CHEMICAL ENGINEERING TRANSACTIONS
VOL. 62, 2017

A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Fei Song, Haibo Wang, Fang He

ISBN 978-88-95608- 60-0; **ISSN** 2283-9216

DOI: 10.3303/CET1762107

Carbon Molecular Sieve (CMS) Design for Air Separation of Buckwheat Hulls

Xinghua Peng, Gaohua Jiang*, Yongze Liu

Department of Resources and Enviroment, Yunnan Vocational Institute of Energy Technology, Qujing 655001, China
jianggaohua@163.com

This paper attempts to prepare a granular CMS for air separation of buckwheat hulls, and analyse the effect of different factors on the air separation effect. With coal tar as the binder, the CMS was created via mixing, extrusion moulding, carbonization and pore regulation. The pore morphology was controlled by the immersion method. The results indicate that the optimal carbonization conditions are the heat treatment at 700℃ for 35mins at the heating rate of 4℃/mins. Under these conditions, CMS reached the best performance (the N_2 can be enriched to 88.5%). The addition of pore-forming agents and medium-temperature coal tar could further improve the air separation performance. With the optimal dosage of these additives, the N_2 can be enriched to 90.5%.

1. Introduction

The carbon molecular sieve (CMS) is a slit-like micro-pore structure of carbon-based adsorbents (pore size: 0.4 nm~0.9nm), capable of separating molecules with different molecular sizes (Ruthven, 1984). Nowadays, commercially available CMSs are mainly produced by Takeda (Japan), BF (Germany) and MAST (UK) (Hu and Vansant, 1995). With a broad range of raw materials, the CMS enjoys many advantages, including but not limited to a large specific surface area, an adjustable pore structure, high thermal and chemical stability, and an excellent adsorption performance (Carrott et al., 2006; Zhao et al., 2015). Over the years, the CMS has been extensively applied in air separation and purification, wastewater treatment and energy storage, particularly in the enrichment of nitrogen from the air (Sevilla et al., 2011; Zhang et al., 2011; Harmas et al., 2016; Thomberg et al., 2011; Zhai et al., 2012). For air separation, the micro-pores of the CMS must be controlled strictly in the range of 0.3nm~0.4nm. Recent years has seen the emergence of a CMS made of renewable cheap carbon containing organic compounds (Titiric and Antonietti, 2010). The samples prepared with the CMS boast well-developed pore structure and stable chemical properties.
This paper attempts to prepare a granular CMS for air separation of buckwheat hulls, a by-product of buckwheat processing. With coal tar as the binder, the CMS was created via mixing, extrusion moulding, carbonization and pore regulation (Liu et al., 2013; Sun et al., 2013; Zhao et al., 2014; Zhang et al., 2010). The pore morphology was controlled by the immersion method. During the research, the author investigated how carbonization temperature, heating rate, soaking time, pore addition agent, dipping solution concentration and the dipping time influenced the air separation performance of the CMS (Sun et al., 2014; Zhang et al., 2010; Wang et al., 2015; Xu et al., 1999).

2. Experiment

2.1 Raw materials, reagents and equipment

The raw materials mainly involve buckwheat hulls, medium-temperature coal tar, high-temperature coal tar, and coal liquefaction residues. The reagents were provided by Zhanyi Coking, including benzene, coal pitch and high-temperature coal tar. The main equipment was a tube-type electric heating furnace, a temperature controller, a pulveriser, a press machine, and a molding machine.

2.2 Preparation

(1) Preparation of buckwheat CMS precursor
The buckwheat hulls were dried at 110 ℃ for 8 hours, and then ground into powders. The pore forming agent was added by a certain proportion and mixed evenly with the hull powders. The mixture was squeezed into 2.5mm-diameter and 4mm-height particles in the moulding machine.
(2) Carbonization and carbon deposition
The precursor of the granular CMS was placed into the tube-type electric heating furnace, and heated up to a certain temperature under the protection of nitrogen. The temperature was maintained constant for a certain period of carbonization. After that, the buckwheat hulls were dipped in different dipping solutions for a certain period of time, and dried again in the furnace. Under high-temperature pyrolysis, the carbon molecules on the organic surface of buckwheat hulls moved freely through the CMS pores.

2.3 Air separation performance test

The single-column breakthrough curve method was adopted to test the air separation performance of the CMS. The adsorption column length was 600mm, the inner diameter Φ was 12mm, and the filling height was 500mm. The bottom of the packed column was covered with a 100mm-tall silica gel. The test pressure, desorption pressure and desorption time were set to 0.3MPa, 0.6MPa and 60s, respectively. The outlet oxygen content of an air separation unit was measured by an oxygen analyser, and the content of non-oxygen gas, i.e., the volume concentration of N_2, was regarded as the detection index of CMS air separation capacity (Mi, 2013; Fu and Guo, 2008).

3. Experimental Results and Discussion

3.1 Effect of carbonization on air separation performance

The carbonization has a major impact on the air separation performance of the CMS for it directly affects the pore structure the sieve. In the carbonization process, the volatile components of CMS precursor particles deposit in various ways, depending on the carbonization temperature, heating rate and soaking time.
(1) Orthogonal test
The effect of carbonization on air separation performance was examined by orthogonal test when the CMS precursor was effectively moulded. The experimental results are shown in Table 1.

Table 1: Results of orthogonal test

No.	Heating rate (℃/min)	Final carbonization temperature (℃)	Temperature constant time (min)	Air separation nitrogen content-82 (%)
1	3	650	30	2.13
2	3	700	35	0.89
3	3	750	40	-0.62
4	4	650	35	4.59
5	4	700	40	1.23
6	4	750	30	-0.13
7	5	650	40	0.38
8	5	700	30	0.97
9	5	750	35	-0.28
K1	2.29	7.08	3.11	
K2	5.62	2.78	5.36	
K3	1.23	-0.87	0.77	
k1	0.75	2.45	1.23	
k2	1.97	0.95	1.69	
k3	0.45	-0.92	0.28	
R	1.37	3.28	1.5	
variance	1.42	9.96	3.41	Q_e=1.568
Degree of freedom	2	2	2	
F	2.28	20.39	6.51	

From Table 1, it can be seen that the range RB > RC > RA, that is, factor B, the final carbonization temperature, has the greatest influence on the air separation performance. The variance FB (2, 6)=19.58>

F0.975(2,6)=6.86 also makes the final carbonization temperature as the leading influencing factor and puts the test accuracy at 97%.

Hence, the variance analysis is consistent with the range analysis. The optimal carbonization conditions were derived as follows. The final carbonization temperature should be 700℃, the soaking time should be 35mins, and the heating rate should be 4℃/min. Under these conditions, the CMS can achieve the best performance, and the nitrogen concentration is up to 88.5%.

(2) Effect of final carbonization temperature of on air separation performance

During the carbonization of buckwheat husks, a large amount of micropores are formed, and the final temperature of carbonization determines the degree of devolatilization and has a significant influence on the pore structure of CMS. The thermal gravimetric analysis of buckwheat husk is shown in Figure 2.1. The heating rate is 4℃/min.

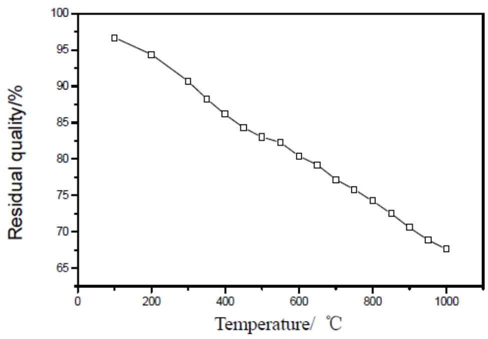

Figure 1: Relationship between thermal weight loss temperature and buckwheat hulls temperature

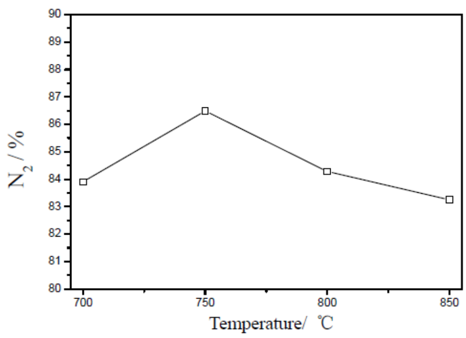

Figure 2: Effect of carbonization temperature on air separation performance

The thermal gravimetric analysis of buckwheat hulls was conducted at the heating rate of 4℃/min (Figure 1), and the effect of carbonization temperature on air separation performance was investigated at the same rate and the soaking time of 35mins (Figure 2).

According to Figures 2.1 and 2.2, the CMS air separation performance was obviously improved as the carbonization temperature increased from 600℃ up to 700℃; meanwhile, the nitrogen concentration increased from 83.5% to 86.5%. The weight loss was close to 22% at 700℃. Further temperature increase led to a substantial decline in air separation performance. The nitrogen concentration was only 83.5% at 900℃.

The trends indicate that 700℃ is the ideal temperature. Any further growth in temperature only induced de-volatilization of buckwheat hulls, and narrowed down the effective pore space for air separation.

(3) Effect of heating rate on air separation performance

The effect of different heating rate on the air separation performance was studied at the final carbonization temperature of 700℃ and the soaking time of 35 mins. The results were illustrated in Figure 3.

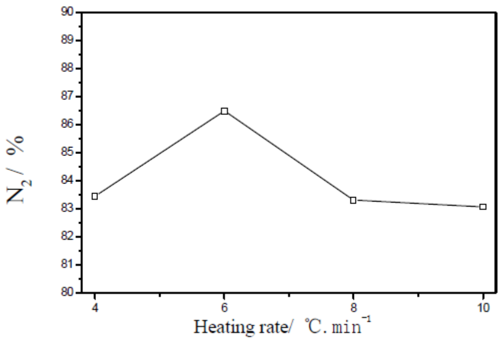

Figure 3: Effect of heating rate on air separation performance

As shown in the figure above, the nitrogen concentration shifted from 83.5% to 86.5% as the heating rate increased from 2℃/min to 4℃/min. As the heating rate continued to rise, the air separation performance entered a downturn. When the heating rate climbed up to 8℃/min, the nitrogen concentration was as low as 83%.

If the heating rate is too slow, the CMS precursor will be poorly heated and the volatility will be rather limited; this condition constrains the development of micro-pores, and, in turn, dampens the air separation effect. If the heating rate is too fast, there will be too many large pores on the CMS, leading to poor selective gas adsorption and subpar air separation performance. Therefore, the optimal heating rate is 4℃/min.

(4) Effect of soaking time on air separation performance

The effect of soaking time on the air separation performance was explored at the final carbonization temperature of 700℃ and the heating rate of 4℃/min. The results are shown in Figure 4.

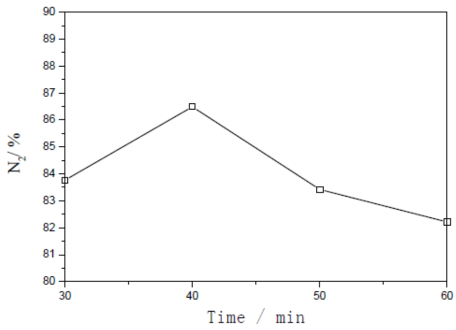

Figure 4: Effect of soaking time on air separation performance

According to Figure 4, the air separation performance increased slightly with the increase of the soaking time before the latter reached 35min. At 35min, the nitrogen concentration reached 86.5%. When the soaking time exceeded 35min, the air separation performance plunged dramatically, as evidenced by the nitrogen concentration (82.3%) at 55min. It is clear that the optimal soaking time is 35min.

After the soaking time, the carbonization temperature reaches 700℃. In this stage, the CMS pores are mainly formed by thermal condensation and cracking of high-temperature coal tar. If the soaking time is too short, there will not be enough contraction of large pores, which hinders the pore adjustment and air separation. If the soaking time is too long, the micro-pores will be over-contracted and evenly plugged by carbon deposition. In this case, the air separation effect is neither desirable.

3.2 Effect of additives on the air separation performance

To improve the air separation performance, several kinds of additives were adopted for this research, including pore forming agent, medium-temperature coal tar, high-temperature coal tar, coal liquefaction residues, etc. Among them, the pore forming agent, consisting of many volatile components, is cheap and convenient to obtain; the coal tars can release free carbon at high temperature and regulate the pores in the CMS.

(1) Effect of pore forming agent on the air separation performance

The pore forming agent mainly encompasses branched hydrocarbons. Most of its components are volatile at 300℃. It can increase the number of micro-pores, thus improve the air separation performance. The effect of pore forming agent was investigated at the final carbonization temperature of 700℃, the heating rate of 4℃/min and the soaking time of 35min (Figure 5).

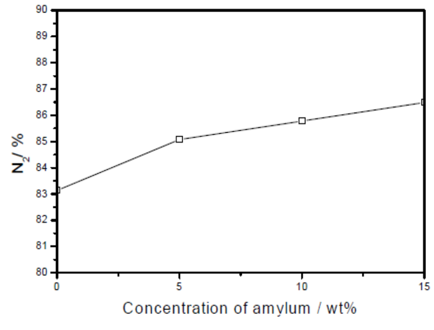

Figure 5: Effect of pore forming agent on the air separation performance

As can be seen from Figure 5, the air separation performance increased with the dosage of the pore forming agent. The trend can be explained by the low volatile point of the agent, which is the mainly cause of pore formation in the CMS. The addition of the agent can increase the number of effective holes and improve the air separation effect. At the dosage of 15%, the CMS had the best air separation performance: the nitrogen concertation was 86.5%, 3.3% higher than that without adding pore forming agent. The dosage should not be further increased. Otherwise, it might affect the strength of the CMS.
(2) Effect of coal tars on air separation performance
The medium-temperature coal tar mainly consists of polycyclic and monocyclic aromatic hydrocarbons. With a complex structure, the coal tar functioned as a bonding agent that enhanced the strength of the CMS in the carbonization process. The high-temperature coal tar also had a strength enhancement effect, as its softening point is as high as 110℃ and its molecular weight is much greater than common coal tar. The coal liquefaction residues, containing 2-3 ring aromatics and cycloalkanes, are an ideal pore-forming agents. The effect of coal tars (and coal liquefaction residues) was tested at the final carbonization temperature of 700℃, the heating rate of 4℃/min and the soaking time of 35min (Figure 6).

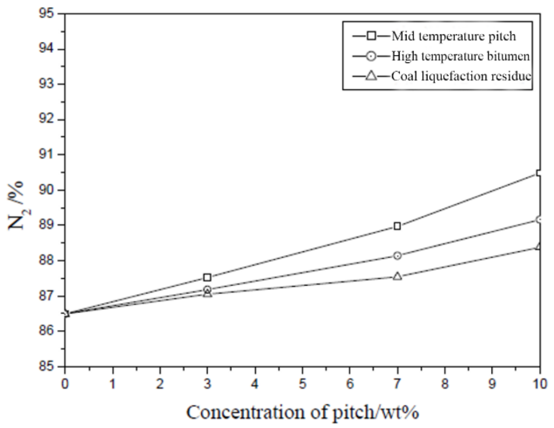

Figure 6: Effect of coal tars on air separation performance

As shown in Figure 6, the air separation performance improved with the increase in the dosage of coal tars. The optimal performance appeared at the dosage of 10%: the nitrogen concentration was 90.5%, 89.2%, and 88.4%, respectively, for medium-temperature coal tar, high-temperature coal tar and coal liquefaction residues, which surpasses that of common coal tar by 3.9%, 2.6% and 1.8%, respectively.
Specifically, the nitrogen concentration in the medium-temperature coal tar case was 1.3% and 2.1% higher than that of the high-temperature coal tar case and the coal liquefaction residues case, respectively. Moreover, the concentration of CMS enriched air of the former case was two times of that of the latter two cases.
The difference is attributable to the high molecular weight and aromatic degree of high-temperature coal tar, which leads to greater porosity after carbonization, and the metal oxide catalyst of coal liquefaction process, which results in the high ash content in the residues. Considering the proportion of buckwheat hulls, the dosage of medium-temperature coal tar should not be further increased. Otherwise, the extrusion will be too difficult to complete.
Through the above analysis, the effect of different carbonization conditions on air separation performance was investigated at the pore forming agent dosage of 15% and the medium-temperature coal tar dosage of 10%. The results show that the optimal carbonization conditions are: carbonization temperature of 700℃, heating rate of 4 ℃/min, and soaking time of 35min.

4. Conclusion

This paper prepares a granular CMS for air separation of buckwheat hulls, and analyses the effect of different factors on the air separation effect. With coal tar as the binder, the CMS was created via mixing, extrusion moulding, carbonization and pore regulation. The pore morphology was controlled by the immersion method. The main conclusions are as follows:
(1) The carbonization conditions have a major impact on the air separation performance. The optimal carbonization conditions are: carbonization temperature of 700℃, heating rate of 4 ℃/min, and soaking time of 35min. Under such conditions, the CMS reached the best performance: the nitrogen concentration was 88.5%;

(2) With the addition of coal tars, the pore structure of the CMS became much more developed. The experiment shows that the optimal dosage of pore forming agent is 15% and that of medium-temperature coal tar is 10%. The corresponding nitrogen concentration is up to 90.5%.

Reference

Carrott P., Cansado I., Carrott M., 2006, Carbon molecular sieves from PET for separations involving CH4, CO2, O2 and N2, Applied surface science, 252(17), 5948-5952.

Fu Z.Y., Guo S., 2008, The study of carbon molecular sieve preparation in the coconut shell of Hainan, Carbon, (2), 30-33.

Harmas M., Thomberg T., Kurig H., Romann T., Janes A., Lust E., 2016, Microporous-meso-porous carbons for energy storage synthesized by activation of carbonaceous material by zinc chloride, potassium hydroxide or mixture of them, Journal of Power Sources, 326, 624-634, DOI: 10.1016/j.jpowsour.2016.04.038

Hu Z., Vansant E.F., 1995, Carbon molecular sieves produced from walnut shell, Carbon, 33(5), 561-567, DOI: 10.1016/0008-6223(94)00141-L

Liu J., Jiang h., Fu T., 2013, Carbon molecular sieve preparation technology research progress and application, Chemical Production and Technology, 20(5), 45-49.

Mi P., 2013, Effect of fabrication processing on structure and properties of mesoporous carbon materials, Dalian: Dalian University of Technology.

Ruthven D.M., 1984, Principles of adsorption and adsorption processes, New York: John Wiley & Sons, 433, DOI: 10.1016/0255-2701(85)80013-1

Sevilla M., Fuertes A.B., Mokaya R., 2011, High density hydrogen storage in superactivated carbons from hydrothermally carbonized renewable organic materials, Energy & Environmental Science, 4(4), 1400-1410, DOI: 10.1039/C0EE00347F

Sun L., Wu D., Li T., Shang N.G., Sun X., 2014, Major influencing parameters of pressure swing adsorption nitrogen generation, Modern Chemical Industry, 34(9), 125-127.

Sun X., Zha Q., Wu M., 2013, The preparation of carbon molecular sieves and surface structure, Journal of Fuel Chemistry and Technology, (6), 569-573.

Thomberg T., Kurig H., Janes A., Lust E., 2011, Mesoporous carbidederived carbons prepared from different chromium carbides, Microporous & Mesoporous Meterials, 141(1), 88-93, DOI: 10.1016/j.micromeso.2010.11.006

Titiric M.M., Antonietti M., 2010, Chemistry and materials options of sustainable carbon materials made by hydrothermal carbonization, Chemical Society Reviews, 39(1), 103-116, DOI: 10.1039/b819318p

Wang J., Hu M., Sun L., Liu X., 2015, Biogas purification using carbon molecular sieves by pressure swing adsorption, Chemical Industry and Engineering Progress, 2015, 34(9), 3452-3455.

Xu S., Wang T., Guo S., 1999, Apricot shell is made of carbon molecular sieve, Journal of Dalian University of Technology, (1), 69-72.

Zhai Y.P., Dou Y.Q., Zhao D.Y., Fulvio P.F., Mayes R.T., 2012, ChemInform abstract: carbon materials for chemical capactive energy storage, Cheminform, 43(2), 4828-4850.

Zhang J., Liang D., Li L., Shang N.G., Sun X., 2010, Research progess and application status of coal-based carbon molecular sieves, Clean Coal Technology, 16(5), 53-56.

Zhang Y., Xu S., Luo Y., Pan S., Ding H., Li G., 2011, Synthesis of mesoporous carbon capsules encapsulated with magnetite nanoparticles and their application in wastewater treatment, Journal of Materials Chemistry, 21(11), 3664-3671, DOI: 10.1039/C0JM03727C

Zhang Y., You L., Hu H., 2010, Study on molecular sieves from phenol-formaldehyde resin, New Carbon Materials, 15(3), 55-58.

Zhao H., Li G., Ren S., Peng F., Ma Z., Dong A., Duan Y., 2015, Research Progress in Preparation and Application of Carbon Molecular Sieve, Anhui Chemical Industry, 41(1), 9-11.

Zhao Y., He Z., Yu Q., Zhuang W., 2014, Preparation and characterization of ordered mesoporous carbon by simple template method, Chemical Industry and Engineering Progress, 33(9), 2392-2397.