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Investigating parameters on the preparation of mesoporous activated carbons by the combination of chemical and physical activations using the Taguchi method

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Abstract Mesoporous activated carbons were prepared from coconut shell by the combination of chemical and physical activation methods. Zinc chloride and CO_2 were used as chemical and physical agents, respectively. Optimum parameters were obtained from investigating the effect of various factors at different levels on the methane storage of wet activated carbons using the Taguchi experimental design method. Soaking time, carbonization temperature, and carbonization time were found as effective parameters in the methane storage. Finally, after achieving optimum levels for each factors based on the enhancement of methane storage, a confirmation experiment was conducted. Methane uptakes of the activated carbons were measured at temperature of 2 °C up to the pressure of 80 bar and it turned out that the maximum amount of methane storage (241 V/V) had a good agreement with the predicted result from the Taguchi method.

Keywords Activated carbon · Mesoporous · Methane storage · Adsorbed natural gas (ANG)

1 Introduction

In recent years, various activated carbons are widely used for different applications, namely catalyst supports, battery electrodes, biomedical engineering and also methane storage as appropriate adsorbents (Tamai et al. 2002; Frackowiak 2007; De la Casa-Lillo et al. 2002; Lin and Teng 2003; Shen et al. 2003). Depending on the preparation method, pores in the activated carbons (*ACs*) structures are divided into three types, micropores with $d \leq 2$ nm, mesopores with $d = 2$–50 nm and macropores with $d > 50$ nm (Aworn et al. 2008). In preparation of appropriate activated carbons, the adsorption capacity of ACs depends on several parameters such as: pore size, pore size distribution, surface area, molecular size of adsorbate, and so on (Lorenc-Grabowska and Gryglewicz 2007). However, the methane storing capacity of final products at wet condition depends on the adsorption mechanism or hydrates formation. Activated carbons can be produced from various materials, e.g. coconut shell, wood, anthracite, polymer materials, nutshell, pistachio shell, etc.; and their final structures are dependent on the activation technique used in the preparation stage (Tamai et al. 2002; Ariyadejwanich et al. 2003; Wu et al. 2005; Mozammel et al. 2002; Su et al. 2003; Daud and Ali 2004; Wu and Tseng 2006).

Methane storage into wet ACs can be regarded as one of the latest application of adsorption method in the automobile industry. In this new method, the combination of adsorbed natural gas (*ANG*) and natural gas hydrate (*NGH*) would enhance the amount of methane storage by formation of hydrate into proper activated carbon (Zhou et al. 2002, 2005; Perrin et al. 2005; Najibi et al. 2008). Methane hydrates are formed in appropriate carbon pores, so the pore size should be suitable for hydrates formation. Generally, type-1 hydrates are formed as methane hydrates with crystal cell dimension of 1.2 nm. Besides, the dynamic diameter of methane is 0.38 nm; consequently, the pore size should not be smaller than 1.6 nm. The advantage of storing methane in pore spaces is based on the interaction of water molecules with surface carbon atoms and this interaction is governed by the Lennard–Jones potential function. Different studies show that two methane hydrates cells are the optimal num-

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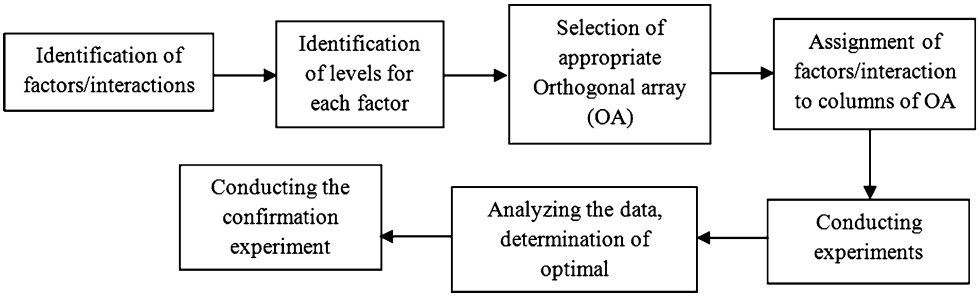

Fig. 1 Scheme of the major steps in implementing the Taguchi method

ber for highest storage because the interaction strength decreases drastically as the distance between opposite carbon surfaces increase and, therefore, the advantage of the storage method will fade. The pore size containing two crystal cells of methane hydrates allow a methane molecule to transport is 2.8 nm. Thus, activated carbons containing optimal pores with dimension of 1.6–2.8 nm are best suitable for methane storage in wet condition (Zhou et al. 2011). Based on the classification of pores mentioned above, the best products for this purpose are mesoporous activated carbons. So, preparing appropriate mesoporous ACs and finding optimum storing conditions were our main objectives in this study.

Various methods have been conducted for the preparation of appropriate mesoporous activated carbons. Some of those methods are activation to high burn-off degrees, application of both physical and chemical activation, catalytic activation in the presence of transition metals, carbonization of polymer blends, carbonization of organic gels, and also template carbonization (Ariyadejwanich et al. 2003; Wu et al. 2005; Mozammel et al. 2002; Su et al. 2003; Daud and Ali 2004; Wu and Tseng 2006; Perrin et al. 2005; Zhou et al. 2005; Najibi et al. 2008; Zhu et al. 2007; Roy 2001), but none of them are examined for methane storage. The key factor in this application is to try different methods for increasing the mesoporous content of ACs.

To prepare an appropriate AC, various factors such as: chemical agent, ratio of chemical to raw material, temperature, and carbonization time can play important roles. Therefore, it is essential to do a variety of experiments. Among several statistical and analytical methods for reducing the number of experiments, Taguchi method is the most practical one.

Taguchi method is one of the designs of experiment (*DOE*) techniques with special application principles. The method was developed by Genichi Taguchi in 1950s in order to improve the quality control in Japan. Taguchi method is a combination of mathematical and statistical techniques used in an empirical study (Roy 2001). Different steps in determination of optimum sample using the Taguchi method is depicted in Fig. 1.

Taguchi method is a technique for designing and performing experiments to investigate processes where the output depends on many factors (different variables and inputs) without having tediously and uneconomically run of the process using all possible combinations of values. By systematically choosing certain combinations of variables, it is possible to separate their individual effects (Lochner and Matar 1990). In the Taguchi method, the favorable design is finalized by selecting the best performance under the given conditions.

In the present study, mesoporous activated carbons were prepared by a combined physical–chemical activation process. In this investigation, CO_2 gas was used as physical agent and $ZnCl_2$ as chemical agent. Coconut shell was also applied as precursor. Chemical agent to precursor ratio, temperature of carbonization, carbonization time, CO_2 flow, and soaking time were investigated as effective parameters in the process. Also, enhancement of methane storage into wet activated carbons with a constant ratio of water to dry samples (equal to one) was selected as a goal. Finally, the Taguchi method was used to obtain optimum parameters.

For further investigation, four best samples with high amount of methane storage were selected to improve their methane uptakes further by altering the ratio of water to dry samples (R). In those experiments, the L7 sample demonstrated the highest amount of methane storage equal to 248 V/V with $R = 1.4$ (Darabi Mahboub et al. 2012).

2 Experimental

2.1 Materials and instruments

Zinc chloride was obtained from Merck. Nitrogen and carbon dioxide gases with purity higher than 99.5 % and methane (>99.8 %) were obtained from Farafan gas company, Iran. All the valves and connections were provided from Parker Company, USA. Pressure transducers and thermocouple were supplied from Lutron Company, Taiwan.

2.2 Preparation of activated carbon

After drying coconut shell as precursor in an oven at 110 °C, raw material was crushed and sieved to uniform size in the range of 1.0–2.0 mm. Then, the granular particles were dried

for additional two hours. After that, they were impregnated with a $ZnCl_2$ solution, and this mixture was dehydrated on a moderate temperature for a certain time (Soaking time). To remove moisture, samples were dried in an oven overnight at 110 °C. Finally, the samples were pyrolysed in a tube furnace under a nitrogen flow of 300 mL min^{-1} until the temperature was reached 800 °C with the slope of 10 °C min^{-1}. Next, N_2 gas was switched to CO_2 and the activation process was continued for certain times. After that, the samples were allowed to cool down to room temperature. Samples were washed with the hot double distillate water and also hydrochloric acid (0.5M) for several times to remove all remaining chemicals. Finally, activated carbon products were dried at 110 °C for 24 h. To obtain methane storage of an AC sample, each adsorbent was first placed in a stainless steel sample holder and then degassed at 220 °C for 10 h. Then, constant mass ratio of water to carbon equal to one was added to the sample. Two pressure sensors and a thermocouple were used to measure the pressure and temperature of the bed. The sampler holder was then put in a water bath of 2 °C to reach the constant temperature. Methane adsorption isotherm was measured volumetrically and the real methane storage at high pressure was obtained by the application of Van der Waals equation of state.

2.3 Density measurement

The density of activated carbon has very important effect in ANG applications, as higher packing density leads to higher methane uptake in the limited vessels. Compacting dry activated carbon samples under pressure is a relevant method to determine the packing density. So, packing densities of samples were measured in a small stainless steel cylinder by applying the pressure of about 335 kg cm^{-2}. It had been shown that pressure up to 550 kg cm^{-2} did not affect methane uptake of the samples (Lozano-Castello et al. 2002).

2.4 Parameters and their levels used in the Taguchi method

By reviewing the results of previous studies and doing some trial and error experiments, effective parameters and their approximate levels were found. The first parameter was zinc chloride to raw material ratio (R), which was varied between 2.5 to 4 based on some trial and error experiments; higher amount did not have any effect on methane storage even altering other parameters. CO_2 was another activation agent that was chosen to change in the range of 105–300 mL min^{-1} based on some trial and error experiments. Also, carbonization time has the best effects in one and two hours, according to several investigations. Finally, temperature of carbonization and soaking time were additional new parameters studied in this investigation and they selected to vary in the ranges of 500–800 °C and 1–2 h, respectively.

Table 1 Different parameters with various levels used in the Taguchi method

Parameters	Level1	Level2	Level3	Level4
R (chemical agent to raw material ratio)	2.5	3	3.5	4
CO_2 flow (mL min^{-1})	105	150	200	300
Carbonization temp. (°C)	590	660	730	800
Carbonization time (h)	2	3		
Soaking time (h)	2	3		

Table 1 shows different selected levels for the mentioned parameters.

The proper orthogonal array for the experiments was determined by the Minitab software. Three parameters in 4-levels and two parameters in 2-levels were positioned in a L_{16} orthogonal array table. By selecting this array, using the five above mentioned parameters and their levels (shown in Table 1), the number of required experiments was significantly reduced from 256 to 16. Suggested experiments that must be examined to obtain the optimum parameters are presented in Table 2.

3 Results and discussion

3.1 Burn-off measurement

One of the most important factors in the preparation of activated carbons is burn-off. Burn-off was determined from the differences between the samples weight before and after activation.

$$\text{Burn-off}\ (\%) = \frac{\text{raw material weight} - \text{activated carbon weight}}{\text{raw material weight}} \times 100 \quad (1)$$

3.2 Iodine number

Another important characteristic of ACs is iodine number. The iodine number is one of the most fundamental parameter used to characterize activated carbon performance. It is a relevant technique applied to determine the adsorption capacity of activated carbons and almost equivalent to their surface areas (Saka 2012). It is defined as the amount of iodine adsorbed by 1 g of carbon at the mg level. The iodine adsorption is usually evaluated using the sodium thiosulfate by volumetric method. The iodine numbers for all activated carbons were determined based on the *ASTM-D4607* standard method (ASTM D4607 1994).

Table 2 Conditions used in the preparation of ACs based on the Taguchi method and their characteristics

Sample	*R*	Flow (mL min^{-1})	Temp. (°C)	Carbonization time (h)	Soaking time (h)	Burn-off (%)	Density (g cm^{-3})	Iodine No. (mg g^{-1})
1	2.5	105	590	2	2	62.4	0.377	1163
2	2.5	150	660	2	2	67.3	0.411	1086
3	2.5	200	730	3	3	75.3	0.376	1250
4	2.5	300	800	3	3	91.0	0.347	1349
5	3	150	590	3	3	65.3	0.427	1208
6	3	105	660	3	3	75.3	0.377	1295
7	3	300	730	2	2	81.1	0.437	1405
8	3	200	800	2	2	84.3	0.402	1843
9	3.5	200	590	2	3	69.3	0.377	1212
10	3.5	300	660	2	3	73.3	0.376	1322
11	3.5	105	730	3	2	88.2	0.414	1343
12	3.5	150	800	3	2	95.4	0.560	1386
13	4	300	590	3	2	79.1	0.377	1264
14	4	200	660	3	2	85.2	0.367	1283
15	4	150	730	2	3	73.9	0.604	1307
16	4	105	800	2	3	75.3	0.369	1321

3.3 Taguchi experimental design

A Taguchi robust design method was applied to select the parameters having the most principal influence on the storage of methane and to find optimal conditions. Table 2 shows structure of the Taguchi orthogonal robust design, burn-off results, and also densities and iodine numbers of all suggested samples.

3.4 Analysis of variance (*ANOVA*)

In designing experiments by the Taguchi method, as these experiments are just part of the whole experiments, ANOVA is applied as a standard mathematical method to survey the results and to investigate different parameters. Also, ANOVA can be used to verify the data (Sharma et al. 2005). To study the effects of different parameters on enhancing methane uptake, two factors of F and P are used. For every parameter, when F is higher and P is lower, it illustrates that this parameter has much effect on increasing methane storage. Figure 2 shows the effect of different parameters for improving methane storage based on the ANOVA analysis.

Figure 2 indicates that the carbonization temperature has the most effect (about 36 %) in increasing methane storage. Soaking and carbonization time are in the second and third order of importance, respectively. Gas flow and $ZnCl_2$/raw material ratio (R) have less effect on enhancing the methane storage.

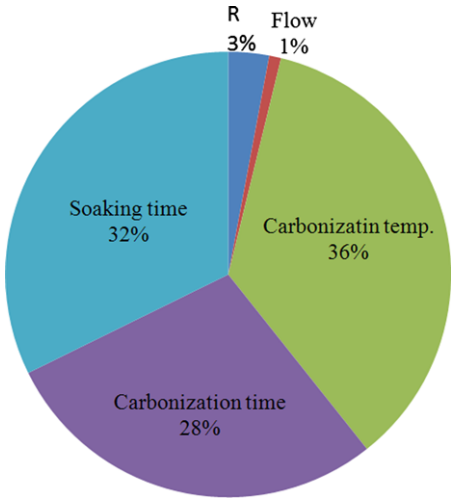

Fig. 2 The effect of different parameters on enhancing methane storage in wet ACs

3.5 Investigating the effect of different parameters on the methane storage enhancement

In the Taguchi method, the terms ‘signal’ and ‘noise’ represent the desirable and undesirable values for the output characteristic, respectively. Taguchi method uses the S/N ratio to measure the quality characteristic deviating from the desired value. The S/N ratios are different according to the type of characteristic (nominal, smaller or bigger is the best) and categorized into three groups (Dobrzañski et al. 2007).

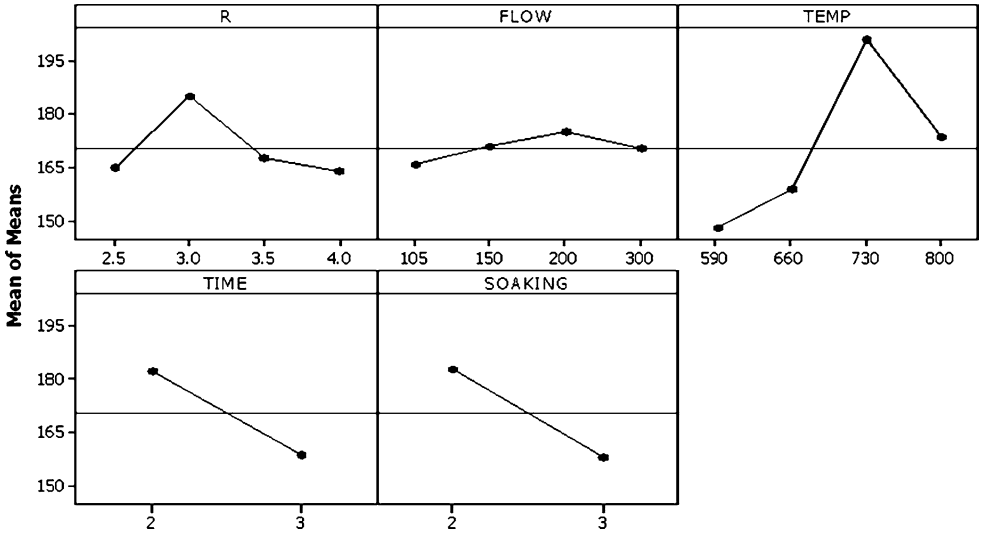

Fig. 3 Effect of different parameters on methane uptake based on the mean value

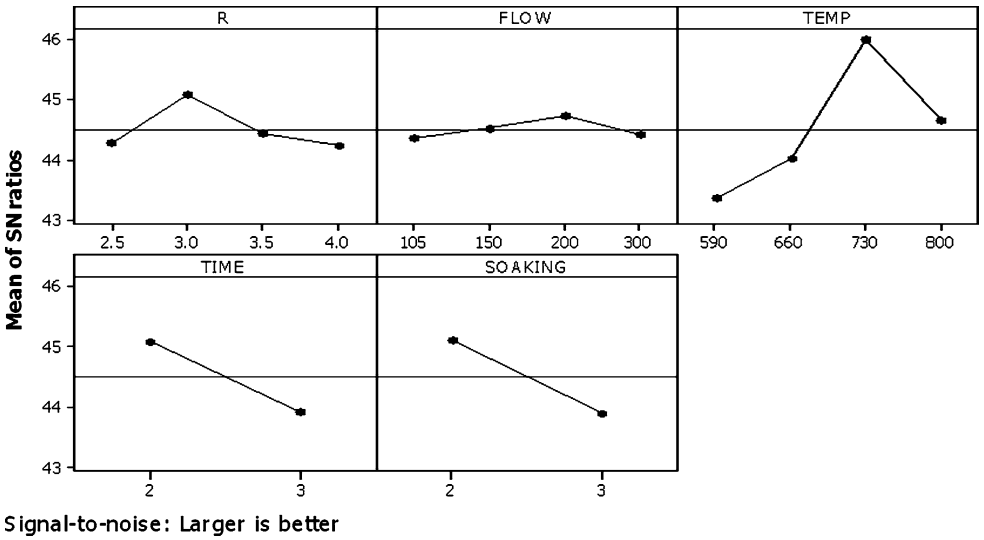

Fig. 4 Effect of different parameters on methane uptake based on the S/N ratio

3.5.1 Smaller-the-better

$\frac{S}{N}$ ratio [dB] $= -10\,\mathrm{Log}_{10}$ [mean of sum of squares of measured data]

This is a chosen S/N ratio for all unfavorable characteristics similar to "defects", for which the ideal value is zero (Dobrzañski et al. 2007). When the ideal value is finite and its maximum or minimum value is defined, such as "maximum purity of 100 %", then the difference between the measured data and ideal value is expected to be as small as possible. The generic form of S/N ratio then becomes:

$\frac{S}{N}$ ratio [dB] $= -10\,\mathrm{Log}_{10}$ [mean of sum of squares of {measured − ideal}]

3.5.2 Larger-the-better

$\frac{S}{N}$ ratio [dB] $= -10\,\mathrm{Log}_{10}$ [mean of sum squares of reciprocal of measured data]

This case can be converted to SMALLER-THE-BETTER by taking the reciprocals of measured data and then taking the S/N ratio as in the smaller-the-better case.

3.5.3 Nominal-the-best

This case increases when a specified value is favorable, meaning that neither a smaller nor a larger value is appropriate.

Figures 3 and 4 show optimum levels for different factors according to mean value and signal to noise ratio (S/N).

Figure 3 illustrates the effect of different quantities of various factors on methane uptake on the basis of mean value. The ratio of $R = 3$, flow of 200 mL min^{-1}, temperature of 730 °C, carbonization time and soaking time of 2 h are optimum values to increase methane storage. These optimum levels are remained the same on the basis of S/N ratio shown in Fig. 4. A confirmation experiment was performed

Table 3 The characteristics of confirmation experiment performed at optimum condition

Sample	*R*	Flow (mL min^{-1})	Temp. (°C)	Carbonization time (h)	Soaking time (h)	Burn-off (%)	Density (g cm^{-3})	Iodine No. (mg g^{-1})
Confirmation experiment	3	200	730	2	2	82.31	0.426	1753

Table 4 Methane storage values for the prepared activated carbons

Sample	*R*	Flow (mL min^{-1})	Temp. (°C)	Carbonization time (h)	Soaking time (h)	Methane uptake (V/V)	Methane release (V/V)
1	2.5	105	590	2	2	168	154
2	2.5	150	660	2	2	172	161
3	2.5	200	730	3	3	179	159
4	2.5	300	800	3	3	139	113
5	3	150	590	3	3	127	97
6	3	105	660	3	3	156	146
7	3	300	730	2	2	237	223
8	3	200	800	2	2	219	197
9	3.5	300	590	2	3	148	134
10	3.5	300	660	2	3	156	142
11	3.5	105	730	3	2	185	167
12	3.5	150	800	3	2	180	159
13	4	300	590	3	2	148	126
14	4	200	660	3	2	151	139
15	4	150	730	2	3	202	186
16	4	105	800	2	3	180	154
Confirmation experiment	3	200	730	2	2	241	229

at this optimum situation and then its characteristics (burn-off, density and iodine number) were determined. Table 3 shows the characteristics of the confirmation experiment.

3.6 Methane storage

One of the most important applications of activated carbon is storing methane as a clean fuel. Methane storage by both NGH and ANG is the new technique for this purpose. In this method, methane storage can be increased by hydrate formation in the mesopores. Therefore, mesoporous activated carbons would be appropriate materials for this purpose. After preparing AC samples, constant amount of water was added to activated carbons and methane adsorptions were obtained at 2 °C up to 80 bar condition similar to the previous investigations for comparison purposes (Ganji et al. 2007; Kim et al. 2010). One of the main advantages of this method is that the released gas is much higher than that of Compressed Natural Gas (*CNG*). Figure 5 shows methane adsorption isotherms of all samples in the wet condition. It is illustrated that at 2 °C, methane uptake increases slowly with the pressure up to a hydrate formation pressure as a result of capturing some pores by water molecules. At this critical pressure, hydrate is formed in the mesopores and isotherms show stepwise behavior, similar to the findings of other researchers (Perrin et al. 2005; Celzard and Marêche 2006; Zhou et al. 2002; Wang et al. 2008). The rapid increase of methane storage occurred at critical pressures that are typically ranged from 25 to 55 bar, depending on the samples. Behavior of the first parts of the isotherms (below the critical pressure) is related to the classical physisorption of methane within the micropores of the adsorbents.

Table 4 shows methane storage and methane release for all mesoporous activated carbons prepared in this study. The U.S. Department of Energy (*DOE*) has suggested the target of 180 V/V for methane storage (De la Casa-Lillo et al. 2002).

On this basis, high methane uptake was achieved by samples L7, L8, L11 and L15 corresponding to 237, 219, 184 and 202 V/V values, respectively.

At constant *R* ratios, as shown in Table 4, with increasing carbonization temperature up to 730 °C , the methane storage was increased for all samples, but at 800 °C it was decreased. This phenomenon can be explained that at temperatures higher than 730 °C, the mesopore volume was diminished. Moreover, by comparison the effect of CO_2 flow

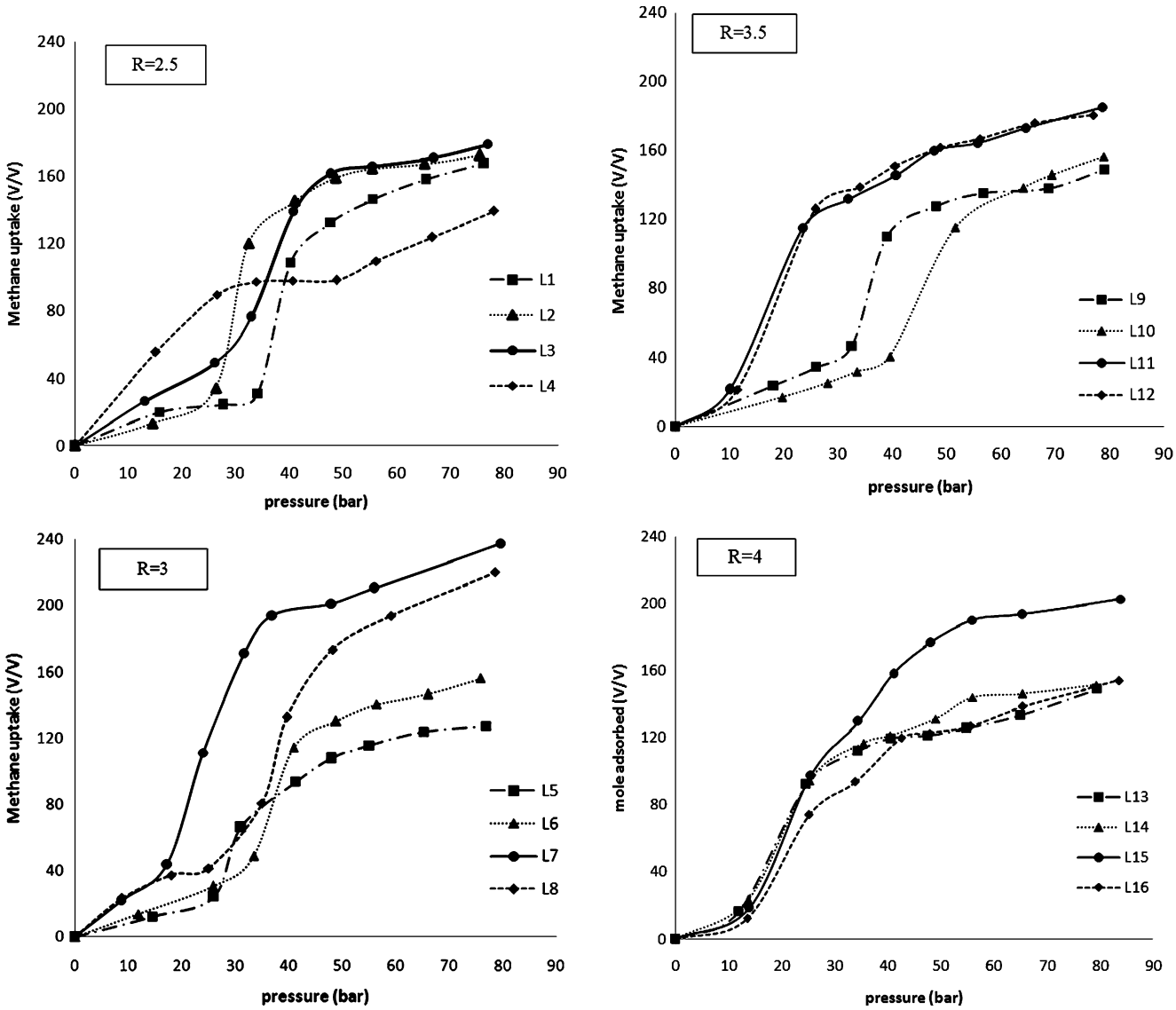

Fig. 5 Methane storage isotherms for all samples

and carbonization temperature on the methane storage, it can be verified that the maximum amount of methane storage was obtained at 730 °C for any CO_2 flow. Besides, if we compare performances of L9 with L13 samples and also L10 with L14 samples, the results illustrated that they have almost equal methane storages, although they prepared at the same R ratio and activation temperature but different values for other parameters. Therefore, it can be concluded that at the same conditions for ratio and temperature, other factors have less effects on improving methane storage. Finally, L4 sample has different behavior in comparison with other samples. This carbon was prepared at lowest ratio and highest amounts of other parameters (R = 2.5, CO_2 flow = 300 mL min^{-1}, temp. = 800 °C, soaking time = 2 h, carbonization time = 2 h), but stored lowest methane. This result can be justified by lacking the mesopore volume to create methane hydrates. It is also clear in Fig. 5 that the methane hydrates could not be created in this sample as most of the pores are micropores. Zhao et al. investigated different parameters such as activation temperature and KOH/anthracite weight ratio (W) to prepare chemically activated carbons for hydrogen storage. Although their investigation illustrated that W had the most effect on hydrogen storage, they just examined two parameters for hydrogen storing in microporous ACs (Zhao et al. 2011). However, in the present study we have investigated the effects of five different parameters and the analysis of results are somehow difficult. On the other hand, preparing mesoporous ACs for methane storage were our main intention; consequently the effects of several parameters could be different from those in preparing microporous ACs for hydrogen storage. It can be seen from the study of Zhao et al. that W had

the most effect on storage, other than in our study R and CO_2 flow had less effects.

4 Conclusion

In this study, mesoporous activated carbons were produced from coconut shell through a combined chemical-physical activation method with $ZnCl_2$ and CO_2 as chemical and physical agents, respectively. AC preparation parameters were optimized using the Taguchi robust design method and methane uptake in the wet activated carbons was utilized as the target. Carbonization temperature, soaking time and carbonization time have most effects for increasing methane uptake. Optimum conditions were obtained as: chemical to raw material ratio of $R = 3$, N_2 flow of 200 mL min^{-1}, carbonization temperature of 730 °C, and carbonization and soaking time of 2 h.

Methane uptake was achieved from 129 to 237 V/V for samples at 2 °C and 80 bar conditions. Taguchi method suggested that the prepared sample from a confirmation experiment under optimum conditions has the highest amount of methane uptake (241 V/V). The results also illustrate that the Taguchi method is an appropriate method for obtaining the best parameters in the preparation of mesoporous activated carbons.

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