields of solid proucts dramatically increased when reaction time increased as shown in Table 7.3. From these findings, the small and uniform particle size and high yield were obtained by operating condition of short reaction time and high temperature.

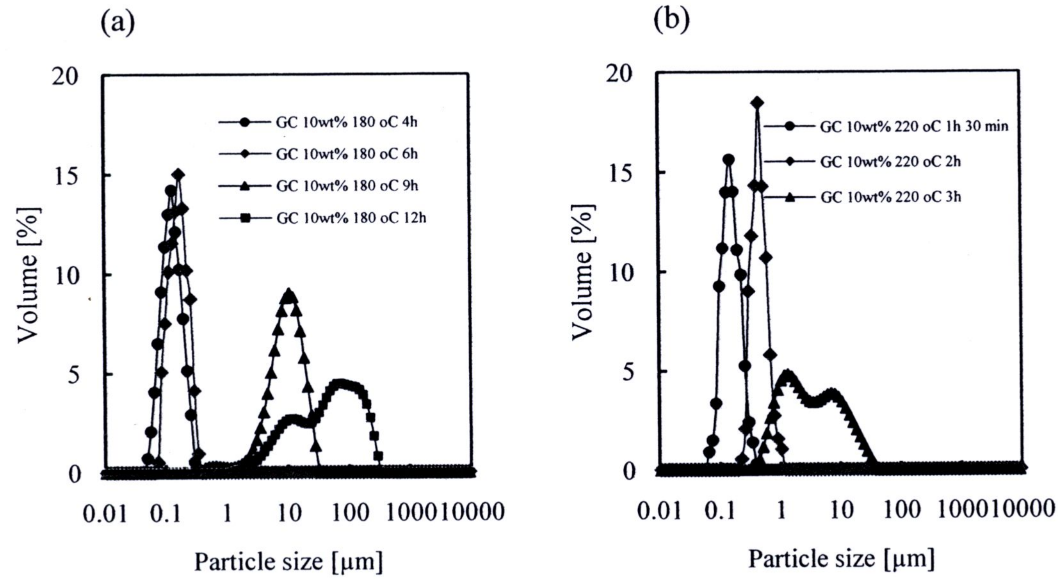

Figure 7.3 Particle size distribution of sythesized CMSs from hydrothermal process of glucose with initial concentration of 10wt% at (a) 180°C and (b) 220 °C in each points of reaction time

In visualized images of particles, it was found that the CMS particle sizes were not actual particle sizes. To exactly reveal particle size distribution of solid product, laser scattering technique was employed to determine an actual particle size using laser scattering technique (Mastersizer 2000). The size distributions were plotted in log-normal distribution as shown in Figure 7.3. At 180°C and short reaction time of hydrothermal process, particle size distributions was steep bell shape which mean narrow particle size distribution [50]. However, the particle size distribution became the narrowest size distribution after 6 hours of reaction time. After reaction time increased to 9 hours, the CMS particles became aggregated which resulted in larger secondary particle size and wider particle size distribution as shown in Figure 7.3(a). According to the irregular shape as shown in Figure 7.1(d), the size distribution became the largest distribution. From these results, it was found that the particle size distributions in both of reaction temperatures (180°C and 220°C) were became wide range when the reaction time increased.

The average value from the particle size distribution is also known as the mean particle size. Normally, size distribution data are available based on the particle mass, volume, projected area, or surface area, so there are multiple measures [48]. Accordingly, the basis for measuring the mean particle size must be specified. According to log-normal distribution characteristics and particle size data in a histogram form (typical for screen analysis where the amount is given for each size interval), the appropriate geometric mean particle size was calculated. To evaluate uniformity of particles, the geometric coefficient of variance was employed which was functioned of geometric standard deviation.

Table 7.2 Summary of morphology, geometric mean size (d_g), geometric coefficient of variance (CV_g), and yield (based on carbon yield) of carbon microspheres from hydrothermal process of glucose with initial concentration of 10wt% at 180°C in each points of reaction time

Samples	Morphology	d_g [μm]	CV_g [-]	yield [-]
Glucose 10 wt%, 180°C, 4h	spherical	0.12	2.74	10.8
Glucose 10 wt%, 180°C, 6h	spherical	0.16	2.52	24.9
Glucose 10 wt%, 180°C, 9h	aggregated spherical	8.77	8.01	39.5
Glucose 10 wt%, 180°C, 12h	irregular	39.94	306.33	51.1

Geometric mean particle size was calculated to compare with the size obtained from SEM micrographs. In comparison with SEM micrographs in Figure 7.1 and Figure 7.2, particle size from geometric mean particle size quite agreed with the size from SEM micrographs. Geometric coefficient of variance (CV_g) was also calculated to criteria uniformity of obtained CMS particles as listed in Table 7.2-7.3. According to these coefficients, it indicated an uniformity of CMSs. A high uniformity is defined as values under 10. From Table 7.2-7.3, CV_g values were low at short reaction time both of 180°C and 220°C which indicated a high uniformity of particles. Yields of CMS samples were also calculated from carbon content in solid product which was analyzed by CHNS/O analyzer as shown and discussed in Chapter 8. The yields in various reaction times were also listed in Table 7.2-7.3.

Table 7.3 Summary of morphology, geometric mean size (d_g), geometric coefficient of variance (CV_g), and yield (based on carbon yield) of carbon microspheres from hydrothermal process of glucose with initial concentration of 10wt% at 220°C in each points of reaction time

Samples	Morphology	d_g [μm]	CV_g [-]	yield [-]
Glucose 10 wt%, 220°C, 1h 30 min	spherical	0.15	2.52	11.8
Glucose 10 wt%, 220°C, 2h	spherical	0.48	2.23	27.8
Glucose 10 wt%, 220°C, 3h	irregular	3.30	74.01	68.8
Glucose 10 wt%, 220°C, 4h	irregular	-	-	79.7
Glucose 10 wt%, 220°C, 9h	irregular	-	-	83.4
Glucose 10 wt%, 220°C, 12h	irregular	-	-	83.5

For the long reaction time, morphology, d_g, CV_g, and yield were not provided and calculated since they absolutely tended to predict from the given results. At 220 °C of reaction temperature, the CMS particles could be obtained in short reaction time (1 hour and 30 minutes). This result implied that temperature strongly accelerated the reaction rate for CMS formation. According to the CMSs at 180°C became aggregated after 6 hours, CMS particles at 220°C became aggregated after only 3 hours. This aggregated behavior came from acceleration of the reactions at high temperature [59].

7.5 Conclusions

Long reaction time and high temperature provided the highest yield (about 80%). Nevertheless, at this condition, carbon microsphere morphology became irregular shape and obtained wide size distribution. In concluding, the smallest and uniform size of carbon microspheres can be obtained by hydrothermal process of glucose the short reaction time and high temperature condition.