Synergy between alkali activation and a salt template in superactive carbon production from lignin

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Abstract

Due to growing demand, the performance of traditional active carbon is insufficient. An innovative solution is superactive carbon with an ultra-high surface area as high as 3000 m² g⁻¹. However, this material is very costly due to the considerable amount of alkali used in its manufacturing. To obtain superactive carbon from lignin, KOH and KCl were used simultaneously. The method was thoroughly studied to describe the mechanism of pore origin and control the pore size. Because of synergy between KOH and KCl, superactive carbon with an ultra-high surface area (2938 ± 42 m² g⁻¹) was obtained at essentially diminished KOH consumption (1 g g⁻¹) in contrast to previously reported methods. The process was optimised using the response surface method. The pore size can be tuned by varying the amount of KOH and temperature. Observed synergy enabled reduced alkali consumption, overcoming the barrier to widespread implementation of superactive carbon.

Supplementary material for this article is available online

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(Some figures may appear in colour only in the online journal)

1. Introduction

Active carbon is a well-known porous solid material with a diverse porous structure and large specific surface area (SSA). There are a variety of applications of active carbon from wastewater treatment to energy storage materials [1]. Active carbon is produced from carbonaceous materials through physical or chemical activation [2]. SSA is a crucial characteristic of active carbon and it is typically between 500 and 1500 m² g⁻¹ for commercial samples. The cutting edge product is superactive carbon that possesses an ultra-high surface area up to 3000 m² g⁻¹ [3]. The ultra-high surface area is beneficial for various applications. For instance, in drinking water purification the adsorption of sodium hypochlorite and chloroform was substantially increased by increasing the surface area [4]. The capacitance of supercapacitors using materials with high surface area is also better than conventional active carbon [5–7]. The increased SSA of superactive carbon is also advantageous for gas storage systems, since a larger volume of natural gas can be adsorbed [8]. As can be seen from these examples, the use of superactive carbon is beneficial in many applications and its use can decrease the needed amount of adsorbent, enabling more sustainable processes. However, improvements to increase the sustainability of the manufacturing process of superactive carbon are still needed.

Superactive carbon was first produced by the AMOCO company (Standard Oil Company) in 1978 by KOH activation using petroleum coke as a raw material [9]. The
superactive carbon of AMOCO is now produced by the Kansai Coke and Chemicals Company under the brand name MAXSORB® [10]. The unique aspect of the process is the use of significant excess of potassium hydroxide per gram of starting material (3–4 g g⁻¹). The superactive carbons produced in the process have a surface area greater than 3000 m² g⁻¹ and rich in micropores. The genesis of a microporous structure is conducted through the interaction of potassium hydroxide with carbon matter, yielding the formation of the corresponding carbonate at temperatures below 700 °C and metallic potassium over 700 °C [11]. The metallic potassium is assumed to be responsible for the origin of micropores through intercalation and by following an expansion of the graphite layers [12]. The micropores and mesopores are generated on the walls of the macropores, which in turn are formed through the self-template of KOH grains [13, 14]. Superactive carbon possesses a versatile porous structure necessary for industrial applications but, since a large amount of KOH is consumed in the process, the material is not affordable and, for most applications, traditional steam-activated carbon is used because of its low price, despite the superior properties of superactive carbon. Studies aiming to reduce alkali consumption in the process of superactive carbon production are therefore essential for technological applications.

Ordered porous carbon can be produced using the so-called template method. A zeolite template is used as a carbon replica for the synthesis of highly ordered porous material with a surface area of 2000–4000 m² g⁻¹ [15]. The polymer solution penetrates the zeolite structure with subsequent carbonisation. The resultant composite contains zeolite and carbon. The zeolite template is removed by leaching using strong mineral acid, and an exact carbon replica is obtained. The template carbon possesses an ordered microporous structure underlying an ultra-high SSA but, for the adsorption applications, a diverse porous structure, containing both mesopores and macropores is needed, and the ordered microporous structure of the template carbon is not porous enough [16]. Moreover, since the raw materials are usually synthetic zeolites and polymers coupled with leaching by a strong acid, the zeolite template carbon is an expensive material with limited applications compared to conventional activated carbon.

There are very few reports that, have demonstrated the use of affordable templates for carbon materials with or without subsequent physical or chemical activation [17–19]. However, the reported materials do not possess an ultrahigh surface area. Our previous studies revealed a novel method for producing microporous carbon by the simultaneous use of NaCl as a template and NaOH as an activator [20]. This method enables production of an active carbon at reduced alkali consumption, but the obtained carbon has a surface area in the range of conventional activated carbon and far below, in contrast to the ultrahigh surface area of the superactive carbon prepared by KOH activation or the zeolite template method.

(Super)active carbon can be made on any carbonaceous materials. The availability and affordability of the potential raw material should be taken into account. The carbon content in the raw material is also important because the higher the carbon content in the raw material, the higher the potential yield of the product. Examples of raw materials for superactive carbons are petroleum coke [10], Spanish anthracite [21] and Kraft lignin [22]. Lignin, as the second most abundant plant polymer after cellulose and having substantial carbon content over 50%, is an advantageous choice among a variety of raw materials [23]. It is also a by-product of the paper industry and ethanol production from wood. Lignin that originates from the kraft process is called kraft or alkali lignin. It is produced, for example, by the LignoBoost® process through precipitation of lignin from black liquor using acid and CO₂ [24]. Despite the straightforwardness of the process, the availability of kraft lignin is still quite limited due to several applications that utilise it and the limited volumes and numbers of commercial-scale producers. Another example of industrial lignin is hydrolysis lignin. This material is a by-product of ethanol production through the hydrolysis of wood carbohydrates. In this process, the carbohydrate part of the wood is hydrolysed for subsequent fermentation while the aromatic part (lignin) remains almost the same. Usually, the hydrolysis lignin is incinerated to produce energy, but the use of lignin for a valuable product like superactive carbon is beneficial compared to incineration. In particular, the price of active carbon is 2–7 times higher than the price of energy obtained after the incineration of lignin [25]. Moreover, there are over 95 million tonnes of lignin waste deposits from the biomass hydrolysis process in post-Soviet republics, leading to environmental problems, so their utilisation is required [26]. Accordingly, hydrolysis lignin is an advantageous raw material for the manufacturing of superactive carbon.

The aim of this study is to intensify the production of superactive carbon by applying the synergy between KOH activation and a KCl template. To optimise the process and obtain superactive carbon at maximum surface area and product yield at minimised alkali consumption, the response surface method (RSM) was applied [27]. Since the control of pore size is important for industrial applications, the tuning of pore size distribution was methodically conducted [28, 29]. In addition, the mechanism of pore formation was investigated revealing the synergy of KOH activation and the KCl template.

2. Materials and methods

2.1. Materials

The raw material is coniferous hydrolysis lignin with a moisture content of 6%. The chemicals such as KOH, K₂CO₃, KCl and NaCl (Sigma-Aldrich) were of analytical purity and dried in a vacuum at 105 °C to remove moisture before use. Deionised water was used to wash the obtained carbon. The nitrogen gas was 99.9999% purity.
2.2. Methods

2.2.1. Producing superactive carbon. The lignin was mixed with KOH and KCl in a mortar. The amount of KOH in the KOH/KCl mixture varied between 0.3 and 1.5 g g⁻¹ while the amount of KCl was 2.7–1.5 g g⁻¹ for each experimental run. The total lignin-to-KOH/KCl ratio was constant at 3 g g⁻¹. The obtained mixture was transferred to a tube furnace and heated at 5 °C min⁻¹ to the target temperatures of 700 °C, 800 °C and 900 °C. Carbonisation was maintained at target temperature for 60 min, and was conducted under nitrogen flow of 21 min⁻¹. Afterwards, the composite of carbon and chemicals was mixed with water. The chemicals were dissolved by washing several times in a Bucher funnel until neutral pH in the washing water was obtained. The produced carbon was dried in a vacuum at 105 °C for 16 h.

For comparison, the KOH-activated carbon (Sample F2007) was prepared according to the procedure adopted from literature [22]. In particular, KOH was mixed with lignin at a ratio of 3.0 g g⁻¹; heated at a ramp rate of 5 °C min⁻¹ to a target temperature of 700 °C and the temperature was maintained for 60 min. The produced carbon was washed several times in water until a neutral pH was obtained in the water. At the same heating rate and dwell time, for the comparison purpose, the carbon sample was prepared at 900 °C by using a mixture of 1.5 g of K₂CO₃ and 1.5 g of KCl (Sample RUN4-K₂CO₃). In the same manner, the carbon sample was obtained by mixing 1.0 g of KOH and 2.0 g of NaCl (Sample PRED1-NaCl). The effect of time (30, 60 and 90 min) was evaluated at 900 °C and KOH/KCl amount was 1.0/2.0 g g⁻¹ (Samples PRED1-30m, PRED1-60m and PRED1-90m).

2.2.2. Optimisation. The process was optimised using the RSM [27] by varying two factors: temperature (A, °C) and the amount of KOH in the KOH/KCl mixture (B, g g⁻¹). Minimum, zero and maximum levels were assigned to each factor: 700 °C, 800 °C and 900 °C for temperature and; 0.3, 0.9 and 1.5 g g⁻¹ for KOH amount. The characteristics of the produced carbon such as SSA (m² g⁻¹) and yield (Yield, %) were selected as responses. To evaluate the reproducibility, the samples were prepared in triplicate at zero level and optimal conditions. The adequacy of the obtained mathematical model was validated by ANOVA analysis.

2.2.3. Characterisation. The produced carbon was studied using N₂ physisorption on a Tristar²® II Plus, Micromeritics. The characterisation was based on N₂ adsorption–desorption isotherms. The values of SSA were estimated using the Brunauer, Emmett and Teller theory [30], applying the recommended procedure for microporous solids [31]. The total pore volume was calculated at p/p⁰ = 0.99. The micropore volume was calculated using the Dubin–Radushkevich equation [32]. The pore size distribution was plotted using non-local density functional theory (NLDFT) for carbon slit-like pores [33]. X-ray powder diffraction was used to investigate the ordered structures of the materials on a high-resolution PANalytical diffractometer. The spectra were recorded from 10° to 120° 2θ degrees applying Co Kα radiation at a voltage of 40 kV. Crystal size was calculated using data from the corresponding diffraction peaks applying the Williamson–Hall method (W–H) [34]. Fourier transform infrared (FTIR) spectroscopy was performed on a Bruker Vertex 70 spectrometer. Scanning electron microscopy (SEM) images were obtained with a JEOL JSM-7900 scanning electron microscope, which was equipped with an energy dispersive x-ray spectrometer (EDS). Transmission electron microscopy (TEM) images were produced with a Hitachi H-7600 transmission electron microscope. Raman spectra were taken with a Horiba HR800 UV (Jobin/Yvon).

3. Results and discussion

3.1. Comparison of NaOH/NaCl and KOH/KCl mixtures

The samples were prepared according to the optimal conditions specified in table 1 of the previously studied method [20]. As seen in this table 1, the use of the mixture KOH/KCl resulted in a larger surface area and greater pore volume than the use of NaOH/NaCl. Figure 1 (the inset) shows the N₂ adsorption/desorption isotherms of the prepared carbons using different starting mixtures. Both of samples demonstrated intrinsic isotherm type I for microporous materials, but the carbon prepared using the NaOH/NaCl mixture demonstrates the hysteresis H4 that could be ascribed to the formed mesopores [35]. The shapes of the isotherm and adsorption hysteresis are attributed to the progressive carbon burn-off that leads to the fusion of mesopores into mesopores [3]. On the NLDFT pore size distribution (figure 1, the inset), the peaks of meso- and macropores are strong for samples prepared using sodium-contained mixtures in contrast to samples prepared using KOH/KCl. Those prepared using KOH/KCl are more microporous while carbons prepared using NaOH/NaCl contain higher amounts of mesopores and macropores. Since the SSA mainly originates from micropores, it is greater for samples prepared using KOH/KCl due to a smaller number of meso- and macropores. This phenomenon can be explained by the assumption that KOH is favourable for micropores origin, while NaOH is responsible for the fusion between micropores into mesopores due to the above-mentioned burn-off [22]. Consequently, since potassium is a more active alkali metal than sodium, the mixture consisting of KOH and KCl is more effective in producing active carbon [36].

3.2. Ultra-high surface area

Since the KOH/KCl mixture is more efficient than the sodium-contained mixture, it was selected for further studies, to produce superactive carbon. At a modest chemical ratio, KOH/KCl-to-lignin of 0.6 g g⁻¹, a larger surface area can be achieved. To obtain carbon with ultra-high surface area by this method at minimum alkali consumption and the highest product yield, the RSM method was employed [27]. In the case of KOH activation, to obtain superactive carbons, the
lignin is 55% consumption. The maximum theoretical carbon yield from chemical ratio should be between 3 and 4 g g\(^{-1}\) [10, 22], so for all the experiments the chemical ratio (KOH/KCl-to-lignin, g g\(^{-1}\)) was maintained constant at 3.0 g g\(^{-1}\). The formation of metallic potassium from KOH is a major activation pathway for an ultra-high surface area [11]. Metallic potassium is produced at temperatures over 700 °C [10, 11], so the temperature regime from 700 °C to 900 °C was selected. Since the dwell time is a less significant factor for producing porous carbon, it was constantly kept at 60 min [20]. Based on the aforementioned information, only two factors were controlled in the experimental plan: KOH amount and target temperature.

At first, the experiments were performed at zero level (RUN0(1–3)). It can be seen that a large surface area (2012 ± 28 m\(^2\) g\(^{-1}\)) can be achieved at moderate alkali consumption. The maximum theoretical carbon yield from lignin is 55% [37], so the product yield (41.51 ± 0.59%) is quite high at zero level. The purpose of the zero level is also to evaluate the reproducibility of the method. Three repetitions were performed indicating good reproducibility. At a minimum level (RUN1), carbon was produced with a moderate value for the SSA (1262 m\(^2\) g\(^{-1}\)), which is appropriate for the conventional active carbon. The results tallied well with the previous results when the alkali consumption was very low [20]. The highest value of product yield (54.41%) was achieved at RUN1 which is close to the maximum theoretical value. The results on a minimum level revealed very modest alkali consumption (0.3 g g\(^{-1}\)) while the surface area is satisfactory for typical active carbons. Moreover, the carbon yield was much higher, exceeding 54% in contrast to the 18% yield of steam-activated carbon with a surface area of 750–800 m\(^2\) g\(^{-1}\) [38]. On a maximum level (RUN4), an ultrahigh surface area was gained (3326 m\(^2\) g\(^{-1}\)) at the lowest carbon yield (15.58%), but the results at maximum level demonstrated the possibility to produce superactive carbon with a SSA exceeding 3000 m\(^2\) g\(^{-1}\) at a KOH amount of 1.5 g g\(^{-1}\) versus the 3.0 g g\(^{-1}\) of the previously reported KOH-activated carbon using kraft lignin [22].

Overall, eight experimental runs were completed. The matrix (table 2) shows that by increasing the amount of alkali and target temperature, the surface area increases, while the yield decreases, which is the usual situation for active carbon production. This approach enables describing the process mathematically within the studied parameters using hydrolysis lignin as a starting material. Using the experimental plan (table 2), the equation of the process can be derived. For the surface area, the mathematical model of the process represents the linear equation:

\[
SSA = 2064 + 486A + 505B + 191AB,
\]

where the value of 2064 is an intercept; A and B are the process factors—temperature (°C) and KOH amount (g g\(^{-1}\)), respectively.

The most essential factor for the SSA is the amount of KOH, while temperature also has a significant influence. According to the equation, all the regression coefficients are positive indicating increasing surface area with an increased level of KOH and temperature. This is also clear from the experimental plan.

The product yield can be described by the following equation:

\[
Yield = 41.77 - 11.18A - 6.92B - 6.34AB.
\]
responses in equations (1) and (2). More specifically, \( R^2 \) is close to unity while the \( p \)-values are far below 0.05, indicating that the models are significant and in agreement with experimental data. The model \( F \)-values of 112.98 and 67.05 for the surface area and carbon yield, respectively, also imply that the models are valid. Moreover, the intercepts of equations (1) and (2) are close to the corresponding average values of surface area and the yield at zero level further proving the adequacy of the models obtained. The aforementioned linear equations can therefore be employed for the prediction of the desired values for SSA and yield. In other words, the optimal parameters of the KOH amount and target temperature can be estimated by the models to achieve the highest SSA and yield.

The ultra-high surface area of 3236 m\(^2\) g\(^{-1}\) was achieved by this method (Sample RUN4). Nevertheless, from the economic point of view, the superactive carbon should be produced at the highest possible yield saving the ultra-high surface area. The RSM method allows optimising the method using the obtained mathematical models (equations (1) and (2)). The prediction was made with the aim of achieving the largest surface area at the highest carbon yield. The purpose was also to minimise the KOH amount since only this chemical is consumed through chemical reactions with carbon. After optimisation, carbon (PRED1-60m) using the optimal process parameters (\( {T} = 900; \text{ KOH(g g}^{-1}) = 1.00 \)) possesses an ultra-high surface area of 2938 ± 42 m\(^2\) g\(^{-1}\) at a good yield of 28.96 ± 0.69%. Moreover, the alkali consumption was considerably reduced (only 1 g g\(^{-1}\)). The optimal conditions can be also used for any other carbonaceous material to produce superactive carbon.

Despite the time being a less significant factor, the effect of time was studied at optimum parameters (table 2, Samples: PRED1-30m, PRED1-60m and PRED1-90m). Compared to the sample PRED1-60m, the carbon prepared for 30 min has a reduced surface area of 2515 m\(^2\) g\(^{-1}\) and a slightly increased yield of 32.94% while sample prepared for 90 min has almost the same surface area of 3009 m\(^2\) g\(^{-1}\) at a reduced yield of 25.41%. Therefore, since the carbon prepared at optimal conditions and for 60 min has the highest values of surface area and yield (Sample PRED1 60 min), the dwell time was correctly selected.

Table 4 shows the comparison between the superactive carbons prepared by this method with carbons from literature prepared by KOH activation. In contrast to the superactive carbons prepared by only KOH activation, the studied material prepared using KOH + KCl also resulted in an ultra-high surface area, comparable total pore volume and micro-pore volume. However, the required KOH consumption using this method is 3–4 times less than those in literature methods. Since the porous carbon with an ultra-high surface area was yielded at a diminished amount of KOH, the new method has a significant advantage compared to the previously reported methods for producing superactive carbons (table 4).

### 3.3. Pore size control

The experimental plan (table 2) allows methodically conducting pore size control. The effects of varying KOH amount and temperature on the pore size distribution and \( N_2 \) adsorption–desorption isotherms were investigated (figure 2). Figures 2(a)–(c) show the effect of increasing KOH amount at
constant temperatures of 700 °C, 800 °C and 900 °C. The adsorption isotherms (the insets) show that the quantity of adsorbed N₂ increases with increasing KOH amount. The pore size distribution shows uniformity at 700 °C, indicating the strongest peak assigned to the size of 1 nm and two others of 1.3 and 1.6 nm. Also, the adsorption isotherms are attributed to type I for microporous materials, which are in good agreement with pore size distribution. However, only for sample RUN3 is there hysteresis type IV, which can probably be attributed to capillary condensation or pore blocking in mesopores [35]. At increased temperatures of 800 °C and 900 °C, a wide micropore size distribution is observed. At a temperature of 800 °C, the micropore size is 1–2 nm with the most probable pore size of 1 nm. At the highest KOH consumption (RUN8), a small number of mesopores is also generated. Moreover, the hysteresis is also observed only for this sample (RUN8) attributed to mesopores. At a temperature of 900 °C the isotherms shapes are similar to type I with the pore filling starting at low pressures \( p/p^* \), indicating micropores. However, the characteristic plateau incipient from medium pressures 0.4–0.7 \( p/p^* \) for samples RUN6 and RUN4, respectively, indicates mesopore contribution [39]. Furthermore, hysteresis type IV also appears, which is peculiar for porous solids containing mesopores. This

### Table 4. The comparison of superactive carbons.

| Reference | MAXSORB® [10] | [21] | [22] | This study* |
|-----------|---------------|------|------|-------------|
| SSA (m² g⁻¹) | 3100 | 3290 | 3100 | 2938 ± 42 |
| KOH amount (g g⁻¹) | 4 | 4 | 3 | 1 |
| \( V_{\text{micro}} \) (cm³ g⁻¹) | — | — | 1.5 | 0.92 ± 0.00 |
| \( V_{\text{total}} \) (cm³ g⁻¹) | 1.5 | 1.45 | 1.7 | 1.29 ± 0.01 |
| Raw material | Petroleum coke | Spanish anthracite | Kraft lignin | Hydrolysis lignin |

*The values were obtained in triplicates.
hysteresis is the most pronounced for the sample RUN4, which was prepared at the highest temperature and KOH amount. Pore size distribution is the most diverse for the samples prepared at 900 °C. In support of the assumed porous structure based on isotherm type and hysteresis, there is a significant number of mesopores clearly observed on NLDFT pore size distribution (figures 2(a)–(c)). Undoubtedly, the samples prepared at the highest temperature and KOH amount possess the widest pore size distribution and the highest N₂ uptake, which result in the ultra-high surface area (table 2). With increasing temperature and KOH amount, the number of mesopores in samples increases, but a more uniform microporous structure can be obtained by reducing temperature or KOH amount. Pore widening occurs due to progressive burn-off of the carbon accompanied by the fusion of micropores into mesopores [3]. Accordingly, by varying the target temperature and KOH amount, superactive carbons can be produced with the desired pore size distribution required in many applications.

The effect of time on the porous structure was studied (figure 2(d)). The N₂ isotherm and NLDFT pore size distribution of superactive carbon prepared at optimal conditions for 60 min (table 2, PRED1-60m) is presented in figure 2(d). The adsorption isotherm shows the shape of isotherm Type I, also indicating the increased curvature of N₂ uptake and a plateau starting at \( p/p^0 > 0.4 \), which can be ascribed to mesopore filling similar to samples RUN4 and RUN6. The NLDFT pore size distribution is also similar to samples prepared at 900 °C indicating the presence of mesopores alongside dominating micropores. At increased dwell time (PRED1-90m) the N₂ uptake and pore size distribution are almost identical indicating a negligible effect of increased time on porous structure. However, at a reduced time (PRED1-30m) the nitrogen uptake is significantly reduced and pores size distribution is more uniform. Therefore, the increased time has almost no influence on the porous structure while decreased time reduces the adsorption capacity and leads to uniform pore size distribution.

3.4. Mechanism of pore formation

3.4.1. Texture characteristics of superactive carbon. The texture of superactive carbon was studied using SEM and TEM (figure 3). The material demonstrates various porous structures. There are macropores of size 1–10 μm, which are intrinsic to KOH-activated carbon from KOH grains (figure 3(a)) [13, 14]. The texture consists of interconnected (figures 3(a)–(d)) and scattered pores (figure 3(e)). In a magnified SEM micrograph of the cross-section (figure 3(b)), the macropores of smaller size 50–500 nm are displayed. A detailed image of this part is shown in figure 3(c) demonstrating the rough surface. In the higher-resolution figure 3(d), the mesopores (10–50 nm) are observed. The scattered mesopores are also clear in figure 3(e) with a
3.4.2. The formation of macropores. Porous carbons produced by KOH activation demonstrated macropore origin through self-templating by KOH grains [13, 14]. In this case, the macropores can be also formed through the KCl template in a similar fashion to the NaCl template [20]. Figure 4 shows, the XRD spectra and SEM images of superactive carbon before leaching. X-ray diffraction peaks (figure 4(a)) are only assigned to the formed KCl crystals (ICSD 98-001-8014). The average crystal size calculated by the W–H method equals 106 nm [34]. In the SEM micrograph (figure 4(b)) crystal size of the same order is observed. Usually, KCl crystals are ordered structures with a cubic shape as shown in figure 4(b). However, here anomalous dendrite-like structures were found (figure 4(c)). Because of the disordered nature, this structure is not observed in the XRD spectra. This kind of structure has been found in KCl or NaCl condensed systems after high-temperature treatment (>800 °C) [41, 42]. Since the temperature of carbonisation is 900 °C, the similarity of the temperature allows assuming the same morphology of KCl. Moreover, the composition of dendrites was also confirmed by EDS spectra and mapping (supplementary material: figure S2). EDS spectra shows the strongest peak of carbon atoms related to the carbon, and the peaks of K and Cl are ascribed to the KCl. In the EDS mapping the distribution of corresponding atoms is observed. Carbon atoms are in the place of macropores frames, while dots assigned to the K and Cl are located exactly on the dendrites-like structures. The composition and distribution from the EDS spectra and the enabling of mapping assume that the dendrites are KCl morphology. Since the size of KCl cubic crystals and the base of the dendrite-like structures are of the same order as macropore size (figure 4), the template mechanism through KCl structures can be assumed. The KOH grains were not observed in figure 4 because the KOH had been decomposed and had interacted with carbon matter through the chemical reactions (discussed in the section ‘3.4.3 The formation of micropores’). In figure 4(d), the structures of KCl around macropores are observed. The KCl is not consumed in the process and remains in the same place, while the KOH grains disappear leaving macropores, which can be seen in figures 4(d) and 3 (after leaching). It can therefore be concluded that the macropore origins are KOH grains and KCl structures.

3.4.3. The formation of micropores. The SSA mainly emerges from micropores while the contribution of
mesopores and macropores is negligible, so the microporous structure is essential for superactive carbon. Micropores are formed by KOH erosion and etching due to chemical reactions between carbon and KOH. According to literature, below 700 °C the KOH is converted to potassium carbonate [10, 11]. At temperatures over 700 °C, a dominating amount of metallic potassium is formed. Metallic potassium is intercalated between graphitic layers with a further drastic expansion of graphite lattice that leads to slit-like micropore formation in the carbon material [12]. Since metallic potassium is a major component for micropore origin, the temperature regime starting from 700 °C was selected [11].

The following chemical reactions were proposed for the activation mechanism by KOH [43]:

$$6\text{KOH} + 2\text{C} = 2\text{K}_2\text{CO}_3 + 2\text{K} + 3\text{H}_2$$

$$4\text{KOH} + \text{C} = 4\text{K} + \text{CO}_2 + 2\text{H}_2\text{O}.$$  (4)

To investigate the products of chemical reactions, the superactive carbon obtained before leaching was validated by FTIR spectra of porous carbon prepared by only KOH activation was also measured (F2007) [22]. The spectra are presented in figure 5. In the present case (PRED1-60m), the potassium carbonate, as was proposed in reaction (3), is not observed, but strong sharp peaks assigned to carbonates at 878 and 1402 cm$^{-1}$ [44] are observed in the sample prepared by the literature method (F2007) only using KOH. This can be explained by the different temperatures of the carbonisation. As was discussed above, the optimal temperature for producing superactive carbon in this study is 900 °C while, for the previously studied method the optimal temperature is 700 °C. For a temperature around 700 °C, chemical reaction (3) is therefore more probable while, for the process at 900 °C, the reaction (4) is more suitable. In other words, at 700 °C the potassium hydroxide is converted to $\text{K}_2\text{CO}_3$, whilst at 900 °C potassium carbonate was not observed and KOH mainly consumed in the formation of metallic potassium. These findings are confirmed by the previously reported mechanism of KOH activation [10, 11]. Furthermore, the reported earlier findings revealed that a higher temperature of activation leads to a higher degree of metallic potassium, which is in good agreement with the results presented here [45].

Since chemical reaction (4) is most probable for the activation process using KOH at temperature 900 °C, metallic potassium is expected to be observed after the process. The boiling point of metallic potassium is 759 °C, which is below the target temperature of 900 °C, so the metallic potassium is in a gas phase in the process and flows away in N$_2$ current from the carbon matter. This explains the voids of macropores observed in figures 3 and 4(d). In the present case, potassium was condensed in the insulation plug of the tube furnace. A considerable amount of potassium was observed. The flash of obtained metallic potassium in contact with water is presented in supplementary material (figure S3). Characteristic yellow–pink formations of potassium dioxide KO$_2$ due to interaction of potassium with the oxygen in the air were found on the walls of the tube furnace and insulation plug [46]. The aforementioned findings allow the assumption of the origin of metallic potassium at a temperature over 900 °C while, at 700 °C KOH was converted to potassium carbonate. These results are consistent with literature [10, 11].

To evaluate the effect of KOH etching on micropores formation carbons prepared using KOH/KCl and $\text{K}_2\text{CO}_3$/KCl mixtures were compared (table 2. Samples RUN4 and RUN4-K2CO3, respectively). Potassium carbonate was selected instead of potassium hydroxide because it is also a source of metallic potassium ($\text{K}_2\text{CO}_3 + 2\text{C} = 2\text{K} + 3\text{CO}$) and has a weaker etching ability compared to KOH [47]. The mass of $\text{K}_2\text{CO}_3$ was the same as KOH used in the experiment. The sample prepared using a mixture containing potassium carbonate has a lower surface area and an insignificantly higher yield compared to the sample prepared with KOH. The results allow assuming that the KOH etching has a significant effect on pore formation.

Because gasification of carbon occurs through a similar mechanism as a micropore formation, KCl can be also involved in this process as a catalyst for gasification [48]. To verify that KCl does not act only as a template and evaluate its catalytic activity, the carbon sample was prepared using KOH/NaCl mixture at the optimal conditions (Sample PRED1-NaCl), because NaCl catalytic activity is lower compared to KCl [49]. The sample prepared by using NaCl instead of KCl demonstrated reduced surface area of 2435 m$^2$ g$^{-1}$ and negligible changes in yield (table 2). Thus, there is a catalytic effect of KCl in micropores formation and KCl is not only a template.

### 3.4.4. The synergy of KCl and KOH in an ultrahigh surface area genesis

To understand why the ultra-high surface area was formed at a substantially reduced consumption of KOH, the synergistic effect of KOH and KCl is discussed here. Based on the mechanism of macro- and micropore formation, a schematic representation of pore origin can be suggested in figure 6. As discussed above, KOH possesses a double role,
being the template for macropores and an etching compound for the micropores through chemical reaction (4). The micropores are schematically represented in figure 6 as slit-like pores. Most of the SSA originates from the micropores [35]. The KCl is responsible for macropore occurrence. It can be seen that micropores are formed around mesopores and macropores. Mesopores around macropores are also observed in figure 3 and discussed in the literature [13, 14], so more macropores provide more possible places for micropores. In KOH activation, the KOH grains are responsible for self-templated macropores [13, 14]. In the present case, KCl also provides additional macropores (figure 3) through a template mechanism (figures 4(b), (c)), so the amount of KOH can be reduced because the KCl can also form the macropores, which provide a place for micropores. In other words, if only KOH is used, alkali is consumed for macropores (self-template) and micropores while, in case of KOH/KCl mixture, the KCl replaces KOH as the origin of macropores.

Since there is a catalytic effect of KCl on micropores formation, the synergy between KOH and KCl that provides enhanced KCl activity can be also assumed in this case. According to previous studies, the catalytic effect depends on the melting point of the catalyst used for gasification [50]. For example, KCl catalytic effect is increased by reducing the melting point of an eutectic mixture containing KCl and vanadium pentoxide [50]. Similar effect can be assumed for KOH/KCl mixture since its melting point is far below pure KCl [51]. Thus, this also assumes a synergistic effect between KOH and KCl and an ultra-high surface area origin at decreased KOH consumption.

4. Conclusion

Superactive carbon with ultra-high SSA was obtained from lignin by the simultaneous use of KOH and KCl. In contrast to previously studied methods, this method enables reducing a 3–4-fold reduction in KOH consumption due to the synergy between KOH activation and the KCl template. Pore size control is feasible by altering the amount of potassium hydroxide and process temperature. The present method allows the manufacturing of superactive carbon in a more cost-efficient and environmentally benign way than KOH activation, due to the reduced KOH consumption and straightforwardness of the process.

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