CHAPTER V

CARBON MICROSPHERES FORMATION FROM NATIVE CORN STARCH AND MODIFIED STARCH

5.1 Introduction

To proof an assumption that carbohydrates will firstly be hydrolyzed to obtain glucose, subsequently glucose dehydrated to form intermediates (furan compound, 5-HMF and TOC), and finally intermediates polymerized to yield carbon microspheres (CMSs) as same as the reaction pathway in the glucose decomposition reaction (discussed in Chapter 7). Therefore, in this chapter, native corn starch was used to synthesize carbon microspheres in order to compare in the reaction pathway with glucose decomposition reaction. Moreover, water-soluble starch (modified starch, HI-CAP®100) was also used to synthesize carbon microspheres in order to reveal effects of hydrolyzed rates of starch on CMS yield rates and CMS morphology. In addition, the effects of reaction time and reaction temperature on morphology, particle size, and particle distributions of CMSs were also investigated to provide comparison between the CMS particles from native corn starch and CMS particle from HI-CAP®100. Finally, synthesized CMS particles were subsequently carbonized under nitrogen atmosphere in order to develop porous structure of the CMS particles. The particularly properties of the porous CMS particle after carbonization process were determined by many techniques which were described in the result and discussion section. To address the reactions and major intermediates during hydrothermal process, the kinetic model of carbon microspheres formation from hydrothermal process of native corn starch were proposed in Chapter 8. In addition, the fitting of kinetic model were also shown in Appendix B as preliminary results.

5.2 Experimental procedures

5.2.1 Hydrothermal process of carbon microspheres

In brief, native corn starch or modified starch (HI-CAP®100) was suspended in de-mineralized water and subsequently filled into the autoclave reactor with 80%v/v fill rate. The autoclave reactor was kept in a hot air oven at reaction temperature (140, 180, and 220°C). After reached desired reaction time (0-1440 min), the reactor was removed from the hot air oven to cool down naturally. The liquid products then were collected by syringe sampling with 0.45 μm polyvinylidene fluoride (PVDF) membrane. The products were filtered with 0.45 μm PVDF membrane and/or were centrifuged to obtain the solid products (CMSs). The gas product analysis was neglected in all experiments because of low gas product formation in this low temperature range (140-220°C).

The glucose and fructose in the liquid products 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 products were also 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). The amount of remain carbon precursor was calculated from product carbon balance.

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

5.2.2 Carbonization process of carbon microspheres

The obtained CMS particles were carbonized in a horizontal tube furnace reactor under nitrogen (N_2) atmosphere. The N_2 flow rate, target temperature, heating rate of the furnace and holding time were 100 mL/min, 600°C, 1°C/min, and 3 hours, respectively (see Figure 5.1). In brief, A 1.0 gram of the CMS particle after drying step was placed in alumina boat. The alumina boat was taken in the horizontal tube furnace reactor which subsequently set to the operating conditions. After the tube furnace reactor cooled to room temperature naturally, the porous CMS particles were collected and weighted for further characterization.

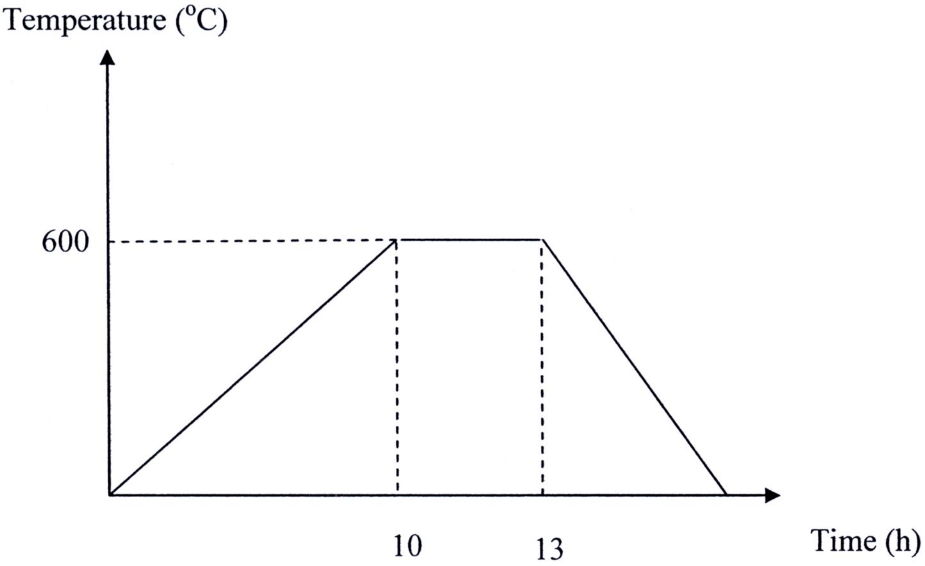

Figure 5.1 Schematic diagram of the carbonization condition

The porous CMS particles were characterized by X-ray diffraction method (XRD) to reveal their crystalline properties. They were determined their specific surface area both before and after carbonization process to reveal the development of porous structure using adsorption – desorption of nitrogen or the Brunauer, Emmett, Teller method (BET method). Moreover, the elemental components of the porous CMS particles were determined by energy dispersive X-ray method (EDX) to demonstrate carbon content in their structure. The transmission electron microscopy (TEM) was used to reveal their internal structure.

5.3 Experimental conditions

The experimental conditions were divided into two processes including hydrothermal process and carbonization process as shown in Table 5.1. In the hydrothermal process, two types of starch which were native corn starch and modified starch (HI-CAP®100) were used as a carbon precursor in these experiments.

Table 5.1 Experimental conditions for hydrothermal and carbonization process of native corn starch and HI-CAP®100

Hydrothermal Process	
Temperature (°C)	140, 180 and 220
Pressure	autogenously
Starch initial concentration (wt%)	1,5,10,15,20
Fill rate in reactor (%v/v)	80
Reaction time (min)	30, 60, 120, 150, 180, 240, 360, 540, 720, 900, 1080, 1260 and 1440
Carbonization Process	
Heating rate (°C/min)	1
Target temperature (°C)	600
Holding time (h)	3
Flowrate of N_2 gas (mL/min)	100

5.4 Results and discussion

Results and discussion structure was divided into two points including hydrothermal process of CMSs and carbonization process of CMSs. The detail of structure was shown in Table 5.2

Table 5.2 Results and discussion structure

5.4.1 Hydrothermal Process of carbon microspheres
5.4.1.1 Effect of hydrothermal reaction temperature of native corn starch on CMS yield rates and CMS morphology
5.4.1.2 Effects of types of starch on CMS yield rates and CMS morphology
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5.4.2.1 Thermal decomposition of carbon microspheres
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5.4.2.6 Elemental components of carbon microspheres

5.4.1 Hydrothermal process of carbon microspheres

5.4.1.1 Effect of hydrothermal reaction temperature of native corn starch on CMS yield rates and CMS morphology

To choose a reaction temperature for synthesizing carbon microspheres from native corn starch, the hydrothermal process was conducted at three points of reaction temperature which were 140, 180 and 220°C with initial concentration of 10wt%. The yield rates of carbon microsphere formation at different points of reaction temperature were comparatively plotted in Figure 5.1. At 140°C of reaction temperature, solid product (CMS particles) could not be obtained during hydrothermal process since the reaction temperature was not enough to dehydrate glucose to intermediates in carbon microspheres formation [32]. This behavior can be also observed from hydrothermal of other carbohydrates (modified starch, amylopectin, amylose, and glucose). Therefore, we only carried out hydrothermal process of other types of carbon precursor at 180°C and 220°C.

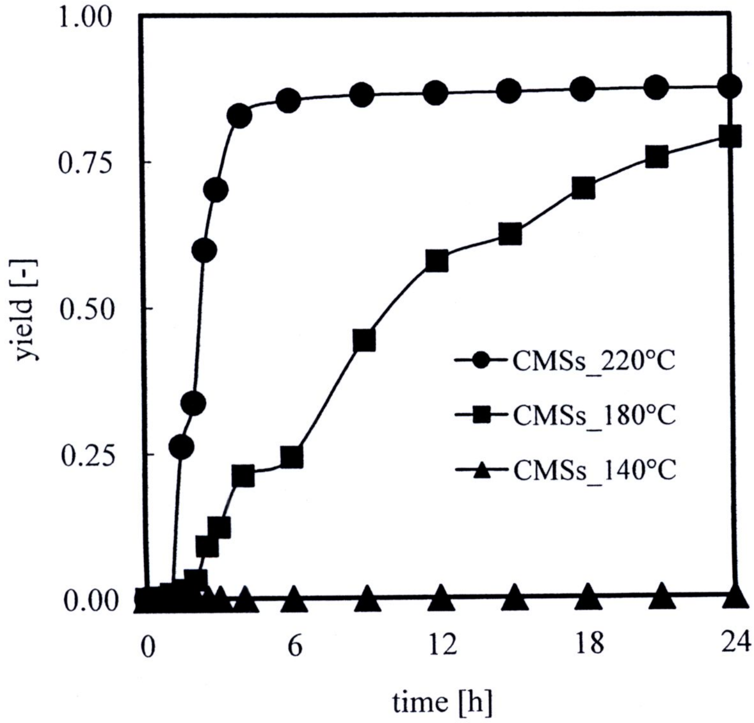


Figure 5.1 The yield rates of CMS formation from hydrothermal process of native corn starch with initial concentration of 10wt% at 140, 180, and 220°C

Nonetheless, CMS particles can be observed at higher temperature (180 and 220°C) than 140°C. At 180°C of reaction temperature, the CMS yield rate gradually increased with increasing in reaction time as shown in Figure 5.1. Although the CMS particles were also obtained from the hydrothermal process at 220°C, the CMS yield rate rapidly increased than the CMS yield rate at 180°C (see Figure 5.1). Moreover, the highest CMS yield was achieved with the short reaction time (after 6 hours) at 220°C. The yield rates of CMS particles strongly depended on reaction temperature [31]. The results can be explained that CMS formation reactions (polymerization and aromatization reaction) were endothermic reactions [33]. Therefore, at the high temperature, the CMS formation reactions might be dramatically accelerated to obtain a high CMS yield rate [15]. From these findings, firstly, the reaction temperature at 140°C cannot produce carbon microspheres, consequently the reaction temperature for hydrothermal process of native corn starch should rise up to 180°C. In the other experiments, we will, therefore, perform hydrothermal process only at 180°C and 220°C of reaction temperature. Secondly, the CMS yield rates strongly depened on reaction temperature and the highest CMS yield could be obtained after 6 hours of reaction time.

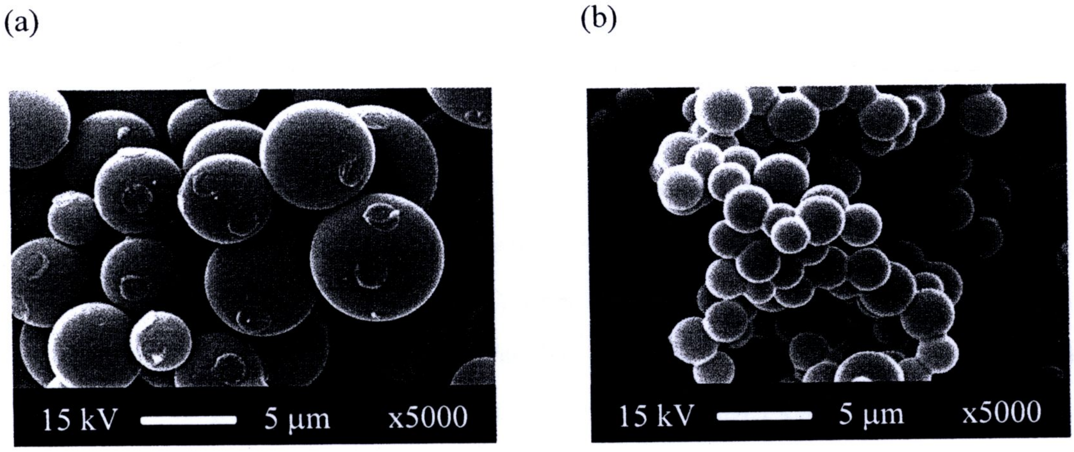


Figure 5.2 SEM micrographs of CMSs particle from hydrothermal process of native corn starch with initial concentration of 10wt% at 180°C (a) and at 220°C (b) for 9h

According to the CMS yield rates strongly depended on reaction temperature as formerly described. Furthermore, morphology and particle size of the CMS particles were focused to also reveal effects of reaction temperature between 180°C and 220°C. The morphology and particle size were observed by scanning electron microscope as shown in Figure 5.2(a)-(b). Formation mechanisms of carbon microspheres can be explained by nuclei formation mechanism and subsequently growth mechanism step [38]. Firstly, the nuclei formation step – during reaction temperature increased, native corn starch was hydrolyzed to yield glucose which subsequently dehydrated to form reactive furan ring compounds before finally polymerized to form CMS nuclei (this mechanism will be discussed in detail in chapter 8) [33]. Secondly, the growth mechanisms step which was the nuclei will grow with deposition and polymerization of later small nuclei on its surface [38]. However, these mechanisms were different when reaction temperature changed [49]. In this study, we, therefore, compared effects of reaction temperature between 180°C and 220°C. At 180°C of reaction temperature, the growth mechanism step plays an important role in carbon microspheres formation [22]. In other word, The nucleus of particles will gradually grow because intermediates gradually were generated from continuously hydrolyzed glucose [22]. Finally, the CMS particles became larger in size and more uniform particle size distribution as shown in Figure 5.2(a). After 24 hours of reaction time, the CMS particle size was constant because intermediates for CMS formation were completely used (carbon microsphere particle development have been discussed in next section) [3].

On the other hand at 220ºC of reaction temperature, CMS particles was smaller in primary particles (~2μm) than the primary CMS particles obtained at 180ºC (~5μm) as shown in Figure 5.2(b). The high reaction temperature accelerated hydrolysis, dehydrattion and polymerization reaction [33]. The nuclei formation rate dramatically increased and the intermediates for CMS formation rapidly decreased [38]. According to this formation behavior, growth mechanism step had a short reaction time to grow particle size consequently the CMS particles were small in primary particle size. However, at this high reaction temperature (at 220ºC), the primary particles became sintered to form aggregated secondary particles as shown in Figure 5.2(b) [8]. In concluding, the reaction temperature inevitably affected on the formation of CMs particles because of the difference in the nuclei formation rate and the growth mechanism rate. The uniform CMS particles with large primary particle size of 5 μm, were obtained at 180 ºC after 12 hours. The aggregated CMS particles with small primary CMS particle size of 2 μm, were obtained at 220 ºC after 9 hours.

5.4.1.2 Effects of types of starch on CMS yield rates and CMS morphology

In the previous section, we have chosen the reaction temperature of hydrothermal process of native corn starch. In this section, non-soluble starch (native corn starch) and water-soluble starch (HI-CAP®100) were used to synthesize carbon microspheres in order to reveal effects of solubility of starch on yield rates and morphology of CMS particles. The solubility of starch will directly affect on hydrolyzed rate of starch [25]. We determined the hydrolyzed rate of native corn starch and HI-CAP®100 from glucose yield rates as shown in Figure 5.3-5.4. The glucose yield rates from hydrothermal process of native corn starch and HICAP®100 at 180°C with initial concentration of 10wt% were clearly different in rate patterns as shown in Figure 5.3. The glucose yield rate of HI-CAP®100 rapidly increased than the glucose yield rate of native corn starch in the beginning of reaction time. Because of its molecular weight and water soluble property, HI-CAP®100 was immediately hydrolyzed to yield glucose [25].

In contradictory, the native corn starch (non-soluble starch) was difficult to be hydrolyzed because they had crystalline structure and high molecular weight [50]. At 220°C, a glucose yield rate of HI-CAP®100 was also faster than native corn starch in short reaction time as shown in Figure 5.4. According to the different hydrolyzed rates of starch as discussed previously, CMS yield rates also strongly depended on the hydrolyzed rates of starch. The differences of CMS yield rates from native corn starch and HI-CAP®100 were plotted in Figure 5.5. At 180°C and initial concentration of 10wt%, the CMS yield rate from HI-CAP®100 was faster than the CMS yield rate from native corn starch and became equal each other after 24 hours of reaction time. From this finding, it was found that the CMS yield rate strongly depended on the hydrolyzed rate of starch. Nevertheless, morphology of carbon microspheres from both hydrothermal process of native corn starch and HICAP®100 was indifferent. The typical morphologies were demonstrated in Figure 5.6(a) and 5.6(b) respectively.

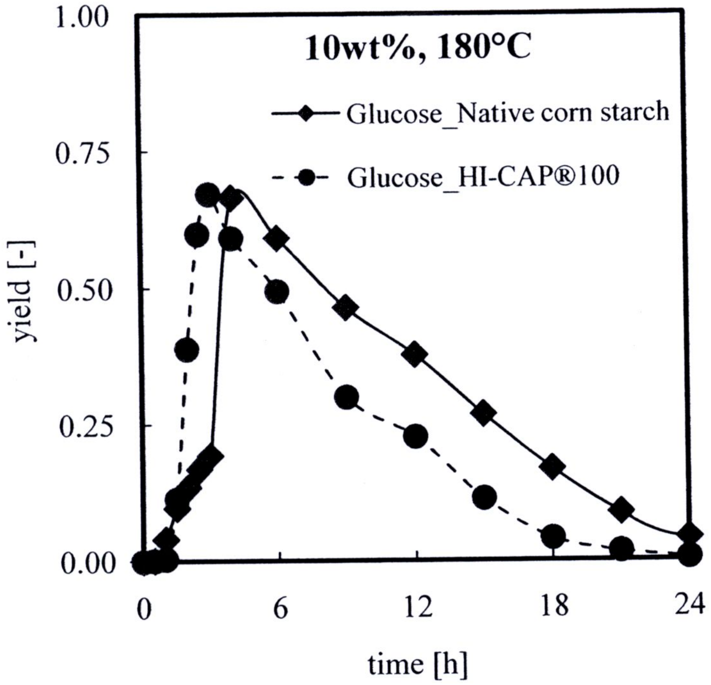


Figure 5.3 Glucose yield rates from hydrothermal process of native corn starch and HI-CAP®100 with initial concentration of 10wt% at 180°C

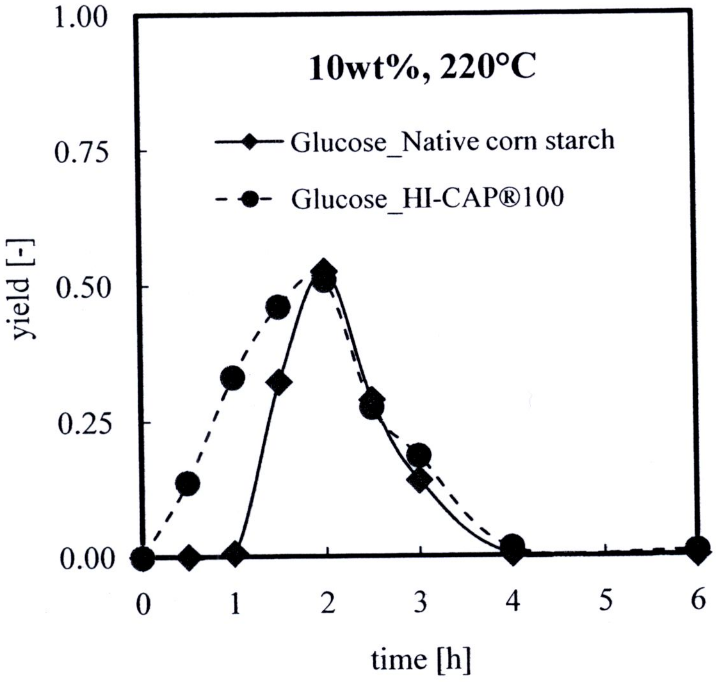


Figure 5.4 Glucose yield rates from hydrothermal process of native corn starch and HI-CAP®100 with initial concentration of 10wt% at 220°C

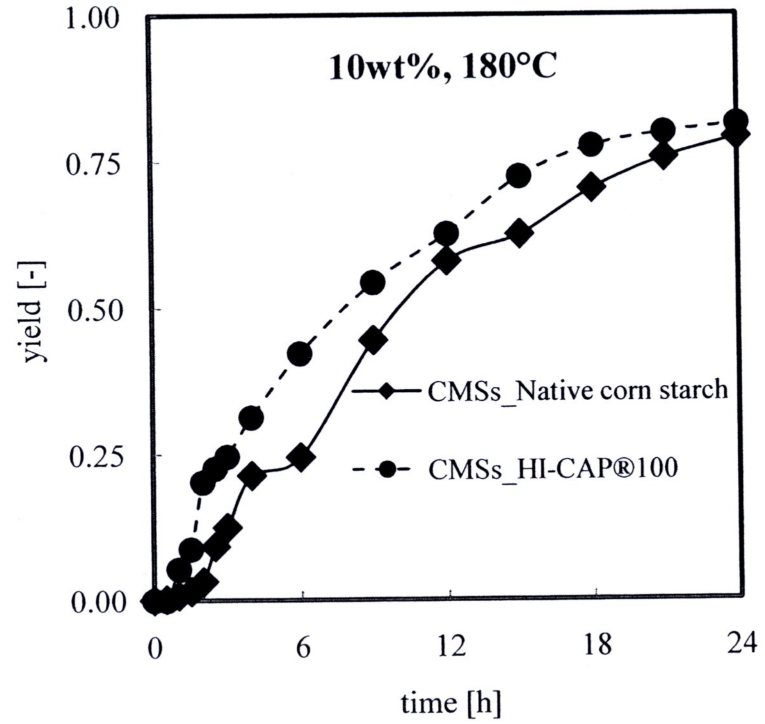


Figure 5.5 CMS yield rates from hydrothermal process of native corn starch and HI-CAP®100 with initial concentration of 10wt% at 180°C

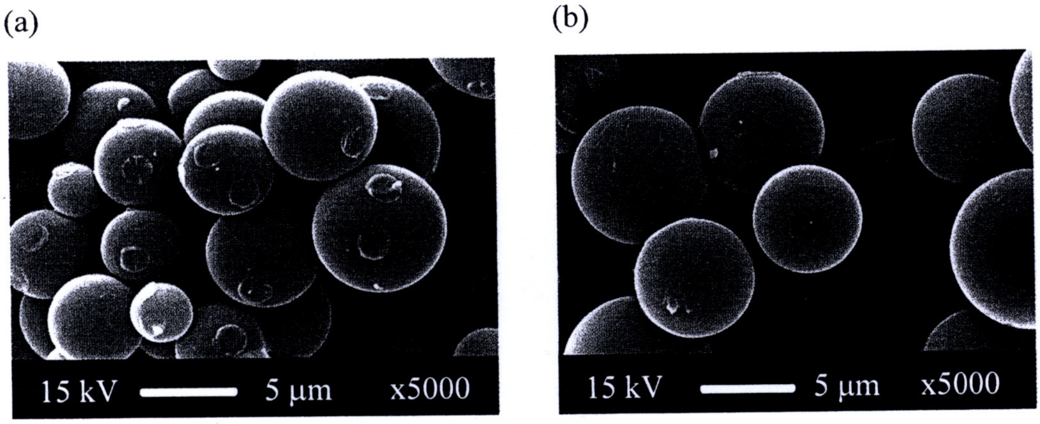


Figure 5.6 SEM micrographs of synthesized CMSs from hydrothermal process of (a) native corn starch and (b) HI-CAP®100 with initial concentration of 10wt% at 180°C for 9h respectively

5.4.1.3 Effects of initial concentrations of native corn starch on CMS yields and CMS morphology

In this section, we will discuss effects of initial concentrations of native corn starch on carbon microsphere yield and carbon microsphere morphology. In this initial concentration parameter, initial concentrations of native corn starch were varied between 1, 5, 10, 15, and 20wt%. The initial concentration of native corn starch at 1wt% gave a low yield of carbon microsphere particles (~20%) as shown in Figure 5.7. When initial concentration of native corn starch increased to 5wt%, the CMS yield rapidly increased to ~ 60% yield. However, the CMS yield slightly increased to 75% yield with increasing in the concentration to 10wt% and became constant when the initial concentration was over than 10wt%. These results demonstrated that reaction rates to form carbon microspheres decreased when initial concentration of native corn starch increased [12]. Therefore, quantity of water-soluble products in liquid products increased [51]. From this results, we had chosen the initial concentration of carbon precursor of 10wt% for synthesizing carbon microspheres in other experiments.

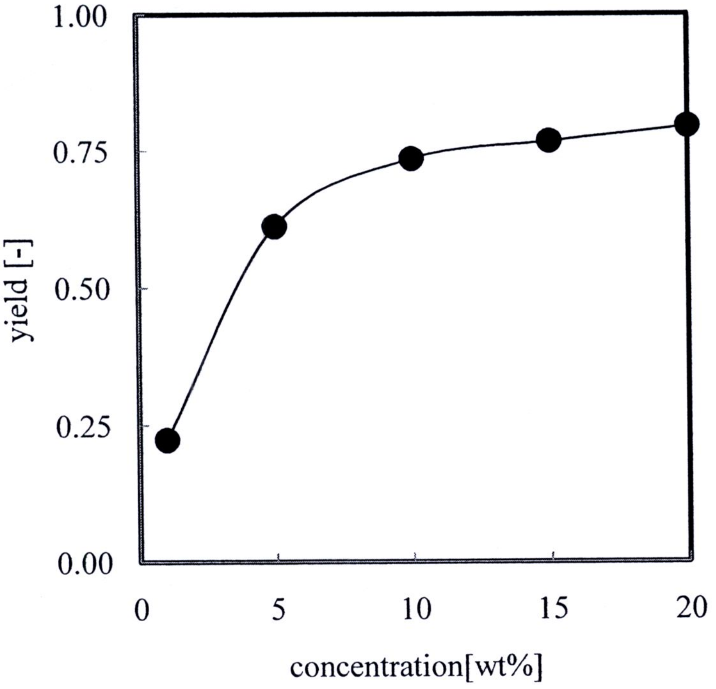


Figure 5.7 CMS yields from hydrothermal process of native corn starch at 220°C for 6h in various initial concentrations (1-20wt%)

At the initial concentration of 1wt%, morphology of carbon microsphere particles was spherical shape and the smallest in size (0.5-1.0 μm) as shown in Figure 5.8(a) because they had a small quantity of intermediates to form and grow their nuclei [52]. Unfortunately, the small CMS particles were difficult to collect because it also was small in quantity. Therefore, we did not carry out hydrothermal process at 1wt% of initial concentration. Similarly, although the CMS particles from hydrothermal process with 5wt% of initial concentration can be collected, at 10wt% of initial concentration gave more CMS yield than at 5wt%. On the other hand, when the concentration increased over 10wt% (15-20wt%), CMS particles became aggregate to form a large secondary particle as shown in Figure 5.8(c). The initial concentration of 10wt% can give both the high CMS yield and the uniform primary CMS particles as shown in Figure 5.8(b).

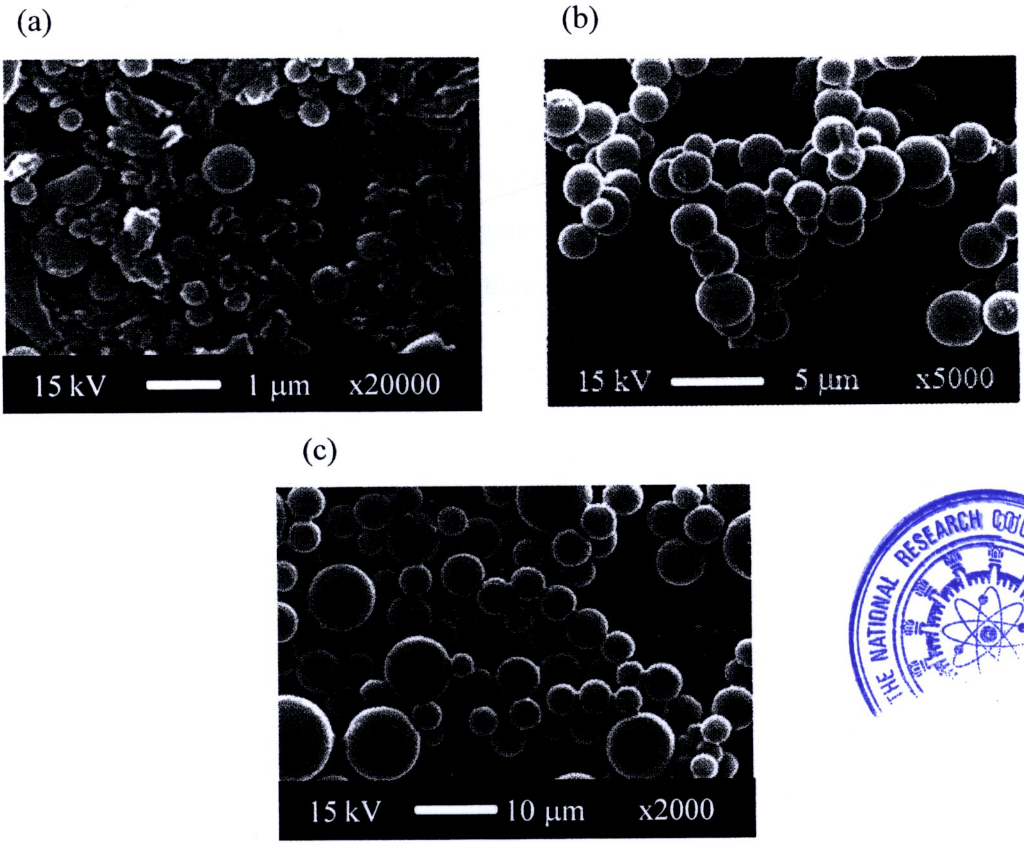


Figure 5.8 SEM micrographs of synthesized CMSs from hydrothermal process of native corn starch at 220°C for 6h with various initial concentrations of (a) 1wt%, (b) 10wt% and (c) 15wt%, respectively

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

Figure 5.9 shows CMS particle development in various points of reaction time of synthesized CMSs from hydrothermal process of native corn starch with initial concentration of 10wt% at 180°C. By varying reaction time at 180°C, the CMS particles were firstly observed after 3 hours of reaction time (as shown in Figure 5.9(a)) but they were polydisperse or irregular shape with primary particle size about 2-3 μm. The short reaction time (3 hours) did not enough to develop the CMS particles to uniform particles because hydrolyzed starch step just began to form glucose and intermediates just polymerized to form the CMS particles [53]. Furthermore, the later nuclei and residue intermediates was likely to polymerize and form the irregular shape particles during cool down step [54]. However, when reaction time increased (4-9 hours), the hydrolyzed glucose increased in the system and subsequently form the intermediates which developed uniformity and larger in particle size as shown in Figure 5.9(b)-(d). They had primary particle size about 3-5 μm [27]. After 12 hours of reaction time, the CMS particles became larger size with primary particle about 4-5 μm (see Figure 5.9(e)-(f)). Fortunately, the increase in reaction time provided more uniform particle size and retained spherical shape [55].

At 220°C, CMS particles became aggregated shape because the high reaction temperature accelerated formation reactions and the CMS particles then sintered together as shown in Figure 5.10. After 1 hours and 30 minutes of reaction time, the CMS particles can be observed with primary particle size about 0.5 μm as shown in Figure 5.10(a)-(c). These CMS primary particles had irregular shape and were likely to aggregate formed the large secondary particles. Nevertheless, these CMS primary particles became large and more uniform when the reaction time increased to 3 hours as shown in Figure 5.10(d). The CMS particles after 3 hours of reaction time had aggregated primary particles with approximate size of 1.0 μm. The CMS development was still undergone to grow in particles size as shown in Figure 5.10(e). Finally, the CMS primary particles were gradually developed to become large and constant particle size with the primary particle of 2.5 μm after 9 hours of reaction time as shown in Figure 5.10(f).

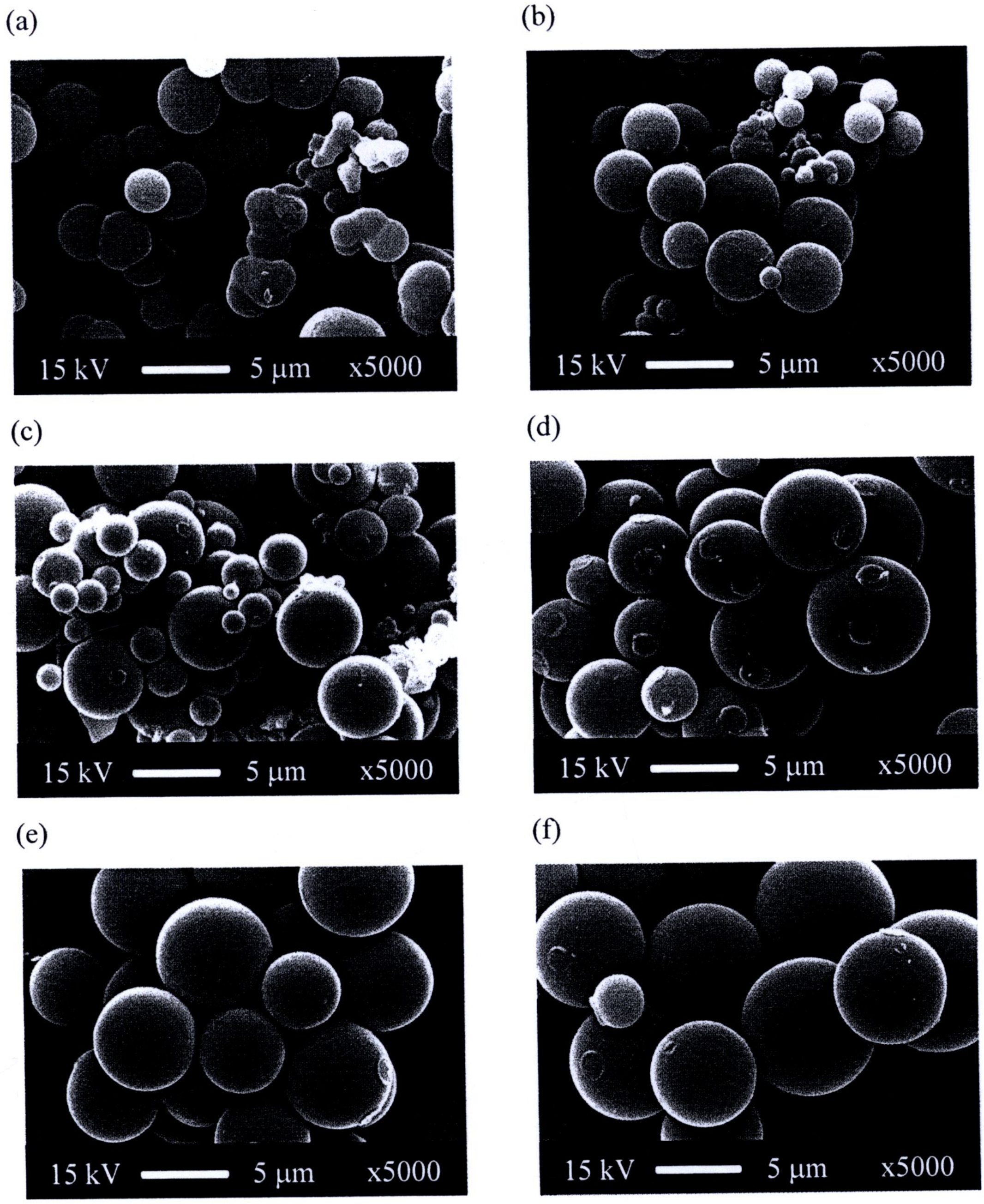


Figure 5.9 SEM micrographs of synthesized CMSs from hydrothermal process of native corn starch with initial concentration of 10wt% at 180°C for reaction time of (a) 3h, (b) 4h, (c) 6h, (d) 9h, (e) 12h, and (f) 24h respectively

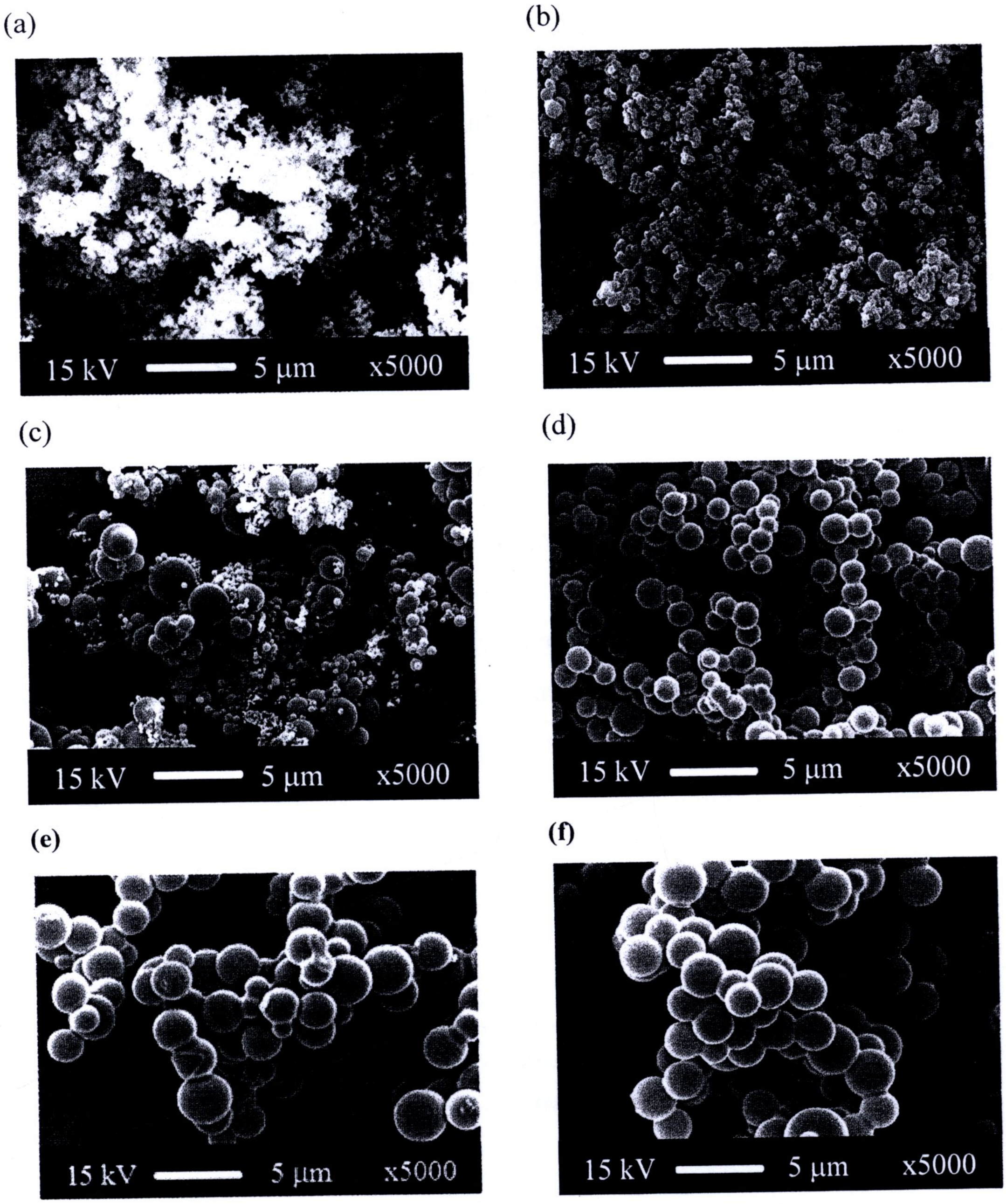
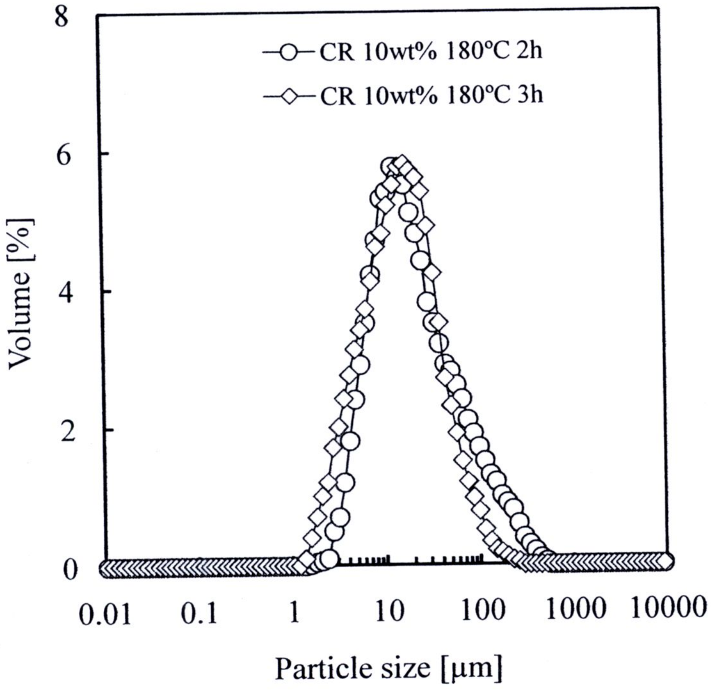


Figure 5.10 SEM micrographs of synthesized CMSs from hydrothermal process of native corn starch with initial concentration of 10wt% at 220°C for reaction time of (a) 1h 30 min, (b) 2h, (c) 3h, and (d) 4h, (e) 6h, and (f) 9h, respectively

According to the CMS particle shape after complete development from both 180 °C and 220°C, the CMS primary particle sizes were approximate 5 μm from hydrothermal process of native corn starch at 180°C and the CMS primary particle sizes were 2 μm from hydrothermal process of native corn starch at 220°C respectively. Since the CMS particles from some conditions (hydrothermal process at 220°C) were likely to aggregate and form large secondary particles, the particle size of secondary CMS particles (aggregated CMS particles) were determined by laser scattering technique to show aggregated CMS particle size and compare with their primary particle size from SEM results. In other words, the particle size both of SEM results and laser scattering results, were compared to reveal their actual particle size. Moreover, uniformity of CMS particle size was determined by geometric coefficient of variance (CV_g) which was calculated from equation (4.3) as provided in Chapter 4. However, the CV_g values did not always demonstrate an uniformity of the primary CMS particles because they may be aggregated CMS particles (the secondary CMS particles). Therefore, the uniformity of CMS particles should be considered with their SEM micrograph which provided they were actual primary or secondary CMS particles. The particle size distributions could be also considered to determine distribution in size and rough particle size.

(a)



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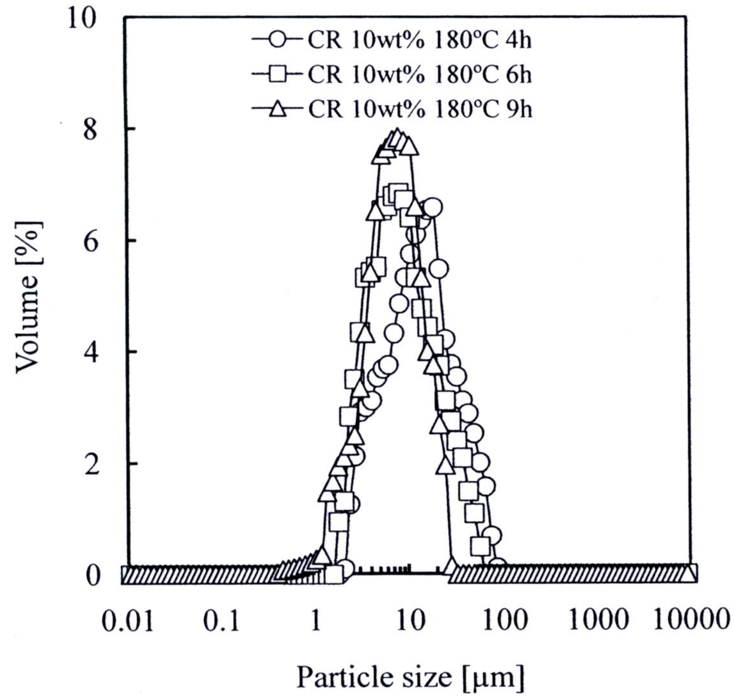

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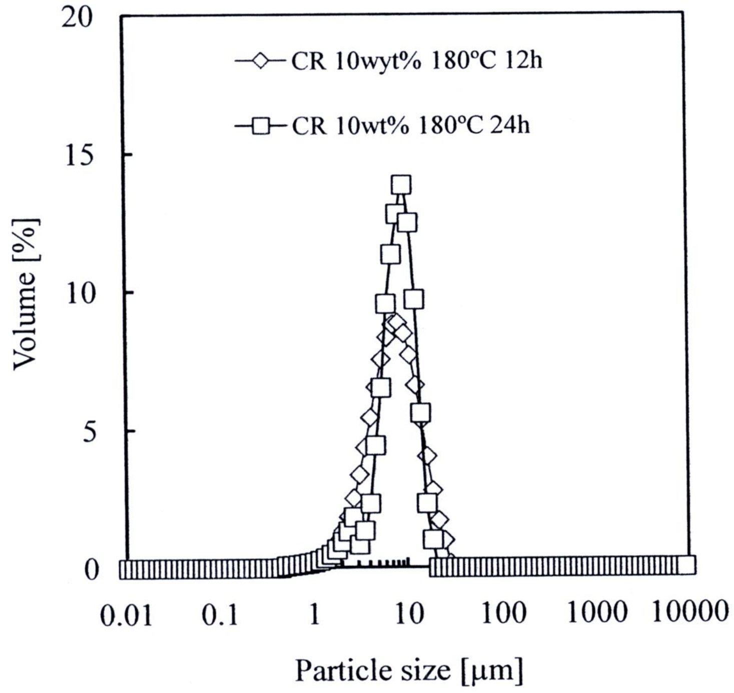

Figure 5.11 Particle size distributions of the CMS particles from hydrothermal process of native corn starch with initial concentration of 10wt% at 180°C in each points of reaction time (CR = native corn starch)

Figure 5.11 shows particle size distributions of the CMS particles at 180°C. In the short reaction time (under 6 hours), the size distributions were broad with high geometric coefficients of variance (CV_g) as listed in Table 5.3. The broad size distributions demonstrated the difference in particle sizes. However,these different CMS particle sizes did not always show that the CMS particles had the considerable difference in primary particle sizes. The SEM micrograph shows that the primary particles did not have the big difference in size. Nevertheless, the particle size distributions of as-prepared CMSs for longer reaction time became narrow size distributions because they became uniform in size [56]. The uniform CMS particle size caused from polymerization of more intermediates in the system (came from dehydration of glucose) when the reaction time increased [11]. After 12 hours, the CMS formation reactions were complete and the CMS particles were uniform [57]. At 220°C, the CMS particle size tended to narrow geometric mean size (d_g) when the reaction time increased as shown in Table 5.3. In short reaction time, the large geometric mean particle size (d_g) may be caused from the reaction was undergoing. Since spherical particle development was not complete. When reaction time increased, the geometric coefficient became small which demonstrated high uniform of the CMS particle size. In Figure 5.12(a)-(b), all particle size distributions were also broad distributions which were confirmed by geometric coefficient of variance (CV_g) (see Table 5.4). As described previously, the particle distributions were broad in the short reaction time because the CMS particles were not complete development [43]. However, the broad distributions at 220°C mainly caused from the sintering CMS particles than incomplete particle development which demonstrated from SEM micrograph. At 220°C of reaction temperature which was high reaction temperature. Therefore, the CMS particles were likely to sinter by the residual monomers and by fast formation reactions [58]. From the results listed in Table 5.4, although the yields of carbon microspheres dramatically increased at 220°C (70% yield after 3 hours), all the CMS morphologies were the aggregated spherical shape. These aggregated CMS particle behavior may be caused from the high reaction temperature which accelerated the reaction rates of CMS formation [59]. At this high reaction temperature, CMS nuclei tended to move rapidly in the solution [38]. Therefore, the CMS nuclei collided each other and linked to form aggregated secondary particles [56]. Nonetheless, the CMS particles were uniform primary particles at 220°C although they were likely to aggregate to form large secondary particles because of high reaction temperature.

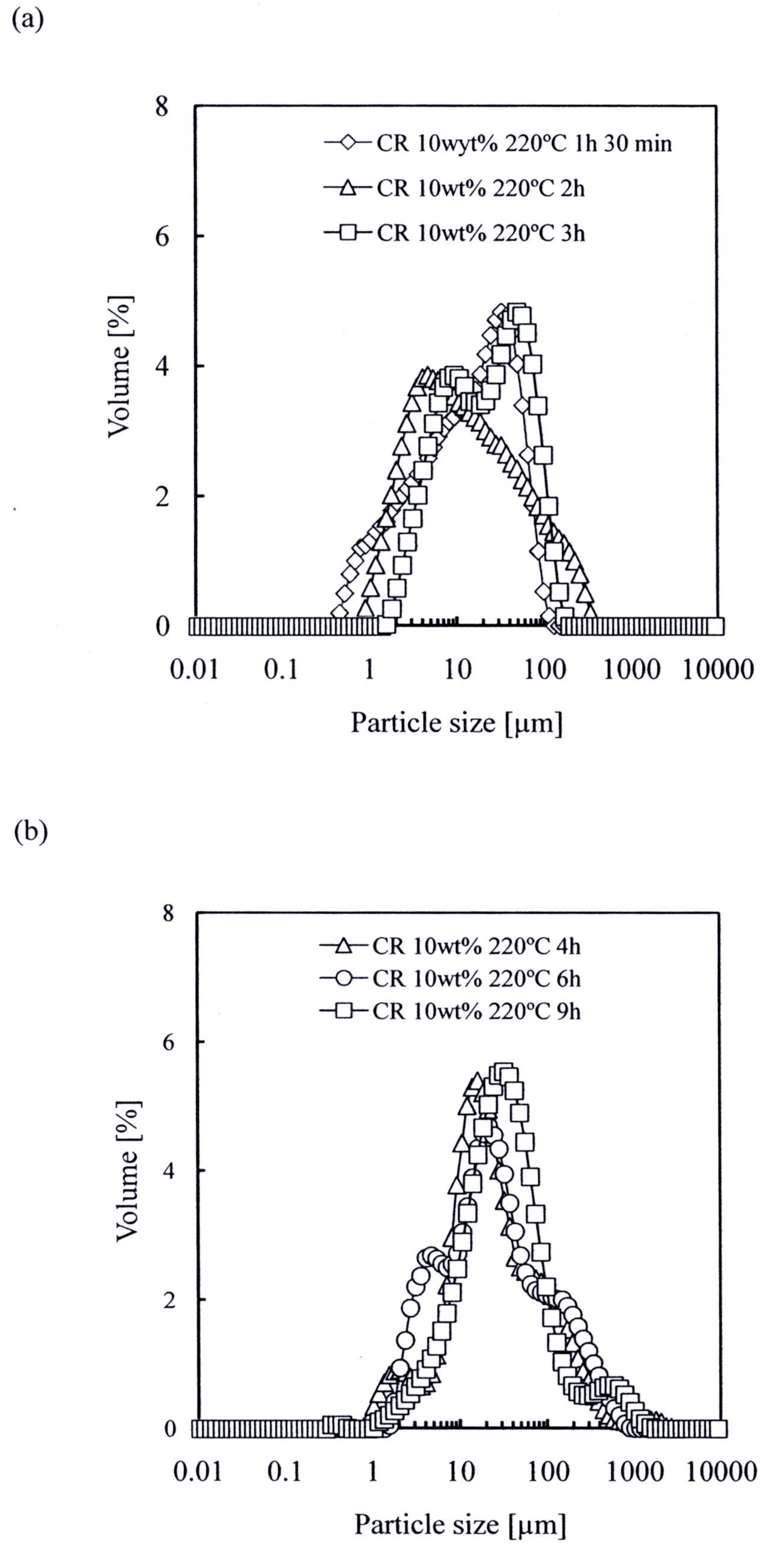

Figure 5.12 Particle size distributions of the CMS particles from hydrothermal process of native corn starch with initial concentration of 10wt% at 220°C in each points of reaction time (CR = native corn starch)

Table 5.3 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 native corn starch with initial concentration of 10wt% at 180°C in each points of reaction time

Samples	Morphology	d_g [μm]	CV_g [-]	%yield [-]
CR 10 wt%, 180°C, 2h	aggregated spherical	19.83	59.79	3.2
CR 10 wt%, 180°C, 3h	aggregated spherical	14.13	27.35	12.3
CR 10 wt%, 180°C, 4h	spherical	12.53	14.25	21.3
CR 10 wt%, 180°C, 6h	spherical	9.51	13.15	24.5
CR 10 wt%, 180°C, 9h	spherical	7.02	8.38	44.4
CR 10 wt%, 180°C, 12h	spherical	6.85	6.12	57.9
CR 10 wt%, 180°C, 24h	spherical	7.66	4.08	79.0

Note: d_g indicates secondary particles when the particles became aggregates

Table 5.4 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 native corn starch with initial concentration of 10wt% at 220°C in each points of reaction time

Samples	Morphology	d_g [μm]	CV_g [-]	%yield [-]
CR 10 wt%, 220°C, 1h 30 min	aggregated spherical	11.69	1124.14	26.3
CR 10 wt%, 220°C, 2h	aggregated spherical	14.19	4558.44	33.7
CR 10 wt%, 220°C, 3h	aggregated spherical	20.07	73.97	70.2
CR 10 wt%, 220°C, 4h	aggregated spherical	22.34	902.55	82.8
CR 10 wt%, 220°C, 6h	aggregated spherical	26.19	2498.34	85.4
CR 10 wt%, 220°C, 9h	aggregated spherical	31.40	283.44	86.3

Note: d_g indicates secondary particles when the particles became aggregates

5.4.2 Carbonization process of carbon microspheres

In carbonization process, CMS particles from hydrothermal process of both native corn starch and HI-CAP®100 with initial concentration of 10wt% at 180°C for 24 hours, were carbonized under nitrogen atmosphere. The N_2 flow rate, target temperature, heating rate of the furnace, and holding time were 100 mL/min, 600°C, 1°C/min, and 3 hours, respectively. Effects of carbonization process on structure of CMS particles were revealed by many analysis techniques in order to understand particular properties of the porous CMS particles. The CMS particles after carbonization process were named the porous CMS particles.

5.4.2.1 Thermal decomposition of carbon microspheres

The as-prepared CMSs from hydrothermal process of native corn starch with initial concentration of 10wt% at 180°C for 24 hours were analyzed by TGA technique to reveal decomposition behavior of the CMS particles under nitrogen atmosphere. The typical decomposition pattern of the CMS particles was shown in Figure 5.13

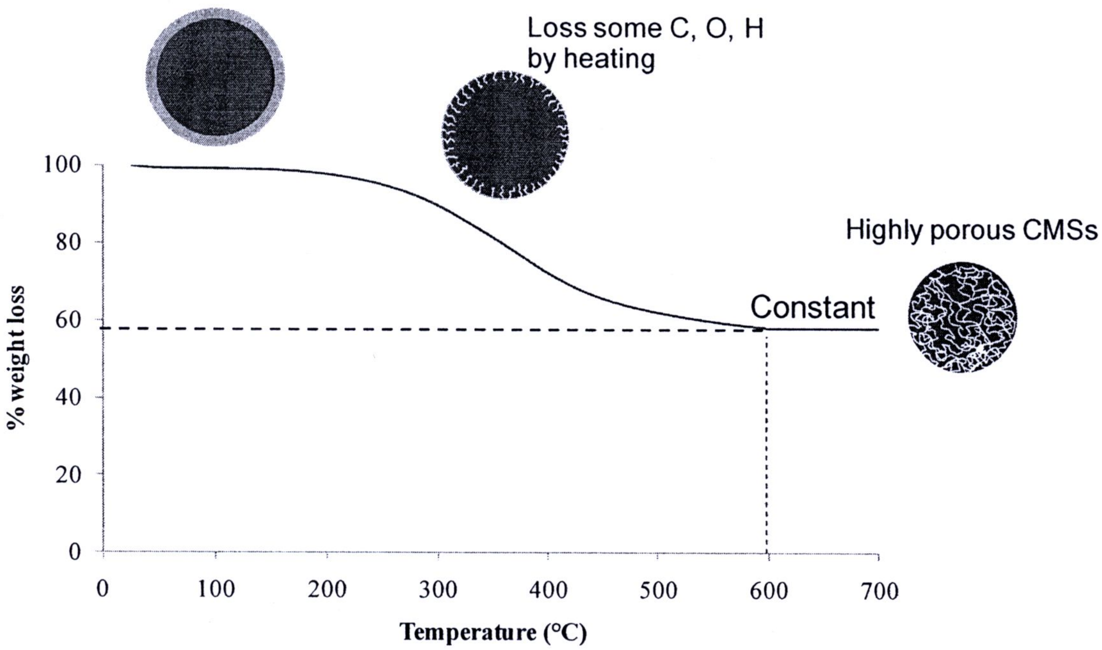

Figure 5.13 Decomposition behavior under nitrogen atmosphere of CMS particles from hydrothermal process of native corn starch with initial concentration of 10wt% at 180°C for 24 hours

In the beginning of the decomposition, the CMS particles lost some moisture and gaseous product residual [11]. The decomposition of C, O, and H was subsequently occurred to form some gaseous product such as CO_2, CH_4 and CO [22]. When temperature reached 600°C, the CMS particle became constant in weight of 60% as shown in Figure 5.13. Finally, the porous CMS particles were obtained. These CMS particles were then stored further characterizations to reveal their many particularly properties.

5.4.2.2 Porosity of carbon microspheres

In the carbonization process, CMS particles from hydrothermal process of both native corn starch and HI-CAP®100 with initial concentration of 10wt% at 180°C for 24 hours, were developed the porous structure by losing some C, H, and O in gaseous byproducts [14]. The porosity of porous carbon microspheres was determined by adsorption-desorption of nitrogen gas at -196°C. Typical isotherms of adsorption-desorption of the porous CMS particles from native corn starch and HI-CAP®100, were demonstrated in Figure 5.14. All isotherms were type I isotherms which indicated micropore structure of the porous CMS samples [22].

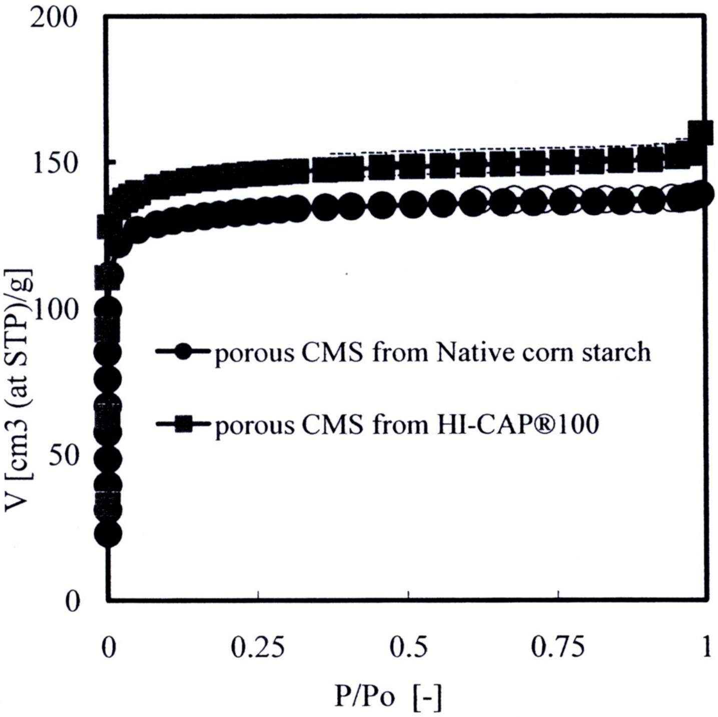

Figure 5.14 N_2 adsorption-desorption isotherms of porous CMSs particles after carbonization process which were from (■) HI-CAP®100 and (●) Native corn starch

An BET equation was used to calculate surface area of the porous carbon microspheres after carbonization process. Specific surface area of porous carbon microspheres from native corn starch and HI-CAP®100, were shown in Table 5.5. All samples have the same range of surface area between 500-600 m^2/g (as shown in Table 5.5). These results demonstrated that the carbonization process gave the same porous structure of carbon microspheres from native corn starch and HI-CAP®100. The same porous structure of the porous CMS particles from different types of native starch was separately shown in Appendix A.

Table 5.5 Specific BET surface area of CMSs before and after carbonization process

CMS particles from	**Specific BET surface area, S_{BET} [m^2/g]**	
	Before carbonization	After carbonization
Native corn starch	3.57	520
HI-CAP®100	4.32	560

Brunauer–Emmett–Teller (BET) surface areas of the CMS particles before and after carbonization processwere also summarized in Table 5.5. The surface areas of the porous CMSs were dramatically increased after carbonization process (from ~10 m^2/g to ~500 m^2/g). The release of H, O and C during carbonization process gave rise to large quantities of micropores throughout the bulk of the porous CMS samples.

5.4.2.3 Functional groups on carbon microspheres

The CMS particles from hydrothermal process of native corn starch with initial concentration of 10wt% at 180°C for 24 hours were characterized by FT-IR technique in order to reveal the reactive functional groups on their surface [60]. Figure 5.15 shows typical FT-IR patterns of carbon microspheres before (red line) and after carbonization process (black line). The bands at 1710 and 1620 cm^{-1} (together with the band at 1513 cm^{-1}) can be attributed to C=O (carbonyl, quinone, ester, or carboxyl) and C=C vibrations respectively, whereas the bands in the 1000–1450 cm^{-1} region correspond to C-O (hydroxyl, ester, or ether) stretching and O-H bending vibrations [15]. The bands at 875–750 cm^{-1} are assigned to aromatic C-H out-of-plane bending vibrations, whereas the bands at approximately 2900 and 3000–3700 cm^{-1} correspond to stretching vibrations of aliphatic C-H and O-H (hydroxyl or carboxyl), respectively [32]. Although carbonization process can develop the porous structure of carbon microspheres, the reactive functional groups on their surface were also removed after carbonization process.

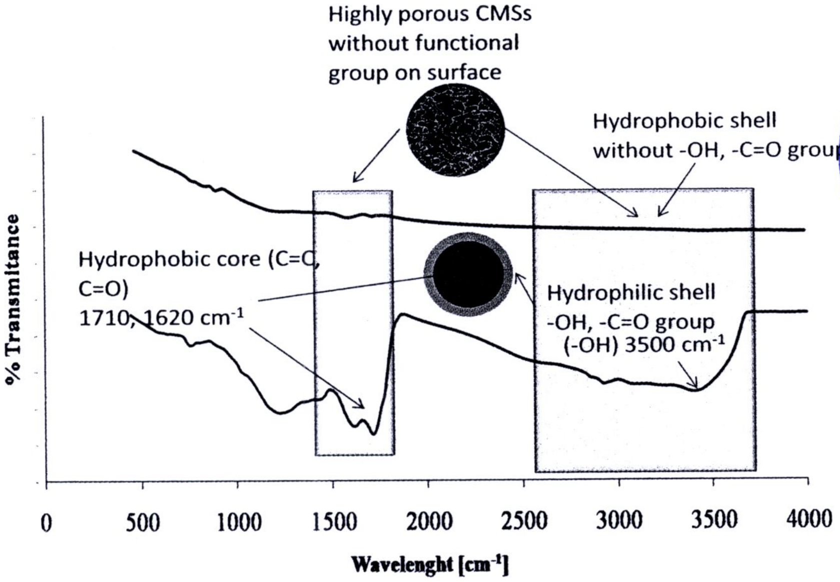

Figure 5.15 FT-IR patterns of CMS particles from hydrothermal process of native corn starch before carbonization process (red line) and after carbonization process (black line)

5.4.2.4 Crystallinity of porous CMS particles

The CMS particles from hydrothermal process of native corn starch and HI-CAP®100 with initial concentration of 10wt% at 180°C for 24 hours were carbonized under nitrogen atmospheres to obtain porous CMS particles. After carbonization process, the porous CMS particles were analyzed by XRD technique to reveal their crystallinity. The XRD patterns both of the porous CMS particles from native corn starch and the porous CMS particle from HI-CAP®100 were shown in Figure 5.16. There were the presences of two broad peaks at 2θ = 24.8 and 43.5 which were reflections from the (002) plane and the (101) plane, respectively [52]. The peaks can be indexed to a hexagonal graphite lattice [54]. The broadening of the peaks suggests the presence of an amorphous carbon phase within the porous CMSs [57]. The XRD patterns from both of the porous CMS particles from native corn starch and the porous CMS particles from HI-CAP®100 had the same crystalline structure characteristics. From these finding, it was found that the porous CMS particle had partial crystalline structure which were suitable for application in electron transfer materials.

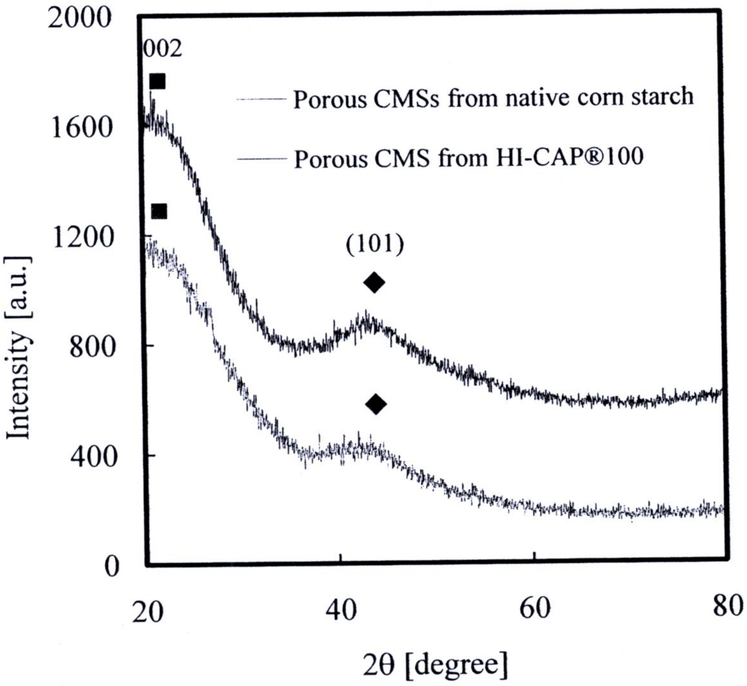

Figure 5.16 XRD patterns of the porous CMS particles from carnonization process of the CMS particles from hyrothermal process of native corn starch and from HI-CAP®100 with initial concentration of 10wt% at 180°C for 24h

5.4.2.5 Internal structure of CMS particle before and after carbonization process

The CMS particles from hydrothermal process of native corn starch with initial concentration of 10wt% at 180°C for 24 hours were characterized by transmission electron microscope (TEM) to reveal their internal and shell structure. The CMS particles have spherical shape and non-hollow structure. The CMS particle after hydrothermal process had dense structure as shown in Figure 5.17(a). The dense structure may compose of aromatic carbon ring compounds which were benzene ring compounds and furan ring compounds as corresponding to FT-IR results and elemental analysis results [56]. The reactive shell of the CMS particles was determined by FT-IR technique. Moreover, the reactive shell can also revealed by TEM results [17]. From the high imagination of TEM observation, the shell had its width of about 8 nm as shown in Figure 5.17(b). After carbonization process of carbon microsphere particles, the particles have a porous structure as described in the previous section [39]. The internal structure of carbon microspheres after carbonization process was revealed by TEM as shown in Figure 5.18(a). The particle has more porous structure which can be seen around perimeter of the sphere. In addition, a sintering particle can be observed when temperature and reaction time increased [61]. Figure 5.18(b) shows a solid bridge between two particles. They have its nucleus which completely separated from each other.

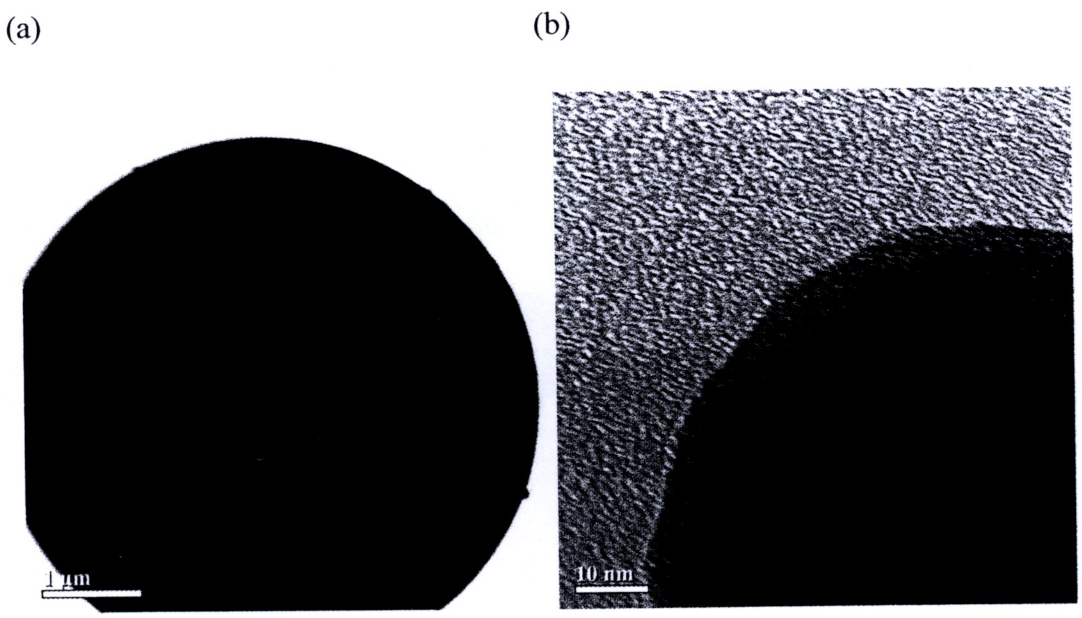

Figure 5.17 TEM micrographs of synthesized CMSs from hydrothermal process of native corn starch with initial concentration of 10wt% at 180°C for 24h

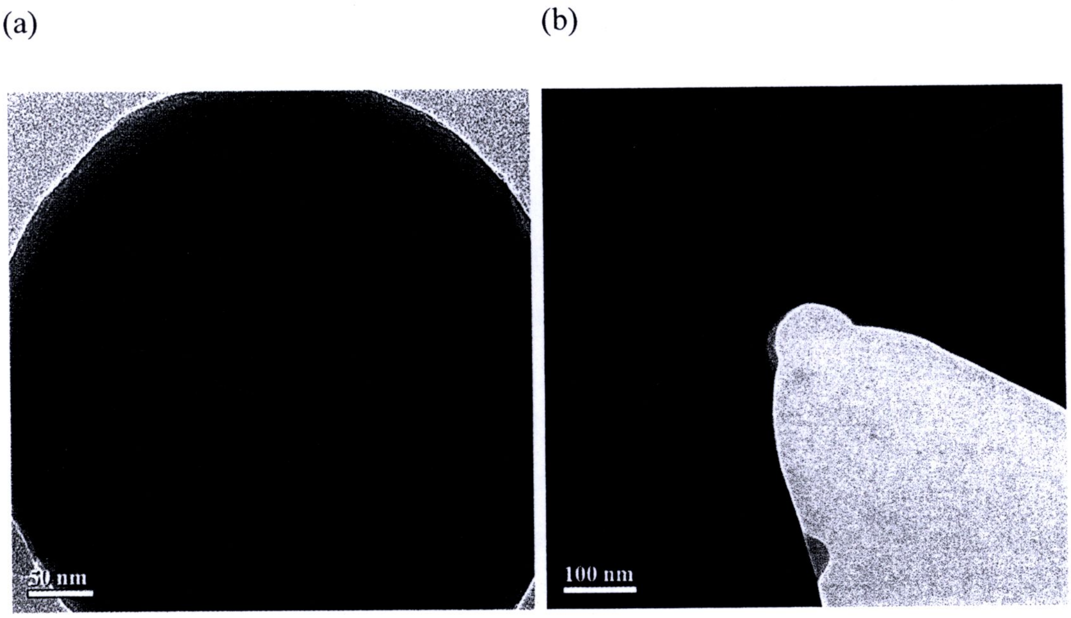

Figure 5.18 TEM micrographs of the porous CMS particles after carbonization process of native corn starch with initial concentration of 10wt% at 180°C for 24h

According to the aggregated CMS particles, the aggregated behavior still observed after carbonization process. It found that the solid bridge has strong structure which did not destroyed during carbonization process. Nanosphere particles can be observed in the hydrothermal process of native corn strach. The particles have particle size in the range of 150-200 nm as shown in Figure 5.19.

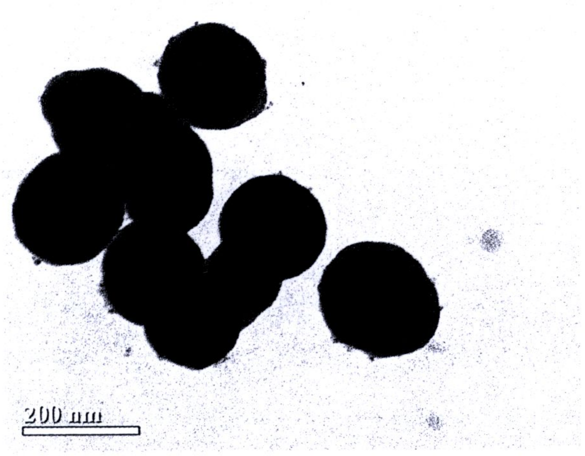

Figure 5.19 TEM micrograph of synthesized CMSs of native corn starch with initial concentration of 10wt% at 180°C for 24h (shown nanospheres)

5.4.2.6 Elemental components of porous carbon microspheres

The energy-dispersive X-ray (EDX) analysis (as shown in Table 5.6.) on porous CMS particles after carbonization process shows that carbon element is the main component of the porous CMSs. The oxygen component may mainly come from the absorbed water molecules on their surface [62]. The carbonization process mainly removed an oxygen and hydrogen components which contained in through the CMS particle structure [36]. The porous CMS particles were increased carbon content in their structures which were particularly inert properties [7]. The particularly properties were inert carbonaceous materials which were suitable for catalyst support application [8]. Although each CMS particles were obtained from different types of starch (native corn starch and HI-CAP®100), they had almost the same carbon content as shown in Table 5.6. All carbohydrates had different structures and compositions but they were hydrolyzed to yield glucose products. The glucose product subsequently dehydrated to form the intermediates for CMS formation. These behaviors were the same which caused almost the same structure of the CMS particles.

Table 5.6 The elemental components of porous CMSs from energy dispersive X-ray

The porous CMS	Carbon (wt%)	Oxygen (wt%)
Native corn starch	66.67	33.33
HI-CAP®100	71.08	28.92

5.5 Conclusions

In summary, the reaction temperature of hydrothermal process of native corn starch should be over up 140°C and the initial concentration were 10wt% for obtaining high yields and uniform spherical shape of CMS particles. The glucose yield rate (the hydrolyzed rate) from native corn starch was lower than the glucose yield rate from HI-CAP®100 because native corn starch was difficult to be hydrolyzed than HI-CAP®100. These hydrolyzed rates was consequently caused the CMS yield rate from HI-CAP®100 faster than the CMS yield rate from native corn starch. The reaction temperature strongly affected on primary particle size and aggregated CMS particles (secondary CMS particles). At 180°C, the primary CMS particles obtained from hydrothermal process of native corn starch with initial concentration of 10wt%, were approximate 5 μm in size after 24 hours of reaction time. The primary CMS particles were gradually developed to form uniform particle size when reaction time increased because of more hydrolyzed glucose in the system. The as-prepared CMS particles, therefore, became more uniform particle size when the reaction time increased to 24 hours. The formation mechanisms can be inferred that growth mechanisms played an important role in formation development of the CMS particles. On the other hand, at 220°C of reaction temperature, the primary CMS particles were approximate small 2 μm. The primary CMS particles were likely to aggregate at 220°C because the starch was rapidly hydrolyzed to yield glucose. Therefore, the hydrolyzed glucose which dramatically increased in the system also accelerated the CMS formation reactions. The fast CMS formation reactions caused the primary CMS particle sintered to form large secondary CMS particles. The large secondary CMS particles were revealed by the broad particle size distribution from laser scattering technique and by coefficient of variance (CV_g). From these results, the reactions in hydrothermal process of native corn starch are consisting of hydrolysis reaction of starch which mainly affected on reactions of CMS formation. Nonetheless, the sintering particles had its own nucleus but they had been only linked by solid bridge. The solid bridge of the aggregated CMS particles were still observed after carbonization process which were clearly evidenced by TEM results. The carbonization process of CMS particles can develop their porous structure. The porous CMS particles had micropore structure and typical specific surface area of 400-500 m^2/g. Moreover, the porous CMS particles also had more carbon content and partial crystallinity of graphite in their structure. Nonetheless, although the CMS particle had many particularly properties, the reactive functional groups on their surface were also removed during carbonization process.