

# Effect of Shear Rate and Soft-Templating Approach on Activated Carbon Microspheres Synthesized by Hydrothermal Carbonization

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## ABSTRACT

Carbon microspheres (CMSs) derived from corn starch were successfully obtained under hydrothermal carbonization (HTC). A 6-blade Pitched blade turbine (PBT) was employed to introduce the controllable shear rate and F127 as the soft template was utilized to find out their effect on the CMSs. The combination of shear rate and soft template method, introducing a controlled flow pattern based on fluid dynamics, provides an alternative to obtain CMSs with wider distribution of pore size and more mesopores, thereby enhancing their adsorption capability. The products were characterized using Scanning Electron Microscopy (SEM), Thermal Gravimetric (TG), and Brunauer-Emmett-Teller (BET) model. The results revealed that the morphology and structure of CMSs were strongly influenced by the shear rate induced by the rotated PBT during the hydrothermal reaction. At a rotating speed of 60rpm, the CMSs showed the maximum CO<sub>2</sub> adsorption rate at 25 °C and 0.15 bar CO<sub>2</sub>, with a specific surface area of 475 m<sup>2</sup>/g and an average pore diameter of 2nm. Furthermore, the diameter of CMSs decreased with an increase of rotating speeds. The assembly of F127 resulted in products with low degree of sphericity forming a chain, which significantly increased the BJH Adsorption/Desorption average pore width (4V/A). Hence, the controllable shear rate offers an alternative approach to explore the property of CMSs.

**Keywords:** carbon microsphere, hydrothermal reactor, soft template, 6-blade PBT, shear rate, fluid dynamics

## NONMENCLATURE

### Abbreviations

HTC	Hydrothermal carbonization
CMSs	Carbon microspheres
MCMs	Mesoporous carbon microspheres

F127	PEO106PPO70PEO106
PBT	6-blade Pitched blade turbine with blade angle of 45°
Re	Reynolds number
<i>Symbols</i>	
$\gamma$	Shear strain rate

## 1. INTRODUCTION

Porous carbons have been widely used in many industries, including gas separation process, water purification, catalyst supports, electrodes for electrochemical double layer capacitors and fuel cells[1]. Previous studies have focused on exploring different biomasses as carbon precursors and optimising synthesis processes to improve the physical and chemical properties of porous carbon. Hydrothermal carbonization (HTC) is a promising method to prepare different carbon materials, such as carbon spheres, carbon nanofibers, and carbon nanosheets. Compared to other carbonisation methods, such as ignition, pyrolysis, and gasification, HTC is a cost-effective and environmentally friendly process that can achieve biomass carbonisation at lower temperatures (< 250 °C). During HTC, biomass is processed in hot self-pressured water, which produces hydro-char, mixed liquid, and gases after hydrolysis, dehydration, decarboxylation, and aromatisation. HTC has been widely used in the production of fuels and other energetic materials in the industry.

Several biomasses have been investigated as carbon precursors to prepare Carbon Microspheres (CMSs) using HTC, including xylose [2, 3], glucose [4-6], fructose [7], sucrose, lignin, cellulose, polydopamine. Starch has a natural spherical structure with heteroplasm content, which results in it could regenerate biomass at a low cost. Starch is an attractive biomass source for carbon materials due to its natural spherical structure with

heteroplasm content. It can be carbonised into special structures (spherical, bowl-shaped, and honeycomb) using a simple procedure and is suitable for large-scale production. The microstructure and number of functional groups on the surface of starch-based CMSs can be controlled by adjusting the synthesis conditions to meet specific requirements. Although starch is a cheaper and more readily available biomass source, it has been rarely studied as a carbon precursor for CMSs using HTC due to its inability to dissolve in water and form a clear uniform solution. However, some recent studies have shown promising results. For instance, Liang and his co-workers [8] obtained a diameter of 10nm of CMSs by adjusting pH value of starch solution during HTC process. Cui et al. [9] used iron oxide nanoparticles and iron ions to synthesise nanosized and micro-sized CMSs from starch using HTC. Zheng et al. [10] regulated the concentration of the starch solution and increased the heating rate and temperature to 600 °C to prepared CMSs. Despite significant efforts, achieving highly purified carbon microspheres using traditional hydrothermal processes remains challenging.

Another major issue with CMSs produced through HTC is their low porosity. Carbon microspheres with pore diameters between 2nm and 50nm are classified as mesoporous carbon microspheres (MCMs) based on their size. The mesoporous texture and specific surface area of MCMs make them excellent absorbents. To control the porous structure of carbon materials and obtain uniform and monodispersed MCMs, a suitable template is required to fabricate a mesoporous structure for carbon microspheres to assemble. There are two types of templates commonly used: hard templates and soft templates. Hard templates, mostly made of silica materials, have a porous structure that serves as a mold for carbon precursors to fill into the pores. There are no chemical interactions between the template and the carbon precursors during this process. Hard templates offer pore structures to carbon precursors and need to be dissolved by hydrofluoric acid or strong base after sol-gel precipitation, chemical vapor deposition, or chemical polymerization filling. The predetermined pore structures and complex preparation process of hard templates have prompted researchers to explore soft templates, which can assemble with carbon precursors during co-condensation and carbonization processes. Soft templates are manipulated by chemical interactions such as hydrogen bonding and ion interactions at the molecular level and space through the self-assembly of carbon precursors and specific organic molecules. The pore structures can be regulated by controlling the

synthetic process, such as adjusting the ratios of biomass/agents, temperatures, and operating processes. Much attention has been given to mesoporous-inducing agents such as PEO<sub>106</sub>PPO<sub>70</sub>PEO<sub>106</sub> (F127) [11-13] and P123 [14, 15] to prepare mesoporous carbon spheres with excellent performance.

In the hydrothermal carbonization process, many factors influence the yield and characteristics of achieved carbon microspheres. Sevilla, M., & Fuertes, A. B. [16] modified the synthesis conditions (temperature, reaction time and concentration) to modulate the diameter of the CMSs successfully. Zheng et al. [10] used alcohol to direct the structure of self-assembled carbon microspheres. Ryu et al. [17] reported a 20% increase in carbon yield by adding phloroglucinol to sugar as the carbon precursor. Most studies published in this area focus on the synthesized materials and chemical reactions. Surprisingly, few studies concentrate on the transport phenomena, for instance, the mechanisms of heat and mass transfer within this system. Most HTC process studies are conducted in non-stirred reactors. The solid-liquid system formed by the raw material in water suspended or precipitated is not uniform in the reactor due to the physical properties of different carbon precursors and water. The concentration gradient of mixture inside the reactor can generate further temperature gradient and aggregation of material during the reaction time. These can significantly hinder the reaction mechanisms, material, and power utilization. Stirring can help maintain a uniform condition of the biomass/water mixture and transport heat to distribute homogeneously, providing different intensities of shear rate to shape the diameter and morphology of the CMSs.

Therefore, the main objective of this study is to use the HTC stirred reactor to carbonize corn starch as the carbon precursor, evaluate the effect of shear rate and a soft template on the characteristics of HTC products, and find a controllable method to obtain uniform size, surface area and pore volume of CMSs. Different rotating speeds were adopted to understand the influence of homogeneity and distribution of biomass with and without a template inside the reactor on the characteristic of products. The carbon derived from the pyrolyzed process was investigated under a series of experimental techniques, including scanning electron microscopy (SEM) for morphology, BET, as well as TGA.

## **2. MATERIAL AND METHODS**

### *2.1 Materials*

F127 (EO<sub>126</sub>PO<sub>70</sub>EO<sub>106</sub>, Pluronic®F-127, Sigma-Aldrich chemical Co., Ltd.), corn starch was kept in an oven overnight at 105°C to remove moisture and maintain a constant weight, deionized water, magnetic stirred (IKA, Germany), ethanol absolute (C<sub>2</sub>H<sub>6</sub>O).

## 2.2 Carbon syntheses

Figure 1 displays the schematic synthesis process of carbon microspheres. The hydrothermal carbonization (HTC) experiments were conducted in a 2L stainless steel autoclave equipped with mechanical stirring. The mass ratio of starch/F127 was 6:1. Typically, the synthesis process was carried out as follows: 3g of F127 was dissolved in 100ml of deionized water at 30 °C using magnetic stirring for 30 minutes. Then, 18g of starch was added to the solution and stirred for another 30 minutes. The above solution was diluted to 300ml, sealed into the autoclave, and treated at 220 °C for 3 hours. After the thermal treatment, the reactor was cooled down to room temperature, and the obtained brown solution with precipitation was taken out, filtered, and washed with water and ethanol to remove the soluble residues. The obtained carbons were dried at 105 °C for 12 hours. Finally, the carbons were carbonized in a tube furnace (KeJing 1400XL) under a N<sub>2</sub> atmosphere (200 ml/min). The heating process was as follows: the temperature increased to 350 °C from room temperature at a heating rate of 5 °C/min and held for 60 minutes, then increased to 800 °C at a heating rate of 10 °C/min and held for 2 hours. After the tube furnace cooled down to room temperature, the CMSs were obtained and designated as CMS-2, CMS-4, and CMS-6 according to the different rotating speeds. CMS-1, CMS-3, and CMS-5 were obtained without adding the soft template F127. The reaction conditions listed in Table 1 were designed through the orthogonal method using the IBM SPSS Statistics software.

## 2.3 Sample characterization

The morphology of the CMSs was analysed by emission scanning electron microscopy (SEM, SU8000 Hitachi) at 15 kV. The surface textural properties of all prepared CMSs were determined from N<sub>2</sub> adsorption-

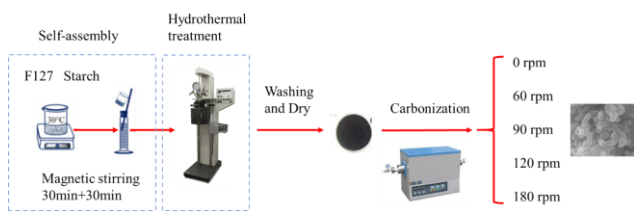


Fig. 1. Preparation process of CMSs and polymerization of precursors.

desorption isotherms obtained at -196 °C using a Micromeritics ASAP2420 instrument. The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) method based on N<sub>2</sub> adsorption isotherms in the relative pressure range of 0.01 to 0.1. The pore size distribution (PSDs) was examined using the Density Functional Theory (DFT) model. Thermogravimetric analysis (TGA, Q500, TA instruments) was used to determine the dynamic CO<sub>2</sub> adsorption properties of the CMSs at 25 °C and 0.15 bar CO<sub>2</sub>.

Table 1. The different reaction conditions of preparing carbon microspheres (CMSs).

Sample	Template F127/Starch	Stirring speed (rpm)	Temperature (°C)	Reaction time (h)
CMS-1	0	0	220	3
CMS-2	1:6	0	220	3
CMS-3	0	60	220	3
CMS-4	1:6	60	220	3
CMS-5	0	120	220	3
CMS-6	1:6	120	220	3
CMS-7	1:6	90	220	3
CMS-8	1:6	180	220	3

## 2.4 Computational approach and methodology

The computational fluid dynamics (CFD) approach was employed to obtain the velocity flow field and shear rate distribution in the hydrothermal carbonization (HTC) process. The simulated HTC setup consists of a reactor vessel, an S-shaped tube, and a six-blade Pitched blade turbine. As depicted in Figure 2, the internal height (H) and diameter (T) of the HTC vessel are 266.7mm and 101.6mm, respectively. The diameter of the impeller (d) is 48mm, and it is oriented at a pitched angle of 45°. The mesh used for simulation was generated using GAMBIT (Version 2.4.6), with a total mesh count of 1.6×10<sup>6</sup>.

To simulate the rotational behaviour of the impeller, two domains were considered: one represents the stationary bulk flow, while the other one encloses the impeller, enabling the modelling of its motion using the Multiple Reference Frame (MRF) method. ANSYS Fluent 2021 R1 was utilized to simulate the mixing phenomena in the HTC. To simplify the simulation conditions and reduce computational expenses, the RNG k-ε model were adopted for the system.

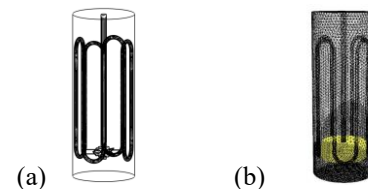


Fig. 2. Internal geometry of the HTC (a), and mesh with rotating region (b) used for numerical simulation.

### 3. RESULTS AND DISCUSSION

#### 3.1 Flow fields in the HTC

Shear is a tangential force that acts on the surfaces that it is applied to. The presence of velocity gradients within the fluid flow gives rise to shear stress. To put it differently, when fluid flows at different speeds in adjacent layers, it causes a slowdown in one layer and an acceleration in another. The rotating impeller in the HTC induces fluid motion around it with a certain velocity, leading to velocity gradients and thus shear force. Consequently, shear force can be linked to the rotating speed of the impeller. Understanding shear rate is essential for two main reasons: (1) shear rate impacts the average turbulent viscosity of non-Newtonian fluids, thereby influencing power consumption, mixing performance, and mass transfer rate [18]; (2) inappropriate shear rate can lead to damage to microorganisms, bioflocs, and other suspended solids [19]. Numerous researchers have correlated shear rate

consumption, which depends on the power number and rotating speed of the impellers. For instance, Pérez et al. [20] investigated the relationship between rotating speed and average shear rate in a stirred reactor and found that the average shear rate  $\gamma$  as a function of the rotating speed  $N$  of the impeller under different conditions. For the laminar flow ( $Re < 10$ ), they found  $\gamma = \text{constant} \times N$ , and for the turbulent flow ( $Re > 10^4$ ),  $\gamma = \text{constant} \times N^{3/2}$ .

Figure 3 presents the simulation results in the HTC at a rotating speed of 120rpm in gas-liquid system. The simulation process focused on the shear force caused by the rotating PBT impeller and ignored heat transfer conditions, maintaining room temperature. The PBT impeller is an axial flow impeller known for its excellent circulation capability, contributing to liquid blending and solid suspension. In Figure 3(a), the velocity flow field shows that the liquid around the PBT impeller has higher velocity, leading to a high strain rate in Figure 3(b), turbulent kinetic energy in Figure 3(c), and turbulent intensity in Figure 3(d). The liquid phase exhibits relatively high turbulent characteristics compared to the gas phase. The forceful discharge flow from the impeller alters the state of the liquid in the reactor from a macroscopic perspective. On a micro level, the shear strain rate generated during the forming process rubs the carbon spheres, influencing the morphology of the obtained CMS.

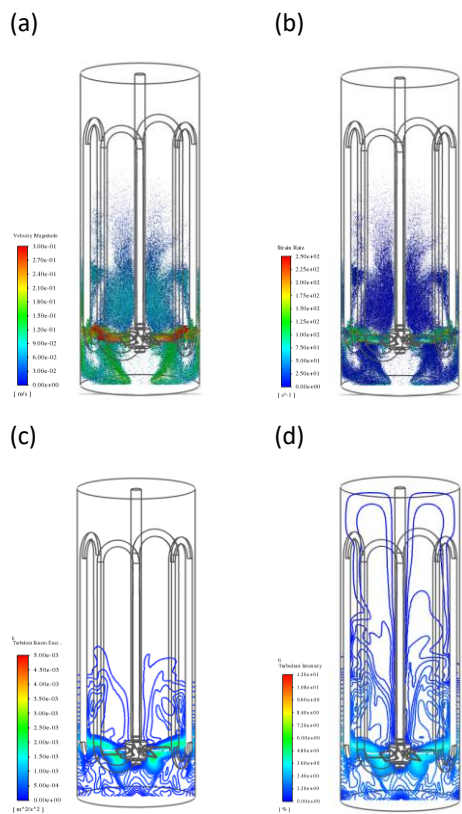


Fig. 3. Simulation results from k-ε model after 12s at x-z plane: (a) velocity vector flow field, (b) strain rate vector field, (c) contour of turbulent kinetic energy, and (d) contour of turbulent intensity.

with the rotating speed of impellers or the power

#### 3.2 Morphologies of obtained CMSs

illustrates the morphology of the CMS-5 and CMS-6 prepared by hydrothermal carbonization at rotating speed of 120rpm. The panoramic SEM images in Figure 4(a) reveal that the samples consist of numerous homogeneous microspheres with an approximate diameter of 0.5μm. Most particles exist as single spheres, and the presence of clumps is not noticeable. These findings align well with the observations made in the study conducted by Zheng et al., (2009). Figure 4(b) shows an enlarged area of Figure 4(a) and demonstrates the perfect spherical morphology of the CMSs with a smooth surface. These microspheres are generally monodispersed, with diameters ranging from 400 to 500nm. Comparatively, Figure 4(c) displays the synthesized CMSs using a soft template under the same rotating speed. A short-chain structure is evident, wherein several CMSs are connected in a chain-like arrangement. It is apparent that the diameter of the

CMSs in Figure 4(d) increases to around 700nm, and their morphology stretches into an oval shape.

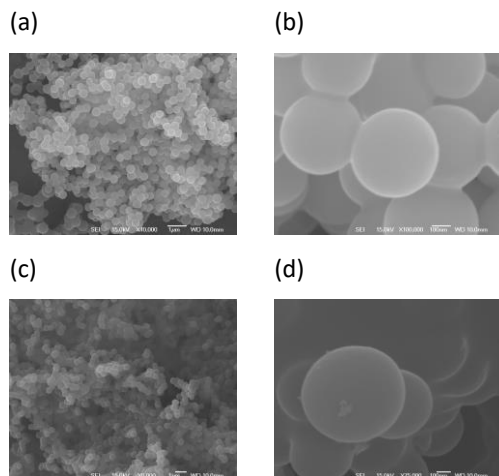


Fig. 4. SEM images of the samples synthesized from the corn starch with and without F127 at rotating speed of 120rpm.

### 3.3 The effect of shear rate on CMSs

In this study, the starch solution under the hydrothermal carbonization process with different rotating speeds at a proper reaction time and temperature yielded highly intriguing results. The rotating speed of the impeller played a significant role in the fluid dynamics within the reactor, affecting the synthesis process of CMSs. Figure 5 displays the CO<sub>2</sub> absorption rate of the CMSs derived from starch with F127 as the soft template under various rotating speeds. As shown in Figure 1, the presence of F127 facilitated an intermolecular condensation process, leading to the transformation of starch into furfural, followed by

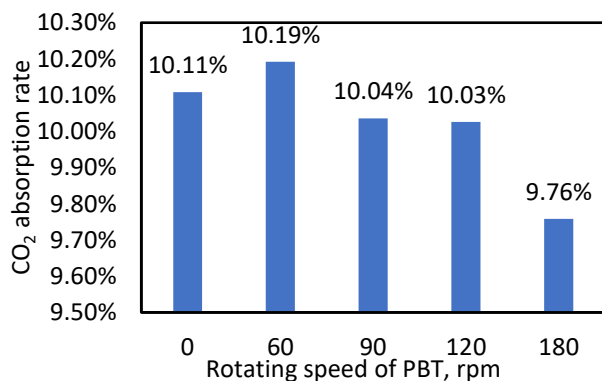


Fig. 5. Effect of rotating speed on the CO<sub>2</sub> absorption rate of CMSs obtained from TG results (reaction conditions: 18g of starch, 3g of F127).

polymerization into a benzene ring structure to create a gel with F127. Subsequently, a high-temperature thermal treatment under a nitrogen atmosphere was employed to remove oxygen and protium from the self-assembly gel. The rotating speed during the HTC stirred reactor played a crucial role in the process of polymerization and fabrication, as demonstrated in Figure 6. When comparing CMS-2 (without stirring) to CMS-4 at a rotating speed of 60rpm, the maximum CO<sub>2</sub> absorption rate measured by TG was found to be 10.19% for CMS-4. This indicates the significance of stirring in enhancing the CO<sub>2</sub> absorption rate during the synthesis process.

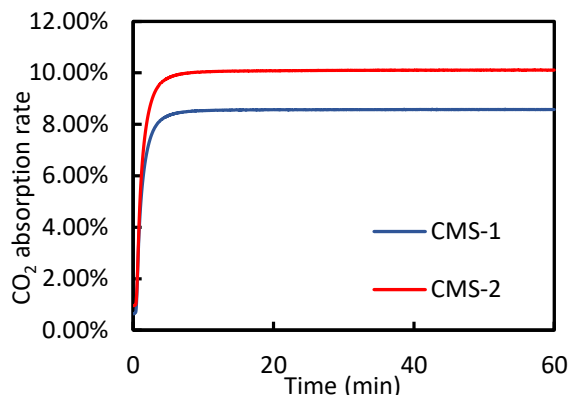


Fig. 6. Effect of the soft template on the CO<sub>2</sub> absorption rate of CMSs obtained from TG results without shear force influence.

Nevertheless, as the rotating speed continues to increase, the CO<sub>2</sub> absorption performance of the CMSs deteriorates. This phenomenon can be attributed to the fact that the starch solution is a typical non-Newtonian fluid, characterized by its viscosity changing in response to pressure or speed variations. With higher pressure or speed, the viscosity of the fluid increases rapidly, and in extreme cases, it can even transiently behave like a solid. This observation explains the diminishing performance

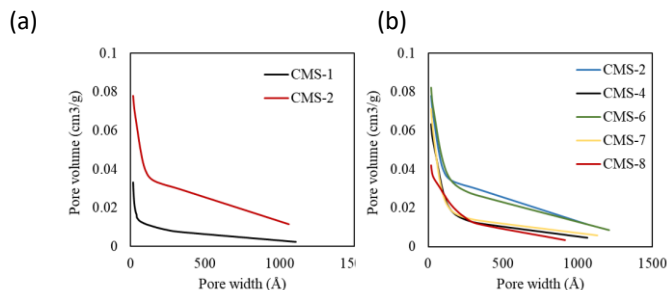


Fig. 7. BJH adsorption cumulative pore volume curve.



Table 2. Specific surface area, pore volume and the DFT pore size distribution information of the CMSs

Samples	SBETa(m <sup>2</sup> /g)	Smicb(m <sup>2</sup> /g)	Sextc(m <sup>2</sup> /g)	Vmicd(cm <sup>3</sup> /g)	BJHadse(cm <sup>3</sup> /g)	BJHdesf(cm <sup>3</sup> /g)	Daveg(Å)
CMS-1	475	469	6.127	0.185	0.033	0.029	16.984
CMS-3	381	379	1.561	0.143	0.010	0.001	15.454
CMS-5	430	427	2.803	0.165	0.014	0.009	15.978

- a BET surface area  
 b Micropore surface area  
 c External surface area  
 d Micropore volume  
 e BJH Adsorption cumulative volume of pores between 19.000 Å and 4,000.000 Å width  
 f BJH Desorption cumulative volume of pores between 19.000 Å and 4,000.000 Å width  
 g Desorption average pore diameter (4V/A by BET)

of the CMSs when the rotating speed surpasses 60rpm. Under high rotating speeds, the intense shear force exerted by the rotating impeller leads to a significant increase in the solution's viscosity within the reactor. This increase in viscosity becomes detrimental to the polymerization and fabricating processes, thus resulting in the worsening performance of the CMSs.

The effect of the template on the performance of CO<sub>2</sub> absorption of CMSs is shown in Figure 7(a) and Figure 8(a) without the influence of stirring. It is obvious that the CO<sub>2</sub> absorption rate of CMS-2 is approximately 20% higher than that of CMS-1 in Figure 7. And the BJH desorption dA/dlog(w) pore area of CMS-2 shows a peak at 40 Å, while that of CMS-1 concentrates on lower power width. The comparisons of the BJH adsorption cumulative pore volume and desorption pore area as a function of pore width among CMS-2 to CMS-8 formed by the starch with F127 at different rotating speeds are shown in Figure 7(b) and 8(b). As rotating speed of the PBT impeller enhanced to largest, CMS-8 displays the

morphology of CMSs appears to be strongly influenced by the rotating speed of impeller. The starch after dehydrating polymerization was integrated with F127 without mechanically stirring and wrapped the F127 micelle, resulting in nonporous carbon spheres. However, the self-assembly process between starch and F127 was completely disorganized with shear force, resulting in a large number of amorphous CMSs rather than carbon spheres. The self-assembly process between xylose and F127 was disrupted to some extent by the axial flow pattern of solutions under a proper rotating speed, leading to a loose spherical composite and porous carbon spheres after carbonization. As a result, a suitable stirring speed aids in the creation of porous carbon spheres with a limited size distribution and homogeneous pores size. A high surface area and fine porosity can offer an effective structure for the accumulation of adsorbed gas.

### 3.5 N<sub>2</sub> adsorption and desorption

The nitrogen adsorption-desorption test was used to measure the specific surface area and pore structure of the prepared carbon material in order to investigate the relationship between the structure of the prepared material and the performance of the adsorption property. Figure 9 shows the N<sub>2</sub> adsorption-desorption isotherms for CMSs. According to the categorization of physical adsorption isotherms by the International Union of Pure and Applied Chemistry (IUPAC), adsorption isotherms can be classified into six types (I-VI) and the hysteresis loop is divided into four groups (H1-H4). As shown in Figure 9, all the hysteresis loops are relatively narrow, and the adsorption-desorption curve display horizontal direction. The loop types agree with I/IV mixture. With increase of pressure, the adsorption volume continuously increases at a slow rate. Compared with obtained CMSs without soft-template in Figure 9(a), the wider hysteresis loops appear between P/P0 values

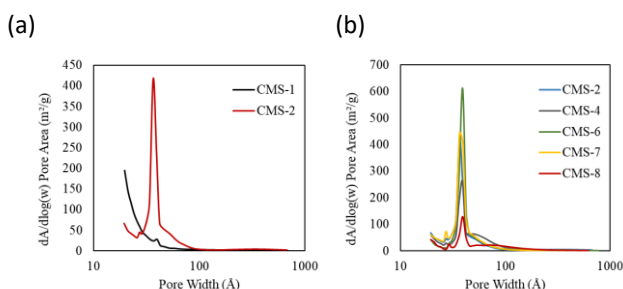


Fig. 8. BJH desorption dA/dlog(w) pore area curve.

smallest the pore volume and pore area. Although the tendencies of them highly display agreements.

### 3.4 Pore size distribution of CMSs

The specific surface area, pore volume and the DFT pore size distribution information of the CMSs are shown in Table 2. The specific surface area for CMS-3 is 381 m<sup>2</sup>/g that is smallest compared with CMS-1 and CMS-5. The

of 0.4 and 0.9, which indicate the wide distribution of particle size and diversified pore types in Figure 9(b). That presents the effect of soft-template on the obtained material, which helps to develop more mesoporous and enlarge the distribution of pore size. The slight H2 type of the hysteresis loop shows the existence of a quantitative mesoporous as well. The prepared material has a multistage structure with microporous, mesoporous, and macroporous pores, which helps to improve the adsorption capability of CO<sub>2</sub>. In addition, the

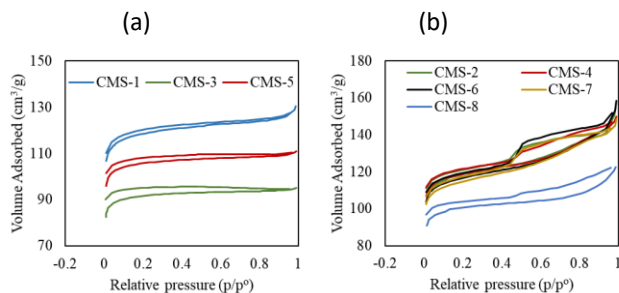


Fig. 9. N<sub>2</sub> adsorption and desorption isotherms for CMSs under different conditions.

lower volume adsorbed value of CMS-8 might be caused by the high rotating speed that leads to high shear force in the HTC during hydrothermal process, which hinders the formation of carbon spheres.

#### 4. CONCLUSION

In summary, a series of CMSs were successfully synthesized from corn starch through a hydrothermal carbonization process, employing various rotating speeds. The results demonstrated that mechanical stirring had a significant impact on the morphology and performance of the CMSs. At a rotating speed of 60rpm, the CMSs exhibited the maximum CO<sub>2</sub> adsorption rate at 25 °C and 0.15 bar CO<sub>2</sub>, with a specific surface area of 475 m<sup>2</sup>/g and average pore diameter of 2nm. As the rotating speed increased, the diameter of the CMSs decreased.

The introduction of F127 during the synthesis process resulted in products with a low degree of sphericity, forming a chain-like structure, leading to a noticeable increase in the BJH Desorption average pore width (4V/A). Furthermore, the study revealed that a small shear rate was conducive to building a spherical structure with a uniform size, while a higher shear rate led to the rapid formation of smaller products with higher pore volume. However, excessively high shear rates were found to have a damaging effect on the CMS structure.

These findings hold promise for the development of novel methods to synthesize CMSs with enhanced

properties for gas separation and purification applications. The ability to control the shear force during the synthesis process offers a valuable avenue for exploring the properties of CMSs and tailoring their characteristics to meet specific application requirements.

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