



HAL
open science

Numerical studies of the effects of process conditions on the development of the porous structure of adsorbents prepared by chemical activation of lignin with alkali hydroxides

Mirosław Kwiatkowski, Vanessa Fierro, Alain Celzard

► To cite this version:

Mirosław Kwiatkowski, Vanessa Fierro, Alain Celzard. Numerical studies of the effects of process conditions on the development of the porous structure of adsorbents prepared by chemical activation of lignin with alkali hydroxides. *Journal of Colloid and Interface Science*, 2017, 486, pp.277-286. 10.1016/j.jcis.2016.10.003 . hal-03563217

HAL Id: hal-03563217

<https://hal.univ-lorraine.fr/hal-03563217>

Submitted on 9 Feb 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

**NUMERICAL STUDIES OF THE EFFECTS OF PROCESS
CONDITIONS ON THE DEVELOPMENT OF THE POROUS
STRUCTURE OF ADSORBENTS PREPARED BY CHEMICAL
ACTIVATION OF LIGNIN WITH ALKALI HYDROXIDES**

Mirosław Kwiatkowski¹, Vanessa Fierro², Alain Celzard^{2*}

¹ *AGH University of Science and Technology, Faculty of Energy and Fuels, al. A.*

Mickiewicza 30, 30-059 Krakow, Poland, tel. (48 12) 617 41 73

² *Institut Jean Lamour - UMR CNRS - Université de Lorraine n°7198. ENSTIB, 27 rue Philippe*

Seguin, CS 60036, 88026 Epinal cedex, France.

* Corresponding author. E-mail: alain.celzard@univ-lorraine.fr (Alain Celzard)

Abstract

This paper presents the results of the application of the advanced LBET and QSDFT methods compared to the BET and DR approach to the comprehensive analysis of the porous structure of activated carbons obtained by chemical activation of demineralised Kraft lignin with potassium and sodium hydroxides. Based on the analysis of nitrogen adsorption isotherms, the influence of the preparation process conditions on the porous structure formation was investigated. Particularly, the impact of the type of activating agent, the activation temperature, the hydroxide to lignin mass ratio, and the flow rate of inert gas on the porous structure formation was assessed. This work proves how useful the used methods of structure analysis are when evaluating the influence of preparation conditions on the formation of the porous structure of activated carbons.

Keywords: adsorption, micropores, chemical activation, Kraft lignin, activated carbons.

1. Introduction

Chemical activation using potassium hydroxide, KOH, or sodium hydroxide, NaOH, as the activating agent is an effective method for producing activated carbons [1-5]. This method proved to be highly advantageous with respect to physical activation with steam or carbon dioxide. Its major advantages are the greater efficiency of the process and the fact that it is carried out in one single stage involving lower temperatures and shorter durations, as well as a significantly enhanced development of the porous structure and the possibility of obtaining a porous structure with a limited range of pore widths. The disadvantages of chemical activation using alkali hydroxides include higher process costs than for physical activation, the requirement of adding a rinsing step, and considerable corrosion due to the use of hydroxides. But, interestingly, the development of the final porous structure can be altered to a considerable degree, depending on the conditions of chemical activation.

As a consequence, the choice of a suitable precursor is not less important than the selection of the adequate production technology and the determination of the optimum process conditions. Therefore, the search for new raw materials is still of interest, and particular attention is being paid in this regard to biomass waste from food and timber industries, and from agriculture. In addition to its physical, chemical and mechanical properties, the key arguments in favour of biomass waste include a relatively low cost and its general accessibility and renewability. From this point of view, plant wastes are very useful as raw materials for the production of activated carbons. Guo et al. [6] presented the results of activated carbons preparation from rice hulls by chemical activation with potassium and sodium hydroxides as activating agents. The research revealed that the materials obtained with KOH usually had surface areas exceeding $3000 \text{ m}^2/\text{g}$, while the surface area of those obtained with NaOH was around $2500 \text{ m}^2/\text{g}$. These results confirmed earlier conclusions from the same group, namely that porous carbons prepared by NaOH activation have larger average

pore diameters than those derived from KOH activation. Additionally, KOH activation produces porous carbons with a higher micropore volume than in the case of NaOH [7].

One of the most promising materials for the production of activated carbons is lignin [8-12], being the second most abundant natural polymer in the world, surpassed only by cellulose. Out of all the polymers found in plant cell walls, lignin is the only one that is not composed of carbohydrate monomers. Lignin is based on up to three different phenyl-propane monomers, depending on the species. Coniferyl alcohol occurs in all species and is the dominant monomer in softwood. Deciduous wood species contain up to 40% syringyl alcohol units while grasses and agricultural crops may also contain coumaryl alcohol units. Concerning the preparation of activated carbons, lignin is particularly advantageous because of its high phenolic content, leading to higher carbon yields than those obtained from the two other main macromolecular compounds of biomass: cellulose and hemicellulose [11,12]. Hayashi et al. also presented interesting results dedicated to chemical activation of lignin with KOH, NaOH, $ZnCl_2$ and H_3PO_4 as activating agents, the weight ratio of the activator to the raw material being 1:1 [13]. From these results, the authors observed that $ZnCl_2$ and H_3PO_4 are effective activating agents at temperatures below 873 K, while KOH and NaOH are more efficient above 873 K [13].

However, generally speaking, optimising activation conditions through the choice of a suitable carbonaceous precursor and that of relevant activation parameters in order to meet given technological, economic and ecological specifications, is a huge experimental task. Many experiments are indeed required before the expected activated carbon designed for a particular adsorptive process is obtained, and a reliable analysis of the obtained results is necessary. However, the tools used for analysing the microporous structure of carbonaceous adsorbents, e.g. based on BET [15] and DR [16] theories, do not provide any information about the effect of the said preparation conditions on the formation of the microporous

structure. This is partly because BET and DR methods are based on too many simplified assumptions, including the supposed homogeneity of the surface of each evaluated material, which can significantly decrease the credibility of the analyses' results. Apart from that, these methods provide few information on the structure of pores and the process of adsorption occurring in them. The information received with the use of the BET and DR methods is useful only in the case of comparative analyses, which are not enough when a precise technology and production conditions of activated carbons, designed for a specific use in advanced industrial processes, have to be chosen.

Consequently, the idea of the present work was, based on nitrogen adsorption isotherms, to carry out comprehensive analyses of the influence of the preparation process conditions on the porous structure formation of activated carbons obtained by chemical activation of demineralised Kraft lignin with potassium and sodium hydroxides.

2. Materials and methods

In our previous work, activated carbons were produced from demineralised Kraft lignin (KL_d) by chemical activation using two hydroxides, NaOH and KOH, as activating agents [14]. The lignin was supplied by Lignotech Iberica S.A (Spain), and underwent an additional process for removing the inorganic matter with the use of H_2SO_4 . KOH and NaOH granules were ground and physically mixed with demineralised kraft lignin KL_d , according to various hydroxide/ KL_d mass ratios R , and next the hydroxide-lignin mixtures were subjected to heat-treatment in inert atmosphere [14]. The activation was carried out in a horizontal furnace flushed with nitrogen at various temperatures T ($^{\circ}C$), hydroxide to raw material mass ratios R (dimensionless), activation times t (min), inert gas flow rates F (cm^3/min), and heating rates r ($^{\circ}C/min$) [14].

At that moment, surface area and pore volumes of the activated carbons, here called, KL_dAC, were determined from the corresponding nitrogen adsorption isotherms obtained at -196°C by using BET [15] and DR [16] simple methods, respectively. Herein two entirely different methods, LBET [17-22] and QSDFT [23-25], were applied to the nitrogen adsorption isotherms for describing the microporous structure of the KL_dAC adsorbents. Those methods of heterogeneous surface assessment of porous materials were especially applied to evaluate the impact of the type of activating agent, the activation temperature, the hydroxide to lignin mass ratio, and the flow rate of inert gas on the porous structure formation. The results of the performed analyses were also compared with the results obtained by means of the BET and DR methods. Such analyses also aimed at comparing and providing information on the usefulness of the used methods of analysis of the structure, i.e., the BET [15], DR [16], LBET [18-22] and QSDFT [23-25] methods, for evaluating of the influence of preparation conditions on the formation of the porous structure, as well as the consistency of the obtained information on the structure of pores and adsorptive properties of materials.

The LBET method was described in detail in former works [19-21]. It is based on the original models of adsorption on heterogeneous surfaces, originating from an unique multilayer adsorption theory, which introduced important generalisations of the BET model [18-22]. In this method, the original numerical fast multivariate identification of the adsorption systems procedure was implemented. The LBET method can be used for analysing the microporous structure of various carbon adsorbents, in which the micropores are a significant part of the overall porosity. The group of analytical models of LBET class is expressed using the following general form [18-22]:

$$\begin{aligned}
\frac{m_a}{m_{hA}} = & (1-\alpha) \left\{ 1 - \frac{1}{\ln(B_{A1}/B_{f1})} \cdot \ln \left(\frac{B_{A1} + \pi}{B_{f1} + \pi} \right) \right\} + \\
& + d \cdot \alpha(1-\alpha)(1 + \beta\theta_{22}) \left\{ 1 - \frac{1}{\ln(B_{A2}/B_{f2})} \ln \left(\frac{B_{A2}(1-\theta_{22})^\beta + \pi}{B_{f2}(1-\theta_{22})^\beta + \pi} \right) \right\} + \\
& + \alpha^{d+1} \left[d + (\beta\theta)^d \left(1 + \frac{\beta\theta}{1-\alpha\beta\theta} \right) \right] \left\{ 1 - \frac{1}{\ln(B_{A2+d}/B_{f\theta})} \ln \left(\frac{B_{A2+d}(1-\theta)^\beta + \pi}{B_{f\theta}(1-\theta)^\beta + \pi} \right) \right\}
\end{aligned} \quad (1)$$

where: m_a is the amount of adsorbate (mmol/g), m_{hA} is the total number of primary sites (mmol/g) such that $m_{hA} = V_{hA}/V_p$, V_{hA} being the first adsorption layer capacity (cm³/g) and V_p being the molar volume of adsorbate (cm³/mmol), θ is a layer coverage ratio, π is the relative pressure, α is the geometrical parameter of the porous structure, β is the pore shape parameter such as $\beta \geq 1$, k is the maximum number of layers, θ_{kj} is the coverage ratio of j -layer at k -type cluster calculated according to the formulas, and $B_{Ak} = \exp(Q_{Ak}/RT)$ and $B_{fk} = \exp(Q_{fk}/RT)$, where Q_{Ak} and Q_{fk} are adsorption energy values for the left and right hand side of the energy distribution, respectively, R is the molar gas constant and T is the absolute temperature. The parameter $B_{f\theta}$ is defined as follows [18-20]:

$$B_{f\theta} \stackrel{def}{=} B_A \exp\left(\frac{Q_{cp}}{RT} \cdot (Z_{A2+d} - Z_{f\infty}) \cdot W_{d\eta}\right), \quad (2)$$

where $W_{d\eta}$ denotes an exponent minimising the approximation error, and Q_{cp} is the molar adhesion energy in ideal adsorbent-adsorbate contacts [J/mol].

The LBET class models have five adjustable parameters: V_{hA} (cm³/g), Q_{Amax}/RT , α , β and B_C which can be adjusted by fitting Eq. (1) to the adsorption isotherm, with a chosen variant of the surface energy distribution function [18-22]. Fitting the theoretical LBET class adsorption models to the experimental adsorption isotherms was realised using the method of non-linear optimisation with limitations, with the using the 30-variant version of the LBET class models in the calculations [18-22]. The adsorption parameters of the analysed system are assumed to be the values obtained for the best-fitted variant of the LBET model.

Another method used for estimating the pore size distribution (PSD) is the one called Quenched Solid Density Functional Theory (QSDFT) [23-25]. It is intended for the pore size analysis of geometrically and chemically disordered micro-mesoporous carbons, and allows the calculation of PSDs from *ca.* 0.5 nm up to *ca.* 40 nm [24]. Owing to the fact that the QSDFT approach explicitly takes into account the effects of surface roughness and heterogeneity, unlike earlier methods, it gives a significant improvement in the agreement between experimental and theoretical adsorption isotherms, in particular in the low-pressure range of the micropore filling. Additionally the QSDFT method eliminates artificial gaps in the PSDs typical for NLDFT calculations [25]. As a consequence, the resulting QSDFT pore size distributions are more reliable.

3. Results and discussion

3.1. Application of adsorption models to nitrogen adsorption data

In [14], a reference sample was prepared in the following conditions: $T = 700^{\circ}\text{C}$, $R = 3$, $t = 1$ h, $F = 200$ cm³/min, $r = 5^{\circ}\text{C}/\text{min}$. All other samples were obtained by changing independently T , R or F , all other parameters being kept constant. The results of all the numerical analyses are presented in Tables 1–3 and in Figures 1–3, respectively, for NaOH activation of demineralised Kraft lignin, and in Tables 4–6 and in Figures 4–6 for KOH activation. The activation conditions are recalled in the top chart of each Figure, wherein the circles mark the experimental nitrogen adsorption (N_2 - KL_dAC) data and the solid lines mark the best-fitted variant of the LBET class model.

The second chart of each Figure presents the adsorption energy distribution on the adsorbent surface determined by LBET method, and the third chart presents pore size distribution (PSD) obtained by QSDFT method.

Table 1. A compilation of the results of adsorption isotherm analyses carried out using the BET, the DR and LBET methods for activated carbons KL_dAC produced by activation with NaOH at different activation temperatures T .

T [°C]	S_{BET} [m ² /g]	V_{DR} [cm ³ /g]	Q_{Amax}/RT	B_C	h	V_{hA} [cm ³ /g]	α	σ_e
600	1896	0.66	11.60	2.81	3	0.808	0.92	0.51
700	2413	0.956	12.40	1.00	1	1.078	0.75	0.64
750	2345	0.81	12.78	1.55	5	0.980	0.97	0.64
800	2433	0.802	10.10	1.01	2	1.068	0.84	0.59
900	2065	0.721	12.18	2.60	3	0.972	0.97	0.54

Table 2. Same as Table 1 but for different hydroxide to lignin mass ratios R .

R	S_{BET} [m ² /g]	V_{DR} [cm ³ /g]	Q_{Amax}/RT	B_C	h	V_{hA} [cm ³ /g]	α	σ_e
2	2288	0,861	14.20	2.60	5	1.096	0.99	0.67
3	2413	0,956	12.40	1.00	1	1.078	0.75	0.64
3.5	2490	0,96	13.14	1.70	5	1.056	0.97	0.59
4	2079	0,834	12.96	1.64	5	0.908	0.96	0.51
5	853	0,254	13.25	1.36	7	0.373	1.00	0.33

Table 3. Same as Table 1 but for different flow rates of inert gas F .

F (cm ³ /min)	S_{BET} (m ² /g)	V_{DR} (cm ³ /g)	Q_{Amax}/RT	B_C	h	V_{hA} (cm ³ /g)	α	σ_e
50	1417	0.516	12.99	3.29	3	0.596	0.91	0.21
200	2413	0.956	12.40	1.00	1	1.078	0.75	0.64
400	2494	1.042	12.56	2.09	3	1.045	0.98	0.54
600	2277	0.796	12.75	2.03	3	1.012	0.97	0.54
800	2121	0.792	14.96	2.57	9	1.037	1.00	0.54

Table 4. A compilation of the results of adsorption isotherm analyses carried out using the BET, the DR and LBET methods as for the activated carbons KL_dAC produced by activation with KOH at different activation temperatures T .

T [°C]	S_{BET} (m ² /g)	V_{DR} (cm ³ /g)	Q_{Amax}/RT	B_C	h	V_{hA} (cm ³ /g)	α	σ_e
600	2307	0,846	12.39	2.54	2	1.172	0.98	0.66
700	3105	0,994	11.49	1.55	3	1.334	0.98	1.1
750	2907	0,915	11.53	1.40	3	1.211	0.97	0.96
800	2804	0,885	11.10	1.13	3	1.092	0.95	0.88
900	2724	0,901	11.42	1.00	5	0.984	0.92	0.63

Table 5. Same as Table 4 but for different hydroxide to lignin mass ratios R .

R	S_{BET} (m ² /g)	V_{DR} (cm ³ /g)	Q_{Amax}/RT	B_C	h	V_{hA} (cm ³ /g)	α	σ_e
2	2431	1.047	14.57	7.73	9	0.490	0.64	0.89
3	3105	0.994	11.49	1.55	3	1.334	0.98	1.1
3.5	2146	0.807	11.35	1.57	2	1.447	0.98	1.05
4	2967	1.143	12.88	2.12	5	1.401	0.99	0.85
5	2062	0.743	13.56	1.80	9	0.970	1.00	0.63

Table 6. Same as Table 4 but for different flow rates of inert gas F .

F [cm ³ /min]	S_{BET} (m ² /g)	V_{DR} (cm ³ /g)	Q_{Amax}/RT	B_C	h	V_{hA} [cm ³ /g]	α	σ_e
50	2889	1.09	-12.50	1.38	5	1.286	1.00	0.67
200	3105	0.994	-11.49	1.55	3	1.334	0.98	1.1
400	2919	0.949	-11.57	1.65	3	1.283	0.98	0.94
600	2774	1.039	-11.52	1.80	2	1.337	0.98	0.94
800	2698	1.076	-11.93	1.48	5	1.173	0.99	0.92

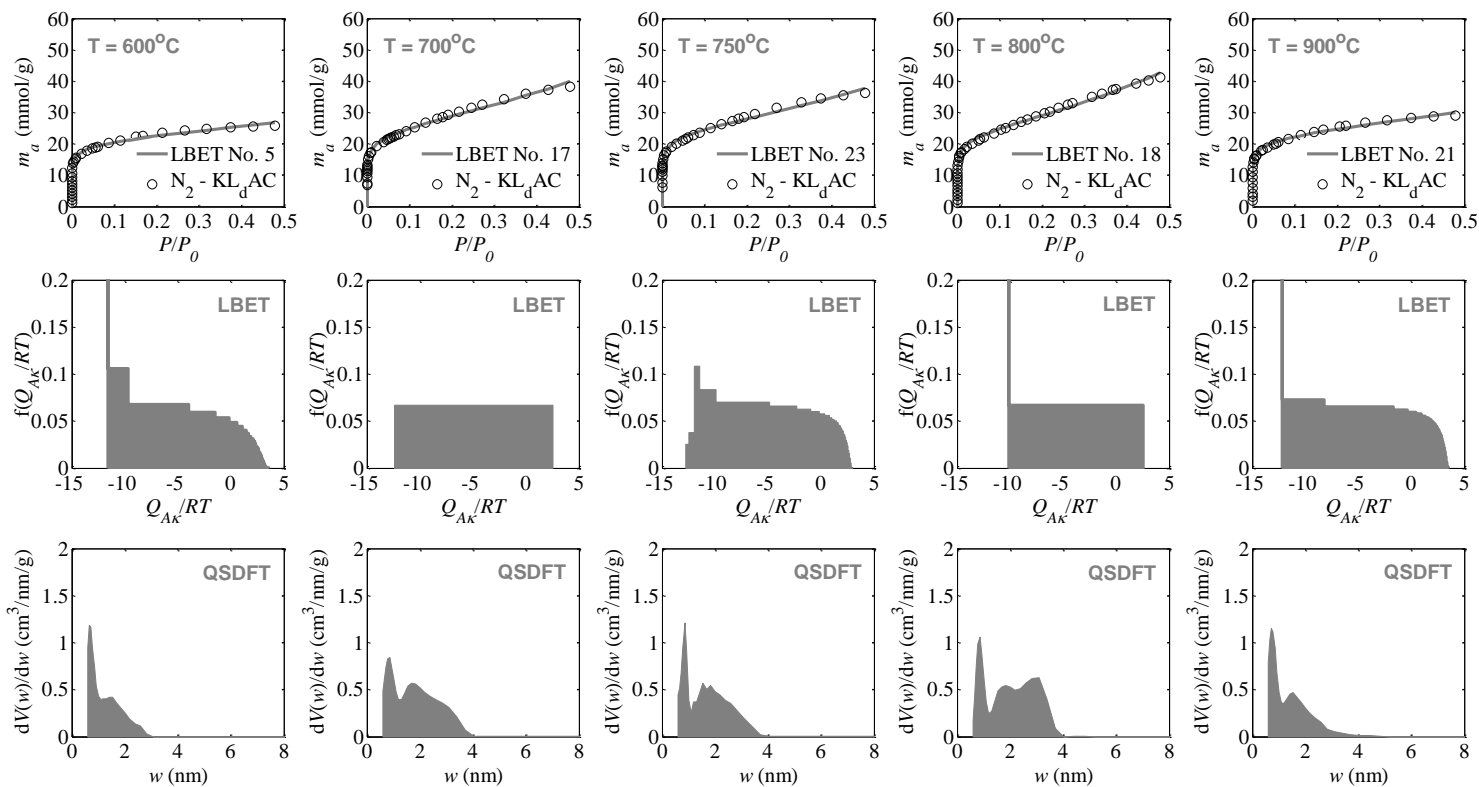


Fig. 1. Nitrogen adsorption isotherms with the best-fitted variant of the LBET model, and their corresponding adsorption energy distributions on the first layer as well as pore size distribution, obtained for the activated carbons KL_dAC produced at different activation temperatures T by activation with NaOH.

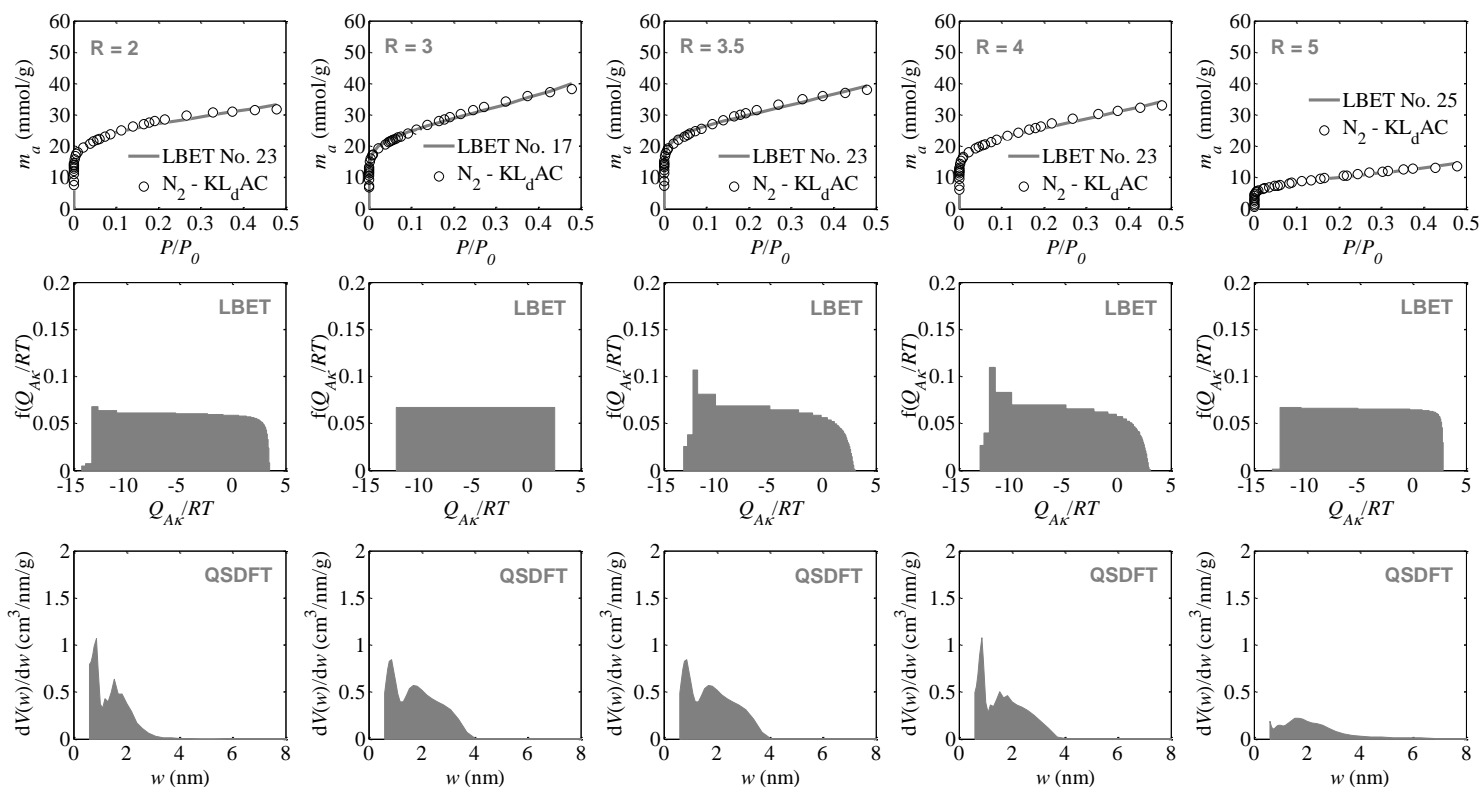


Fig. 2. Same as Fig. 1 but for different hydroxide to lignin mass ratio R .

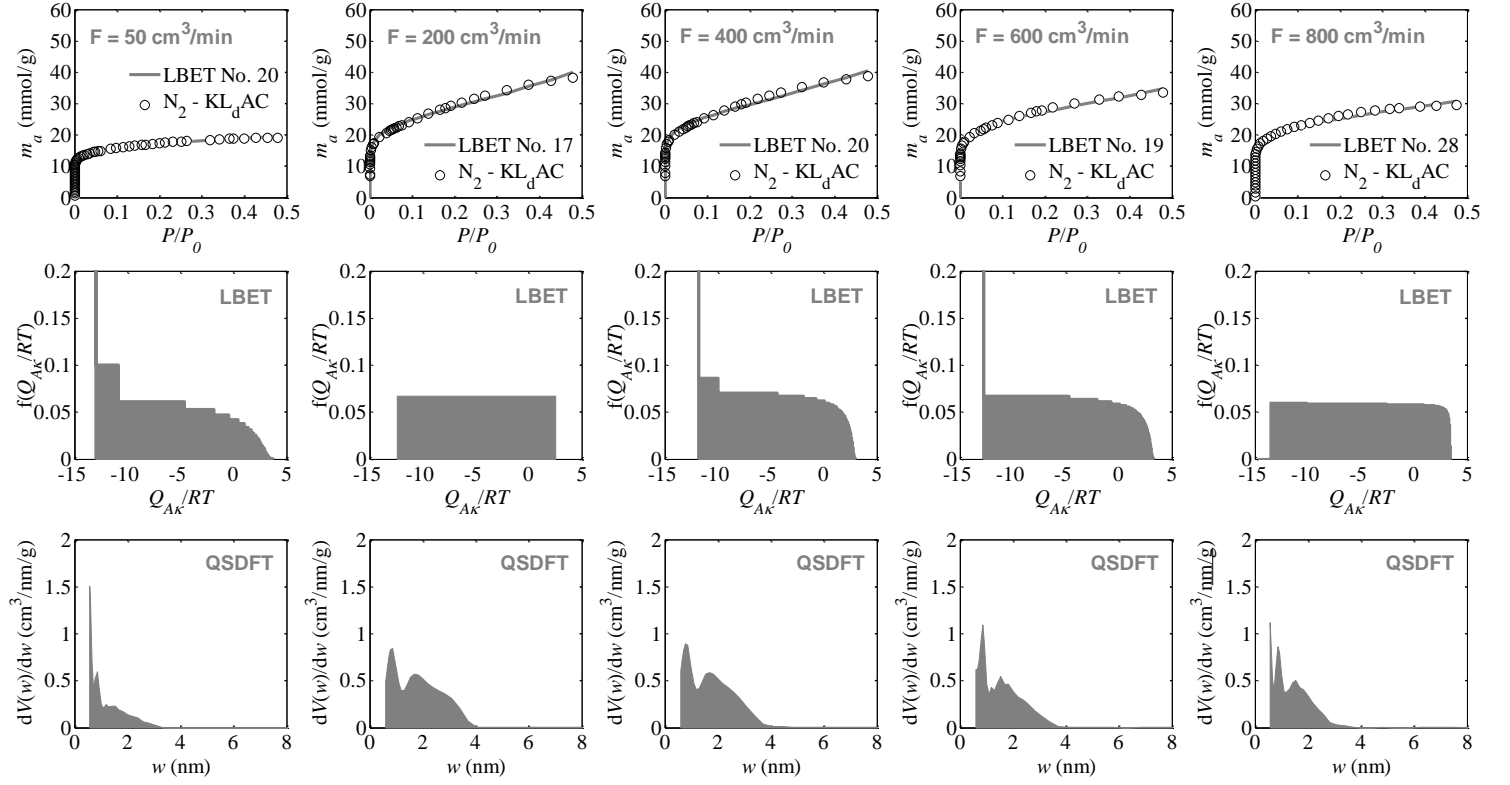


Fig. 3. Same as Fig. 1 but for different flow rates of inert gas F .

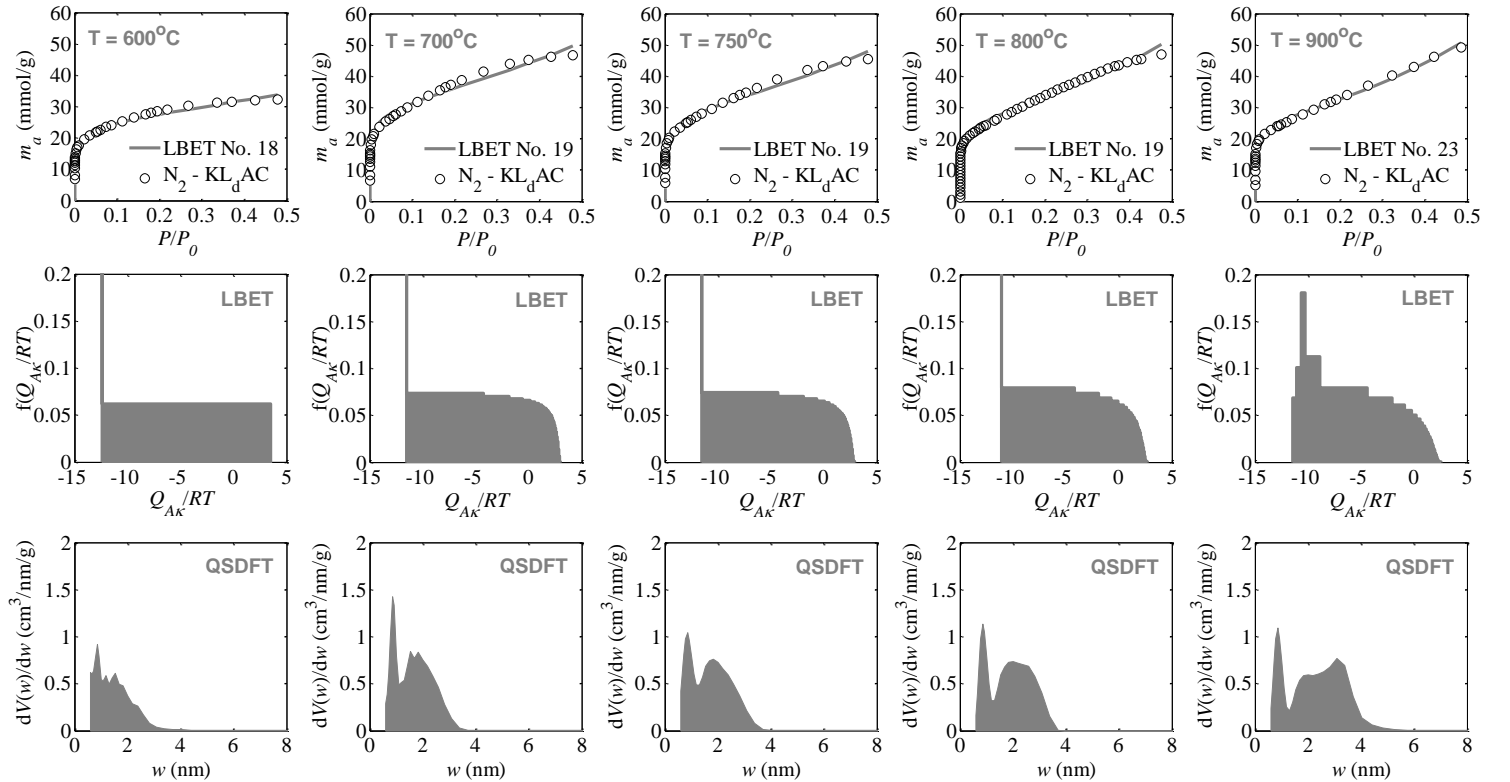


Fig. 4. Nitrogen adsorption isotherms with the best-fitted variant of the LBET model, and their corresponding adsorption energy distributions on the first layer as well as pore size distribution, obtained for the activated carbons KL_dAC produced at different activation temperatures T by activation with KOH.

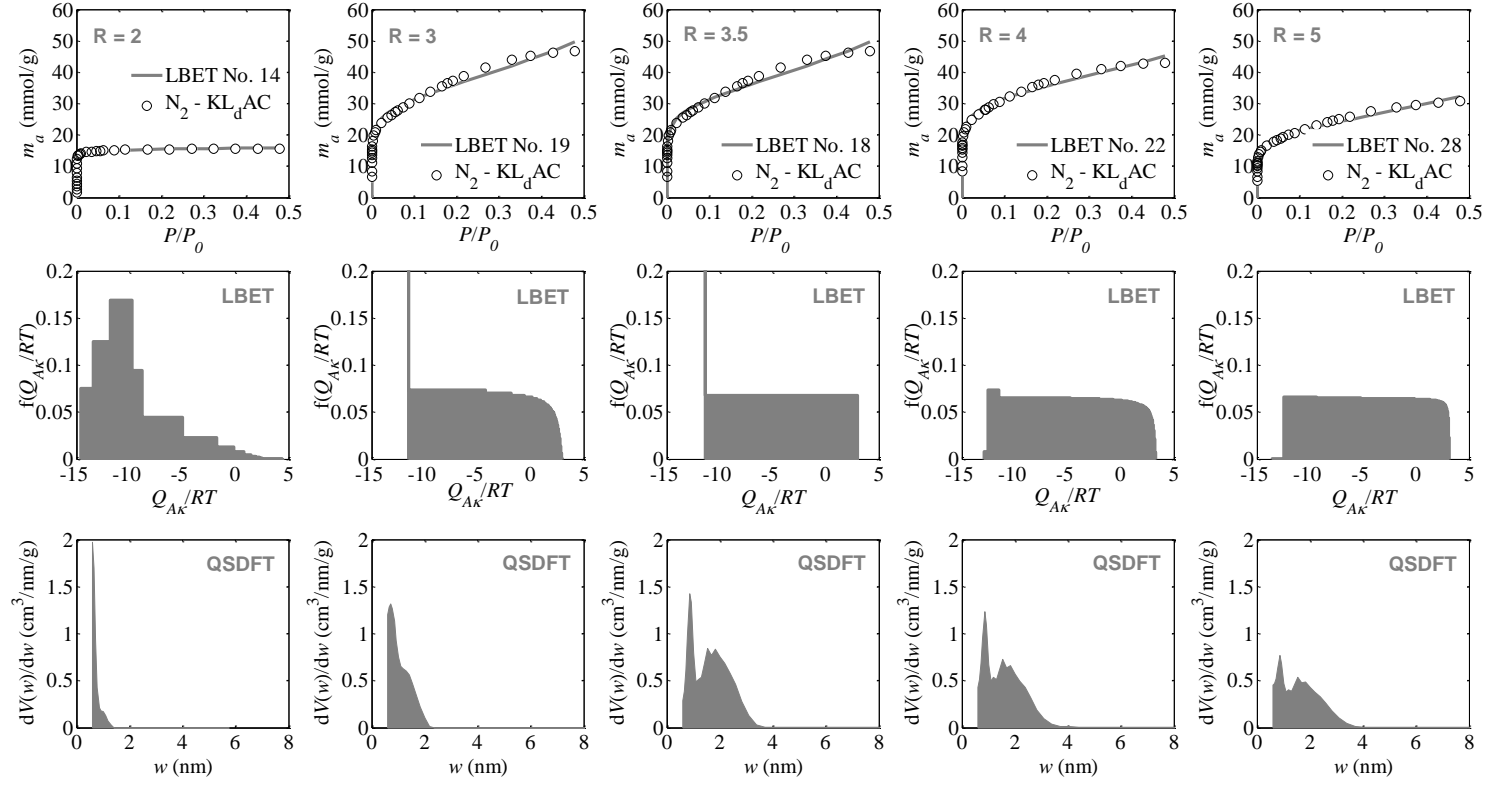


Fig. 5. Same as Fig. 4 but for different hydroxide to lignin mass ratio R .

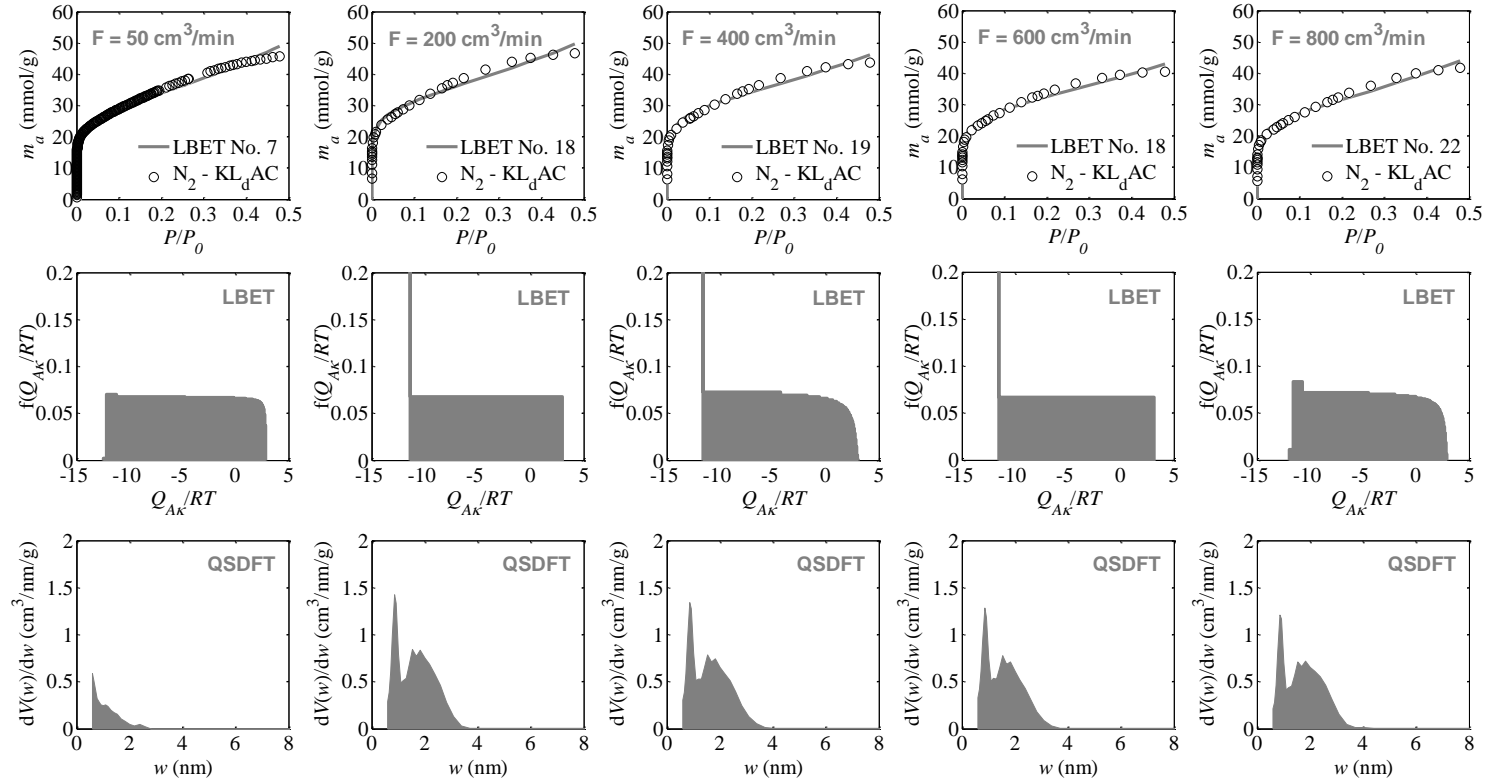


Fig. 6. Same as Fig. 1 but for different flow rates of inert gas F .

On the basis of the results and computer analyses presented in these tables and figures, it can be observed that the methods for analysing nitrogen adsorption isotherms, i.e., BET, DR, LBET and QSDFT, are mutually complementary. They indeed provide a full spectrum of information about both the porous structure of KL_dAC and adsorption processes, useful for scientists and technologists. Using all these methods at the same time for analysing the porous structure of adsorbents allows verifying the obtained information and evaluating their credibility. It also significantly facilitates the interpretation of the obtained results.

From the LBET method, the value of the width parameter of clusters of adsorbate molecules ($\beta=1.00$) has been obtained for all the analysed samples of activated carbons. Therefore, such information was not given in the tables. The estimated value of the β parameter indicates that not branching clusters of adsorbate molecules are created in the micropores of the obtained activated carbons. It means that only one molecule of a higher layer can adsorb onto each molecule of a given layer.

3.2. Effect of activation temperature

Based on the results gathered in Table 1 and in Figure 1, it can be observed that the sample of KL_dAC obtained by activation NaOH at 600°C shows the lowest value of specific surface area ($S_{BET} = 1896 \text{ m}^2/\text{g}$), micropore volume ($V_{DR} = 0.66 \text{ cm}^3/\text{g}$) and capacity of the first adsorption layer ($V_{hA} = 0.808 \text{ cm}^3/\text{g}$) out of all other analysed samples, as well as the highest value of energetic parameter for the higher levels ($B_C = 2.81$). The surface of the analysed sample is heterogeneous, which is indicated by the parameter value $h = 3$, and high, not branching clusters of adsorbate molecules are created in the micropores of this material. The number of the best adjusted model of the LBET class namely LBET No. 5, suggests growth limitations of clusters of adsorbate molecules, which result from the competitive expansion of the neighbouring clusters of the adsorbate molecules. The shape

of the graph of adsorption energy distribution on the first adsorbed layer indicates that, on the surface of the same material (KL_dAC obtained with NaOH at 600°C), there is a narrow fraction of pores of sizes comparable to those of the adsorbate molecules, and of equal adsorption energy. Moreover, there is a group of adsorptive sites of narrow energy spectrum, and the remaining part has a very wide range of adsorption energies. In turn, on the graph of pore size distributions (PSDs) estimated from the QSDFT method, we can observe a dominant presence of narrow micropores in the overall porosity, and hence, in the sample of the analysed material there were preferential conditions for an expansion of clusters of adsorbate molecules, at the expense of the formation of new clusters.

The results of the analysis of the first sample show the advantages of using both LBET and QSDFT methods, as the information obtained with the use of the BET and DR methods alone, i.e., the specific surface area S_{BET} and the micropore volume V_{DR} , is not enough for a complete description of the porous structure of activated carbons, of the properties of their surface and the related adsorption processes. An analysis of the nitrogen adsorption isotherm of the sample produced by NaOH activation at $T = 700^\circ\text{C}$ with the use of BET and DR equations showed that the surface area of the said sample was $S_{BET} = 2413 \text{ m}^2/\text{g}$, while the pore volume was $V_{DR} = 0.956 \text{ cm}^3/\text{g}$. These values are significantly higher than those obtained for the sample prepared at 600°C. The usual conclusion is that the microporosity simply increases with the activation temperature. However, such statement is not precise enough and no other effect of the increase of the activation temperature by 100°C can be deduced. Only using the LBET and QSDFT methods applied to the same isotherm enabled obtaining a broader spectrum of information about surface heterogeneity and adsorption processes.

Thus, it is observed that the value of the parameter V_{hA} increased from 0.808 to 1.078 cm^3/g , whereas the parameter α , i.e., the height of adsorbate molecules clusters (related to

the number of adsorbed layers), decreased from 0.92 at 600°C to 0.75 at 700°C. On the other hand, the value of the dimensionless parameter B_C , i.e., the parameter of adsorption energy for the higher layers, dropped from 2.81 to 1.00, along with an increase of maximum energy of adsorption on the first layer Q_A/RT from 11.60 up to 12.40. This fact can be explained by the fact that an increase of activation temperature resulted in the development of more adsorption sites on the surface of the material and in an increase of adhesive forces, offering more favourable conditions for the development of new clusters at the expense of the development of the already existing ones.

The value of the parameter $h = 1$ and the shape of the adsorption energy distribution diagram (see Fig. 1) evidence that the distribution of adsorption energy on the surface of the sample prepared with NaOH at 700°C is uniform for all the clusters of adsorbate molecules. Also, the number of the best-fitted LBET class model, namely LBET No. 17, shows that the limitations on cluster growth result from limited pore geometry. The shape of the graph of adsorption energy distribution on the first layer indicates that there are very similar micropores on the surface of this material, of very similar energetic properties of the surface. Based on the analysis of the KL_dAC sample obtained at 700°C with the use of the QSDFT method, we can observe a the presence of more and broader mesopores than in the sample obtained at 600°C. This also confirms the results of the analyses obtained with the use of the LBET method, which indicate that in the case of the KL_dAC obtained at 700°C, there were better conditions for the creation of new clusters of adsorbate molecules , at the expense of the development of the existing clusters.

Very interesting results were obtained for the sample of activated carbon KL_dAC produced at 750°C. More specifically, compared to the sample discussed above produced at 700°C, an increased value of the adsorbate molecules cluster height parameter was obtained ($\alpha = 0.97$), as well as higher maximum adsorption energy for the first layer ($Q_{Amax}/RT =$

12.78). Lower values of the volume of the first adsorbed layer ($V_{hA} = 0.980 \text{ cm}^3/\text{g}$), and higher value of the adsorption energy for the layers above the first layer ($B_C = 1.55$) were also found, as well as a significantly higher degree of surface heterogeneity ($h = 5$). The number of the best adjusted model of the LBET class (No.23), indicates the presence of dominant geometric growth limitations of clusters of adsorbate particles. The shape of energy distribution of the material obtained at 750°C shows a significant energetic diversification of the original adsorption sites. As can be observed, a small modification of activation temperature resulted in a considerably different structure of micropores compared to the sample produced at 700°C . Judging from the results of the analyses, the sample produced at 750°C developed a heterogeneous microporous structure offering conditions for the growth of high clusters of adsorbate molecules, owing to the higher energy of adsorption in the upper layers.

The results obtained from the LBET method also confirmed those from the QSDFT. Namely, the latter led to a PSD at 750°C showing a more significant presence of micropores (between 0.6 and 1.2) and a less significant rate of the mesopore volume to the total pore volume than at 700°C . These results also correlate with values of specific surface area $S_{BET} = 2345 \text{ m}^2/\text{g}$ and micropore volume $V_{DR} = 0.81 \text{ cm}^3/\text{g}$. However, it is worth mentioning that the analysis based on BET and DR methods is virtually useless, as it only yielded information on the decrease of the S_{BET} and V_{DR} , which could suggest only slight changes in the structure of pores and in the properties of the surfaces. However, as suggested from LBET and QSDFT methods, an increase of activation temperature to 750°C actually resulted in significant changes in the structure of the surface of the examined KL_dAC sample and of its adsorption properties.

The analysis of the results obtained for the activated carbon produced at 800°C , yielded equally interesting results, some of them being close to those obtained for the sample

produced at 700°C. The value of the maximum energy of adsorption on the first layer was indeed $Q_{Amax}/RT = 10.10$, namely the lowest of all the analysed samples. The surface heterogeneity parameter was $h = 2$, pointing out the fact that for the individual adsorbed molecules the surface was homogeneous, and all the adsorbate molecule clusters had a uniform distribution of adsorption energy, which is also reflected in the shape of the adsorption energy distribution on the first adsorbed layer. Analogically to the previously described sample, the number of the best adjusted LBET model, No. 18, indicates dominant geometric growth limitations of clusters of adsorbate molecules, in the evaluated activated carbon. The analysis of the PSD chart indicated that mesopores between 3 and 4nm in size have developed in this material to a much greater extent than in the former samples. This aspect had not been detected neither by BET nor DR methods, however a change of shape of the graph of adsorption energy distribution, obtained with the use of the LBET method, might evidence that. This confirms the need of associating LBET and QSDFT to more usual methods, which complement each other, thereby allowing a complete and credible picture of the analysed porous structure.

In the case of the results obtained for the sample obtained at 900°C, it is worth pointing out the significantly lower values of specific surface area S_{BET} , micropore volume V_{DR} and volume of the first adsorbed layer V_{hA} , as well as a more significant diversification of the right side of the adsorption energy distribution. The analysis based on the QSDFT showed that there is much fewer of the largest micro and mesopores, especially from the range between about 3 to 4 nm, in the sample prepared at 900°C.

Based on the above, it can be observed that a higher the degree of surface heterogeneity leads to a greater the discrepancies between the results obtained from LBET and QSDFT on one hand and those from BET and DR methods on the other hand. This is

logical as the general assumption of BET and DR models considers that the adsorbent surface is homogenous.

3.3. Effect of activation ratio

The effect of the NaOH to demineralised Kraft lignin mass ratio, R , on the development of the microporous structure of the activated carbons is now considered. The analysis was carried out for the samples produced at activation temperature $T = 700^\circ\text{C}$ and, again, with activation time t , inert gas flow rate F and heating rate r of 1h, 200 cm³/min and 5°C/min, respectively. The results of analyses of the corresponding adsorption isotherms are given in Table 2 and in Fig. 2. For the sample obtained at a mass ratio $R = 2$, the specific surface area had the value of $S_{BET} = 2288 \text{ m}^2/\text{g}$, and the micropore volume was $V_{DR} = 0.861 \text{ cm}^3/\text{g}$. Application of the LBET class models showed that the surface is heterogeneous, as evidenced by the parameter $h = 5$, while very high, stack-like clusters of adsorbate molecules ($\alpha = 0.99$) developed in the micropores of the material. Equally noteworthy were the high values of maximum adsorption energy for the first layer and the upper layers, described by means of their respective parameters Q_{Amax}/RT and B_C . The shape of the adsorption energy distribution indicates a wide range of adsorption energy in micropores. The analysis of the PSD graph, obtained with the use of the QSDFT method, in turn showed a dominant presence of micropores in the total pore volume, although the distribution is bimodal.

Interesting results were obtained for the sample produced at $R = 3$, which was much more homogeneous than the sample discussed above ($h = 1$). Besides, significantly lower adsorbate molecule clusters were formed in that material, as evidenced by the value of the α parameter ($\alpha = 0.75$). Also, the said sample was characterised by a very large volume of first adsorbed layer ($V_{hA} = 1.078 \text{ cm}^3/\text{g}$), of specific surface area ($S_{BET} = 2413 \text{ m}^2/\text{g}$) and of micropore volume ($V_{DR} = 0.956 \text{ cm}^3/\text{g}$). The analysis with the use of the QSDFT method

indicated a much more significant presence of mesopores between 2 to 4 nm in the overall porosity with respect to the sample prepared at $R = 2$.

An analysis of the values of specific surface area S_{BET} and micropore volume V_{DR} determined from BET and DR equations, respectively, may suggest that the KL_dAC sample produced at the mass ratio $R = 3.5$ is characterised by the best adsorptive properties ($S_{BET} = 2490 \text{ m}^2/\text{g}$, $V_{DR} = 0.96 \text{ cm}^3/\text{g}$). However, it was only when the more advanced LBET method was employed that the surface heterogeneity of the said sample became significant ($h = 5$), which completely changes the interpretation of the results of calculations. As it can also be observed, the graph of adsorption energy distribution is highly asymmetric, which indicates a very broad spectrum of adsorptive sites. In turn, the analysis performed with the use of the QSDFT method evidenced more mesopores between 2 and 4 nm in comparison to the material obtained at a $R = 3$.

At $R = 4$, the sample had much smaller values of specific surface area, micropore volume as well as volume of the first adsorbed layer and, interestingly, a more significant presence of micropores in the total pore volume, including the micropores between 0.6 to about 1 nm. The results for $R = 5$ indicate a destructive impact of sodium hydroxide. As a result of this, an adsorbent of relatively small values of structure parameters, i.e., S_{BET} , V_{DR} , V_{hA} , and with a highly inhomogeneous surface ($h = 7$) and a wide distribution of adsorption energy on the surface, was produced.

3.4. Effect of inert gas flow rate

The effect of the inert gas (nitrogen) flow rate F on the development of the microporous structure was analysed in the range from 50 to 800 cm^3/min for KL_dAC samples produced in the following activation conditions: $T = 700^\circ\text{C}$; $R = 3$; $t = 1 \text{ h}$; and $r = 5^\circ\text{C}/\text{min}$. Based on the results compiled in Table 3 and presented in Fig. 3, it has been found that the

sample obtained at $F = 50 \text{ cm}^3/\text{min}$ had lower values of S_{BET} , V_{DR} and V_{hA} , as well as an inhomogeneous surface ($h = 3$), and a broad range of adsorption energies in the micropores. It would therefore be easily claimed that it is the worst out all the analysed samples of KL_dAC activated carbons obtained at various inert gas flow rates. However, only the analysis with the use of the QSDFT method indicated that there is dominant presence of a fraction of very narrow micropores in the structure of this material, which is often very desired in many adsorption processes. Once again, it confirms the need for performing a complex analysis of the porous structure with the use of the LBET and QSDFT methods, along with standard analyses performed with the use of BET and DR. Only doing so one can obtain a complete information of the porous structure and the geometric and energy properties of the material's surface, which is required for selecting precise preparation conditions and thereby getting a final product of strictly determined adsorptive properties.

The material produced at $200 \text{ cm}^3/\text{min}$ was characterised by the highest volume of the first adsorbed layer ($V_{hA} = 1.078 \text{ cm}^3/\text{g}$) and the most homogeneous surface ($h = 1$), as well as by high values of specific surface area ($S_{BET} = 2413 \text{ m}^2/\text{g}$) and of microporous volume ($V_{DR} = 0.956 \text{ cm}^3/\text{g}$). However, its parameters α and B_C were the lowest among the analysed samples ($\alpha = 0.75$ and $B_C = 1.00$). On the basis of the graph of adsorption energy distribution, estimated with the use of the LBET method, it can be concluded that there is a very wide spectrum of adsorption energy in the micropores of this material, showing a high presence of wide micropores. On the other hand, on the basis of the graph of pore size distribution, much more wider micropores and mesopores between 2 to 4 nm than in the former sample can be observed. This confirms the aforementioned observations from the analysis performed with the LBET method. The sample produced at $400 \text{ cm}^3/\text{min}$ had admittedly the highest values of surface area ($S_{BET} = 2494 \text{ m}^2/\text{g}$) and of microporous volume ($V_{DR} = 1.042 \text{ cm}^3/\text{g}$) out of all analysed samples, but was characterized by a heterogeneous surface ($h = 3$).

A further increase of F from 600 to 800 cm³/min resulted in materials of slightly lower surface area and micropore volume as indicated from BET and DR methods. The analysis with the use of the LBET method led to comparable values for the volume of the first adsorbed layer V_{hA} , and hence of corresponding growth limitation of clusters of adsorbate molecules resulting from geometric limitations. However, in the case of the activated carbon obtained at 800 cm³/min, a significantly greater value (9) of the h parameter was obtained, showing a very significant surface inhomogeneity. In the case of the samples obtained from the F value equal to respectively 600 and 800 cm³/min, on the graph obtained by QSDFT method it can be seen also smaller participation of the volume of mesopores in the total pore volume and a larger part of the narrowest micropores.

From the results presented in Tables 1–3 and Fig. 1–3, it can be concluded that the best adsorptive properties are those of the activated carbon KL_dAC obtained by the reference sample, i.e., the one produced in the following conditions of the activation: $T = 700^{\circ}\text{C}$, $R = 3$, $t = 1$ h, $F = 200$ cm³/min, $r = 5^{\circ}\text{C}/\text{min}$, provided that the maximum adsorptive capacity is assumed to be the key criterion, with the maximum degree of homogeneity of the surface of the material. Similar computer analyses as those detailed above were carried out for activated carbons KL_dAC produced from chemical activation of demineralised Kraft lignin KL_d with potassium hydroxide KOH, and the results are detailed below.

3.5. Effect of the nature of the activating agent

NaOH or KOH are now compared for developing the microporous structure of activated carbons based on demineralised Kraft lignin, and the corresponding results are gathered in Tables 4-6 and Fig. 4-6. As before, a reference sample was produced by KOH activation in the same conditions as for NaOH i.e., $T = 700^{\circ}\text{C}$, $R = 3$, $t = 1$ h, $F = 200$ cm³/min and $r = 5^{\circ}\text{C}/\text{min}$.

Considering all results presented so far, a significant influence of the nature of the chemical activating agent can be easily noticed, as expected from the broad former literature on this topic. Especially, based on adsorption isotherm analyses carried out with BET, DR and LBET methods for KL_dAC activated carbons at different activation temperatures, KOH clearly led to definitely larger S_{BET} , V_{DR} and V_{hA} values with respect to NaOH. The energy parameters Q_{Amax}/RT and B_C , however, were comparable, except at $T = 900^\circ\text{C}$ for which a higher B_C value was observed with NaOH. On the other hand, values of the heterogeneity parameter h after NaOH activation were different for various temperatures, and no correlation with the temperature of the activation process was seen. This indicates that the progression of reactions is uncontrollable with NaOH compared to carbons obtained by KOH activation, for which the degree of heterogeneity globally increased with the activation temperature.

However, as calculations demonstrated, NaOH activation at 700°C produced the materials with the lowest degree of surface heterogeneity. In a similar way, the analysis of the α parameter values indicates that there is no correlation of this parameter with the increase of temperature for activated carbons obtained with NaOH. In contrast, the order of clusters of the adsorbate molecules defined by α significantly decreased as the temperature increased for KOH activation.

Examining now the effect of mass ratio (see Table 2 and 5, as well as Fig. 2 and 5), it can also be concluded that KL_dAC activated carbons were obtained with a higher degree of surface heterogeneity when prepared with KOH and, at the same time, with higher values of S_{BET} , V_{DR} and V_{hA} . However, it should be noticed that, for KOH activation, S_{BET} and h were very sensitive to changes of the R mass ratio.

Examining the effect of the flow rates of inert gas F during NaOH and KOH activation (see Table 3 and 6), the same kind of conclusions can be obtained, i.e., KL_dAC activated carbons were obtained with a higher degree of surface heterogeneity when prepared with

KOH and, at the same time, with higher values of S_{BET} , V_{DR} and V_{hA} . On the other hand, the impact of F on the microporosity was much lower when KOH was used.

The present analyses therefore suggest that KOH generally allows producing activated carbons characterised by a considerably higher microporosity, i.e., with higher values of: volume of the first adsorbed layer V_{hA} , specific surface area S_{BET} , micropore volume V_{DR} and first adsorption layer capacity V_{hA} , however, with a higher degree of surface heterogeneity h . A conclusion is that KOH performs better as an activating agent than NaOH, owing to the fact that the potassium cation is characterised by a higher radius (0.2666 nm) than that of sodium (0.190 nm). Moreover, in the case of reaction with biomass, potassium hydroxide has stronger dehydrating and oxidising properties than sodium hydroxide, hence its ability to enhance the development of the microporous structure of activated carbons produced from this type of raw materials. Accordingly, the activated carbons obtained from demineralised Kraft lignin by KOH activation present a higher degree of surface heterogeneity and higher values of Q_{Amax}/RT maximum adsorption energy with respect to those obtained from NaOH.

4. Conclusion

Based on the porous structure of activated carbons obtained in various preparation conditions, precisely determining the optimal conditions for producing them is expected to be possible, taking into account all technical, energetic and economic aspects in order to obtain materials having strictly determined properties for given adsorption processes. However, doing so requires the necessary skills for correctly interpreting the obtained results, as well as a very good knowledge of the calculation tools and the models of pore structure and the adsorption processes occurring inside it.

Thus, the nature of the methods of pore structure analysis from the nitrogen adsorption isotherms influences the quality and the credibility of the obtained results. Especially the use

of the BET method for determining the specific surface area of microporous activated carbons can be criticised. If, however, the obtained information is used in the framework of a purely comparative analysis, it remains highly valuable due to the attachment of the scientific and industrial communities to the BET equation. Results derived from the DR equation, i.e., the micropore volume, should be approached with caution, due to the fact that this method assumes, among others, surface homogeneity, which is not correct in most of the cases such as those reported herein. However, just like for BET, the DR method is also a standard method for describing the microporous structure of carbonaceous adsorbents.

We have shown that the application of only BET and DR methods to nitrogen adsorption isotherms of activated carbons is not enough for a credible description of the pore structure and adsorption processes occurring in them, the knowledge of which might allow the optimisation of preparation conditions. Thus, it is recommended to use more advanced methods of pore structure and adsorption process analysis, such as LBET or QSDFT methods.

The LBET method was shown here to be especially suitable for the analysis of the microporous structure of activated carbons such as KL_dAC, and it was indeed initially developed for analysing microporous materials. KL_dAC activated carbons were indeed found to be ideal materials for verifying the LBET method, as evidenced by the excellent fits of the LBET class models to the nitrogen adsorption isotherms, and further confirmed by the low error standard fitting deviation σ_e .

The QSDFT method was also proved to be highly useful for determining credible pore size distributions thanks to the assumption of surface heterogeneity and coarsness. None of the artefacts known from the former NLDFT method was observed, and the information on the shape of the PSD allowed a more thorough and relevant description of the pore structure, and hence a more reliable evaluation of the impact of the activation conditions on the porous structure formation.

As demonstrated here, the best is therefore to combine the use of all four methods, i.e. BET, DR, QSDFT and LBET, because of their mutual complementarity, thereby leading to a full spectrum of useful information both for scientists and for technologists. Moreover, these methods allow crosschecking the obtained results, from which calculation errors can be avoided. Finally, the present work revealed complex interrelations concerning the effect of preparation conditions on the development of the microporous structure of activated carbons produced by chemical activation of demineralised Kraft lignin with potassium hydroxide and sodium hydroxides.

Acknowledgment: The research is led within the AGH University of Science and Technology in Krakow grant No. 11.11.210.217.

References

1. I.I. Salame, T.J. Badosz, *Ind. Eng. Chem. Res.* 39 (2000) 301.
2. J. Sreńscek-Nazzal, B. Michalkiewicz, *Polish J. Chem. Technol.* 13 (2011) 63.
3. K. Kante, C. Nieto-Delgado, J.R. Rangel-Mendez, T.J. Badosz, *J. Hazard. Mater.* 201-202 (2011) 141.
4. J. Sreńscek-Nazzal, W. Kamińska, B. Michalkiewicz, Z. C. Koren, *Ind. Crops. Prod.* 47 (2013) 153.
5. K.Y. Foo, B.H. Hameed, *Chem. Eng. J.* 173 (2011) 385.
6. Y. Guo, Sh. Yang, K. Yu, J. Zhao, Z. Wang, H. Xu, *Mater. Chem. Phys.* 74 (2002) 320.
7. Y. Guo, S. Yang, J. Zhao, *Chem J. Chin. Univ.* 21 (2000) 335.
8. L. Manjarrez-Nevárez, L. Ballinas-Casarrubias, A. Celzard, V. Fierro, V. Torres-Muñoz, A. Camacho Davila, R. Torres-Lubian, R. Ibarra-Gómez, G. González-Sánchez, *Carbohydr. Polym.* 86 (2011) 732.

9. L. I. Grischechko, G. Amaral-Labat, A. Szczurek, V. Fierro, B. N. Kuznetsov, A. Celzard, *Micropor. Mesopor. Mater.* 168 (2013) 19.
10. M. A. Anwer, H. E. Naguib, A. Celzard, V. Fierro, *Composites Part B: Engineering* 82 (2015) 92.
11. V. Fierro, V. Torné-Fernández, A. Celzard, *Micropor. Mesopor. Mater.* 92 (2006) 243.
12. V. Fierro, V. Torné-Fernández, A. Celzard, *Stud. Surf. Sci. Catal.* 160 (2007) 607.
13. J. Hayashi, K. Muroyama, V.G. Gomes, A.P. Watkinson. *Carbon* 40 (2002) 617.
14. V. Fierro, V. Torné-Fernández, A. Celzard, *Micropor. Mesopor. Mater.* 101 (2007) 419.
15. S. Brunauer, P. H. Emmett, E. Teller, *J. Am. Chem. Soc.* 60 (1938) 309.
16. M.M. Dubinin, *Chem. Rev.* 60 (1960) 235.
17. J.T. Duda, M. Kwiatkowski, J. Milewska-Duda, *J. Mol. Model.* 11 (2005) 416.
18. M. Kwiatkowski, *Langmuir* 23 (2007) 2569.
19. M. Kwiatkowski, *J. Colloid Interface Sci.* 313 (2007) 428.
20. M. Kwiatkowski, *J. Mol. Model.* 14 (2008) 183.
21. M. Kwiatkowski, *Appl. Surf. Sci.* 257 (2011) 8912.
22. M. Kwiatkowski, A. Policicchio, M. Seredych, T. J. Bandoz, *Carbon* 98 (2016) 250.
23. P.I. Ravikovitch, A.V. Neimark, *Langmuir* 22 (2006) 11171.
24. A.V. Neimark, Y. Lin, P.I. Ravikovitch, M. Thommes, *Carbon* 47 (2009) 1617.
25. J. Landers, G.Y. Gor, A.V. Neimark, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 437 (2013) 3-32.