

## Production of adsorbents from "End of Life" tyres and characterization of their porous structure

L. Gonsalvesh<sup>1\*</sup>, M. Dimov<sup>2</sup>, S. P. Marinov<sup>3</sup>

<sup>1</sup>Central Scientific Research Laboratory, Assen Zlatarov University, Burgas 8000, Bulgaria

<sup>2</sup>Department of Physical and Organic Chemistry, Assen Zlatarov University, Burgas 8000, Bulgaria

<sup>3</sup>Institute of Organic Chemistry with Centre of Phytochemistry, BAS, Sofia 1113, Bulgaria

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*Dedicated to Acad. Ivan Juchnovski on the occasion of his 80<sup>th</sup> birthday*

The valorisation of waste tyres into adsorbents, i.e. technical and activated carbons, is considered in the current research. The technical carbons (TCs) are prepared through treatments with conc. HNO<sub>3</sub>, conc. HNO<sub>3</sub> + conc. H<sub>3</sub>PO<sub>4</sub> or conc. HNO<sub>3</sub> + C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> and subsequent Soxhlet extraction with acetone, while activated carbon (AC) is obtained through physical activation of TCs in a stream of water vapour. Using low temperature N<sub>2</sub> adsorption and Surfer apparatus of Thermo Scientific, the adsorption isotherms of samples under consideration are measured and used for assessment of porous structure. It has been revealed that TCs are mesoporous material characterized by "poor" porous structure since calculated  $S_{\text{BET}}$  and  $V_{0.95}$  are rather low, i.e. up to 63 m<sup>2</sup> g<sup>-1</sup> and 0.205 cm<sup>3</sup> g<sup>-1</sup>, respectively. Thus further processing as physical activation is required in order to improve their porous texture characteristics and respectively their adsorption abilities. The obtained AC exhibits much better developed porous structure represented by micro- and the mesopores. The calculated  $S_{\text{BET}}$  and  $V_{0.95}$  are 527 m<sup>2</sup> g<sup>-1</sup> and 0.489 cm<sup>3</sup> g<sup>-1</sup>, respectively. This determines the promising features of prepared AC to be used as an adsorbent.

**Key words:** „end of life” tyres, technical and activated carbons, N<sub>2</sub> adsorption isotherms, porous structure

### INTRODUCTION

The outstanding increase in the number of vehicles worldwide and the lack of adequate processing of the "end of life" (waste tyres), define the last as a serious ecological problem in terms of waste disposal. Consequently, the increased ecological concern has led to environmental legislation norms that limits the landfill of "end of life" tyres [1] and policies that encourage the valorisation of this waste stream and has driven the tyre sector towards recovery and recycling [2]. However, since tyres are complex materials designed to be resistant to severe mechanical stress and different weather conditions their recycling and further processing is not an easy task.

Tyres are a mixture of constituent components such as rubbers (60-65 wt.%, in the form of natural rubber and synthetic rubber, i.e. butyl rubber and styrene-butadiene rubber), carbon black (25-35 wt.%), steel, textiles and some inorganics acting as accelerators and fillers [2-4]. The tyre manufacturing process involves vulcanization during which irreversible reactions between elastomers, sulphur and other reagent take place and creates a three-dimensional chemical network

through formation of crosslinks between the elastomer molecular chains [4]. Thus created cross-linked elastomers are solid, insoluble and infusible thermoset materials that define high strength and elasticity properties to tyres and hinder their decomposition.

Recently, the European tyre industry has been trying to move towards a zero-waste scenario and increased valorisation of "end of life" tyres through their recycling or usage for energy recovery [2]. From recycling point of view, the tyres recovered rubber can be incorporated in asphalt and concrete and thus lighten material with high durability and increased resistance to cracking, deformation, and aggressive reagents can be obtained [2]. The steel elements recovered from tyres can be reused for production of new steel and reinforced concrete. However, the level of contamination of recovered components, i.e. rubber or steel, is a critical factor affecting the quality of the obtained end product.

The energetic valorisation is a valuable use of "end of life" tyres [5]. In this sense, the thermochemical methods as combustion, gasification and pyrolysis have been studied [4-6]. The incineration or combustion are considered as the easiest and cheapest processes for production of energy from tyres [6]. However both are rather not

\* To whom all correspondence should be sent:  
E-mail: lenia\_gonsalvesh@abv.bg

advisable due to the release of serious poisonous emissions as NO<sub>x</sub>, CO/CO<sub>2</sub>, SO<sub>2</sub>, PAH, which are higher even in comparison to combustion of fossil fuels. Gasification and pyrolysis are more attractive approaches to tackle the waste tyres valorisation due to the less environmental impact. Additionally, value added products are produced. Pyrolysis results in high-energy-density volatile gases (condensable and non-condensable) that can be used as a fuel or chemical feedstock and solid carbonaceous fraction, named char or pyrolytic carbon black, that can be used as a fuel, carbon black or adsorbent. However, the use of pyrolytic char as a fuel and carbon black is limited. The combustion of tyre char is rarely applied due to required long residence times at elevated temperature and high rate of unburned particle [4]. The char is not often reused as carbon black as well due to the presence of organic impurities, high ash content, low surface area, large particle size, and due to the fact that it does not seem to have the particle structure desired for rubber compounding [7]. The most proper application of pyrolytic char seems to be as adsorbent after its upgrade at higher temperature by means of physical [8-11] or chemical treatment [12-15] into activated carbon (AC). Thus prepared ACs can be used as cheap adsorbents with broad applications, i.e. environmental protection and recovery of chemicals with added value. However, the specific application of tyre based ACs depends on their characteristics, i.e. porous texture and surface chemistry, determined by the composition and peculiarities of the initial precursor, nature of activating agent and process parameters [3,4,16].

It has been found that immediate reaction of tyre wastes with concentrated nitric acid undergoes through nitration, oxidation and destruction processes that leads to formation of polyfunctional products (PFPs), low-molecular carboxylic acids and carbonaceous solid residue (technical carbon, TC) after subsequent extraction with a suitable organic solvent [17]. PFPs have been reported to be used as a growth stimulators and as an incubation medium for microorganisms, while the TC has been tested as an adsorbent for removal Cu<sup>2+</sup> ions from aqueous solution [17-19].

The objective of the current research is to characterize the porous structure of carbonaceous solid residues produced by oxidative destruction of waste tyres and an activated carbon obtained on their basis and to assess the possibility of their usage as adsorbents.

## MATERIALS AND METHODS

### Precursor and applied treatments

"End of life" tyres (with an average particle sizes of 0.2-0.4 mm) supplied by A Factory of Rubber Productivities-LTD, Yambol, Bulgaria were used as a carbon precursor feedstock. The tyre particles (10 g) were gradually added with an average rate of 0.2 g min<sup>-1</sup> to 30 ml 65% HNO<sub>3</sub> (p.a., Merck) (treatment A) or its mixture with 20 ml 85% H<sub>3</sub>PO<sub>4</sub> (p.a., Merck) (treatment B) or with 20 ml C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> (p.a., Merck) (treatment C) as described in Fig. 1. The treatments were conducted at 60 °C and continuous stirring for 2h. The reaction products were cooled down and subjected to filtration. Low-molecular dicarboxylic acids were leached in the filtrate, while the solid residue is an oxygenated vulcanized rubber, comprising the mixture of PFP and TC [18]. The obtained solid residue was extensively rinsed up to neutral reaction and dried at 60 °C up to constant weight. For separation of PFP and TC, the solid residues were placed in a Soxhlet thimble and extracted by acetone (~300ml), with a reflux process continuing for about 24 h. The concentrated after vacuum distillation acetone extracts were poured into water and PFP precipitates were formed. The TC residues, i.e. TC-A (obtained after treatment A, Fig.1), TC-B (obtained after treatment B, Fig.1) and TC-C (obtained after treatment C, Fig.1), left in the Soxhlet thimble were dried and subjected to porous structure characterization and further processing in the current study.

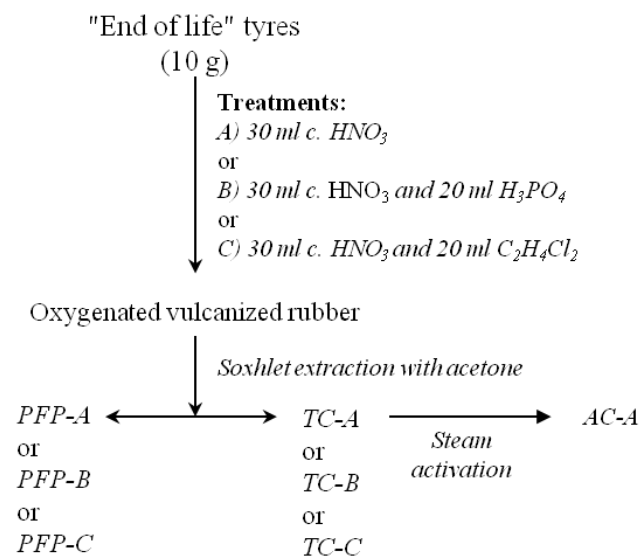


Fig. 1. Experimental strategy

Preparation of activated carbon (AC) through physical activation typically comprises a two-stage pyrolytic process. Carbonization of the precursor is carried out in the first stage, while in the second step the physical activation of the resulting char is performed in the presence of suitable oxidizing gases such as water vapour, CO<sub>2</sub> and others. In the present study a relatively new, one-stage pyrolysis process in the presence of water vapour is applied [20]. The technical carbons (particle size <0.2 mm) were pyrolysed in a stainless steel reactor at the following experimental conditions: heating rate of 10 °C min<sup>-1</sup> in an inert atmosphere up to 400 °C, kept isothermal for 15 min, then heating continued up to activation temperature of 800 °C, kept isothermal for 30 min. When the activation temperature was reached, the inert atmosphere was switched to steam with a constant water vapour flow of 2 ml min<sup>-1</sup>. The process was ended with the cooling of the reactor in an inert atmosphere and drying of the resultant AC at 110 °C.

#### Characterization of the samples under study

The TC and AC samples were subjected to thermogravimetric analysis (TGA) for obtaining data of proximate analysis (i.e. moisture (*W*), volatile matter (*VM*), fixed carbon (*C<sub>fix</sub>*) and ash (*A*) contents) using a Netzsch STA 449 F3 Jupiter thermogravimetric analyser as described in Gonsalvesh et. al. [21,22]. A porous textural characterization was carried out by measuring nitrogen adsorption isotherms at -196 °C on an automatic apparatus Surfer sorption analyzer (Thermo Scientific). The surface area of the TCs and AC is determined by the BET method (*S<sub>BET</sub>*) using data from the adsorption isotherms in the range of relative pressures up to 8.3.10<sup>-2</sup> (for hybrid type isotherms I-IV) or from 0.05 to 0.28 (for isotherms type IV) [23,24]. The total pore volume, known as volume of *Gurvich*, is determined based on the volume of adsorbate *V<sub>0.95</sub>*, recorded on the desorption branch of the adsorption isotherm at a relative pressure  $P_i/P_0 = 0.95$ . The micropore volume (*V<sub>DR,micro</sub>*) is calculated by using the Dubinin-Radushkevich equation up to  $P_i/P_0 \leq 0.15$  [25]. The pore size distribution and pore diameters *L<sub>0</sub>* are obtained by applying the Non Local Density Functional Theory (NLDFT) on N<sub>2</sub> adsorption data [26].

## RESULTS AND DISCUSSION

The proximate analysis and yields of TC samples are gathered in Table 1. Apparently the obtained TCs are carbon-enriched products as *C<sub>fix</sub>*

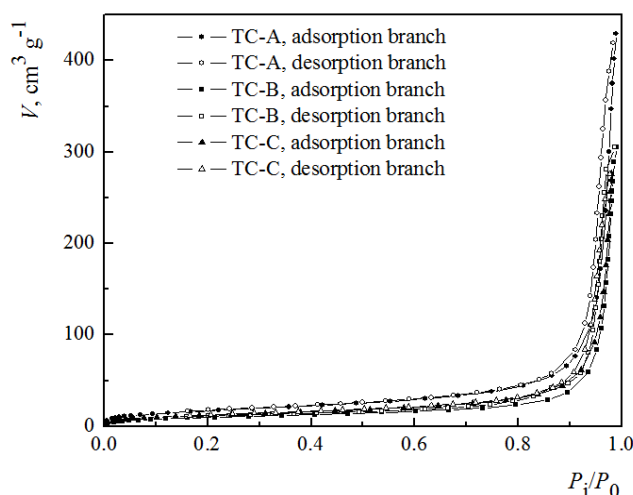
**Table 1.** Proximate analysis and recoveries of samples under consideration in wt.%

Sample	<i>W</i>	Ash <sup>db</sup>	VM <sup>daf</sup>	<i>C<sub>fix</sub></i> <sup>daf</sup>	Re
TC-A	3.5	9.2	7.4	83.4	35.6
TC-B	4.3	13.5	11.7	74.8	32.0
TC-C	5.1	3.4	7.1	89.5	31.0
AC-A	12.0	5.5	7.5	87.0	49.0*

<sup>db</sup>-dry basis; <sup>daf</sup>-dry ash free basis; \*calculated based on TC-A sample.

content varies in the range of 74.8 to 89.5 wt.%. The highest *C<sub>fix</sub>* content and lowest VM and Ash contents are registered for TC-C sample, while TC-B sample is characterized by the highest VM and ash contents and lowest *C<sub>fix</sub>* content. Consequently it can be assumed that applied treatments for production of TC samples somewhat influence their proximate characteristics. The recoveries of obtained TCs are in the range of 31.0 - 35.6 wt.%. It should also be mentioned that both proximate characteristics and recoveries of studied TCs are comparable to that of pyrolytic carbon black [3,4,27,28]. This largely means that TCs obtained by applying our experimental strategy have relevance and applications commensurable with that of pyrolytic carbon black.

The N<sub>2</sub> adsorption isotherms of TC samples are shown on Fig. 2.



**Fig. 2.** N<sub>2</sub> adsorption isotherms of TCs obtained from "end of life" tyres

It can be seen that TC samples are characterized by adsorption isotherms of type IV according to

classification of IUPAC, which are typical for mesoporous materials. The existence of discrepancy between the adsorption and desorption branches of the isotherms, i.e. hysteresis loop, is an indication for differences in the mechanisms of pore filling with an adsorbate and its evaporation and the presence of mesoporous structure in which a capillary condensation of the adsorbate occurs. The type of hysteresis loop for various mesoporous materials can be different, depending on the nature of mesoporous material and the shape and size of its pores. In our study hysteresis loops of type H-1 according to classification of IUPAC are observed in the course of all isotherms of TC samples. This can be related to cylindrical geometry of the mesopores and the high degree of uniformity of the pore sizes. Inasmuch as registered hysteresis loops are pulled to the high relative pressures it can be assumed that the size of the mesopores is rather large.

Pore size distribution of investigated TCs is assessed as well by applying NLDFT theory. Inasmuch as cylindrical geometry of mesopores is supposed, the *n2c77\_cyl* kernel developed for carbon materials with cylindrical pores is used for NLDFT computation. The theoretical adsorption isotherms described by using this kernel is in best agreement with the registered experimental adsorption isotherms of the TCs. The obtained pore size distribution of TCs is presented in Fig. 3. The maximums in the pore size distribution curve correspond to the prevailing pore sizes of the investigated samples. It can be clearly seen that pore size distribution curves, built according to NLDFT computational procedure exhibit a bimodal distribution of the pore volumes with a predominant  $L_0$  about 32.34 and 43.36 nm.

The monolayer capacities  $\alpha_m$  of the TC samples, on the basis of which the specific surface areas and physicochemical constants  $C$  are calculated, are determined using the linear form of the BET adsorption isotherm (Fig. 4). The obtained results together with the total pore volume of *Gurvich* and micro- and mesopore volumes of investigated TCs are summarized in Table 2.

Analysis of the obtained data confirms aforementioned peculiarities: i) porous texture characteristics of prepared TCs do not differ considerably; ii) indeed the prepared TCs are mesoporous materials since  $V_{meso}$  (about 90%) significantly prevails over  $V_{DR,micro}$ . However, the calculated  $S_{BET}$  and  $V_{0.95}$  are rather low, which hinder adsorption abilities of prepared TCs and thus further processing is required in order to improve

their porous characteristics.  $S_{BET}$  and  $V_{0.95}$  varied in the range of 36 - 63  $m^2 g^{-1}$  and 0.121 - 0.205  $cm^3 g^{-1}$ , respectively, as both parameters maximizing in the case of TC-A sample. This is an indication that among applied treatments, i.e.  $HNO_3$ ,  $HNO_3+H_3PO_4$  and  $HNO_3+C_2H_4Cl_2$  (see Fig.1), the one using only  $HNO_3$  leads to better development of mesoporous structure. Therefore exactly TC-A samples is subjected to further processing into AC.

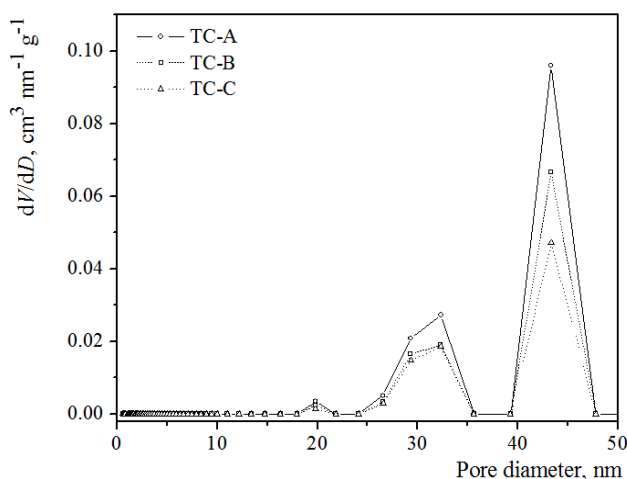


Fig. 3. Pore size distribution of TCs obtained from "end of life" tyres

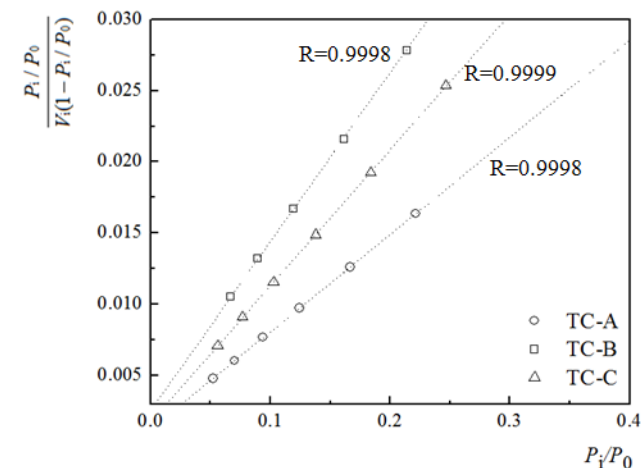


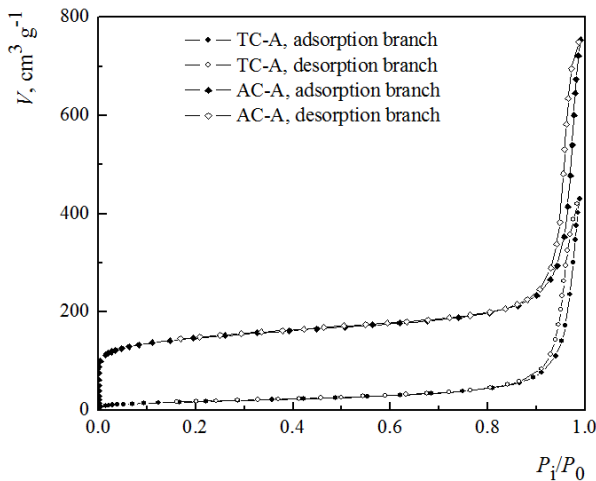
Fig. 4. The linear form of the BET equation for TCs.

The proximate analysis and the yield of AC-A sample are presented in Table 1. Clearly, a good yield of AC (49.0 wt.%) with relatively low ash content (5.5 wt.%) is obtained. However, of utmost importance is the porous structure. The  $N_2$  adsorption isotherms of AC-A sample is visualized on Fig. 5 together with  $N_2$  adsorption isotherms of TC-A sample for better comparison and clearness of presentation.

**Table 2.** Textural properties of prepared TCs and AC

Sample	$V_{0.95}$ ( $\text{cm}^3 \text{g}^{-1}$ )	$S_{\text{BET}}$ ( $\text{m}^2 \text{g}^{-1}$ )	$C$	$V_{\text{DR,micro}}$ ( $\text{cm}^3 \text{g}^{-1}$ )	$V_{\text{meso}}^*$ ( $\text{cm}^3 \text{g}^{-1}$ )	$V_{\text{mezo}}/V_{0.95}$	$L_0$ (nm)
TC-A	0.205	63	56.1	0.021	0.184	0.90	32.34
							43.36
TC-B	0.121	36	47.3	0.012	0.109	0.90	32.34
							43.36
TC-C	0.148	48	55.6	0.015	0.133	0.90	32.34
							43.36
AC-A	0.489	527	2240.8	0.207	0.282	0.58	1.68
							2.11
							2.82
							43.36

$$V_{\text{meso}}^* = V_{0.95} - V_{\text{DR,micro}}$$



**Fig. 5.**  $\text{N}_2$  adsorption isotherms of AC-A and TC-A samples

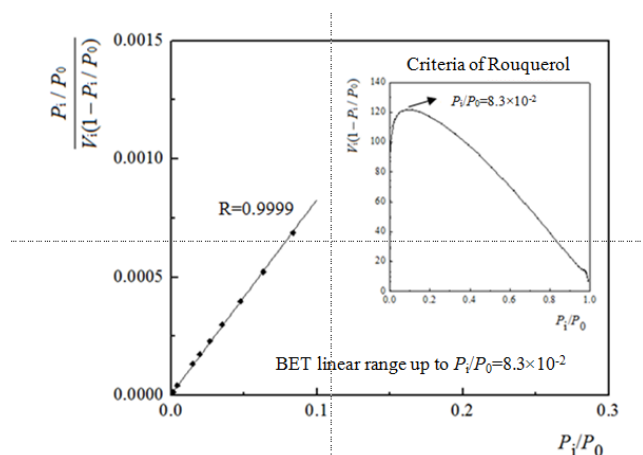
According to IUPAC classification  $\text{N}_2$  isotherm of AC-A sample represents a hybrid type I-IV. The adsorption isotherm manifest a steep rise at low relative pressures, sharp shoulder/knee in the relative pressure  $P_i/P_0$  about 0.01 and almost parallel to the abscissa course at medium and high relative pressures. In the course of the isotherm a hysteresis loop of the type H-1 is also observed.

This behaviour of the adsorption isotherm reveals that the porous structure of AC-A is represented by both micro- and the mesopores. The isotherm of AC-A sample compared to that of TC-A sample displays an increase of the adsorbed  $\text{N}_2$  which is caused by the appearance and development of microporosity, and an increase in mesoporosity with preserved cylindrical geometry

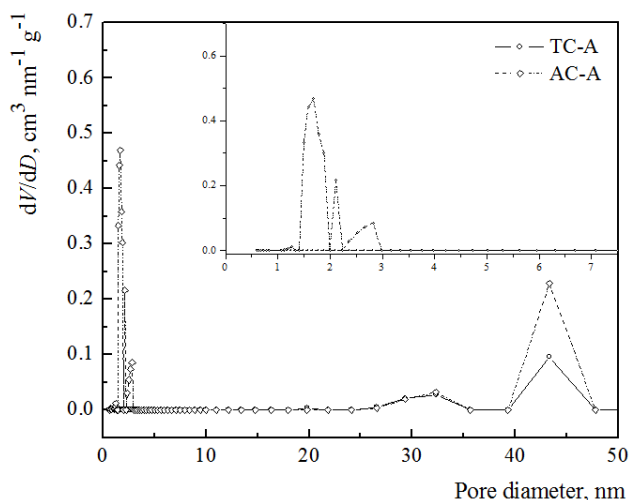
(hysteresis loop of H-1 type is observed in the isotherms of AC-A and TC-A samples). Apparently, physical activation of TC-A sample in a stream of water vapour had gasified some of the carbon, which gave rise to more deeply developed porosity.

The specific surface area  $S_{\text{BET}}$  of AC-A sample is determined using the linear form of the BET adsorption isotherm. In general, BET equation is applicable for determining the specific surface area of non porous, macro- and mesoporous materials consisting of pores with large diameter, but its application to determine the specific surface area of microporous adsorbents is problematic due to difficulties to distinguish mono- and polylayer adsorption of micropores volumetric filling, which generally ends at relative pressures less than 0.1 [29]. Therefore, the specific surface area of microporous materials obtained by the BET method does not reflect the true internal surface area, and should be regarded only as a reference, or a kind of equivalent BET surface. In this case, it is obligatory to note the range of relative pressures in which linear BET dependence occur. In general, linear BET dependence for microporous materials is shifted to a significantly low relative pressures compared to mesoporous material and can be determined by applying Rouquerol criteria [30]. The linear form of BET equation and criteria of Rouquerol for AC-A sample are shown on Fig. 6. Based on them  $S_{\text{BET}}$  of  $527 \text{ m}^2 \text{g}^{-1}$  is calculated, which is significantly higher compared to TC-A precursor characterized by  $S_{\text{BET}}$  of about  $63 \text{ m}^2 \text{g}^{-1}$ .

Total pore volume,  $V_{0.95}$ , is also higher (double) for the activated carbon, which is mainly due to the development of microporous structure (micropores with diameters  $L_0$  of 1.68, 2.11 and 2.82 nm are registered, Fig. 7) and to a lesser extent due to widening of mesoporous structure (mesopores diameter  $L_0$  is 43.36 nm, Fig. 7).



**Fig. 6.** The linear form of the BET equation for AC-A by applying criteria of Rouquerol.



**Fig. 7.** Pore size distribution of TC-A and AC-A samples.

However, the contribution of the mesopores to  $V_{0.95}$  is still prevailing as about 60% of AC-A pores are presented by mesopores. Thus, as a result of the detailed description of porous texture characteristics of prepared AC, it can be concluded that porous structure of AC-A is rather different to that of commercial activated carbons which are mainly microporous, but similar and comparable to that of other activated carbons derived from "end of life" tyre wastes [11,15,16,31].

## CONCLUSION

The current study, focusing on valorisation of "end of life" tyres, reveals that these wastes can be successfully used for production of adsorbents. The technical carbons, prepared by treatments tyre wastes with  $\text{HNO}_3$ ,  $\text{HNO}_3+\text{H}_3\text{PO}_4$  or  $\text{HNO}_3+\text{C}_2\text{H}_4\text{Cl}_2$  and subsequent Soxhlet extraction with acetone, are mesoporous material characterized by "poor" porous structure since calculated  $S_{\text{BET}}$  (varying in the range of 36 - 63  $\text{m}^2 \text{g}^{-1}$ ), and  $V_{0.95}$  (varying in the range of 0.121 - 0.205  $\text{cm}^3 \text{g}^{-1}$ ), are rather low. This hinder their adsorption abilities and thus further processing as physical activation is required in order to improve their porous texture characteristics. The obtained AC through activation of TC-A sample in a stream of water vapour exhibits promising porous texture features and demonstrates promising abilities to be used as an adsorbent. The AC-A sample is characterized by porous structure represented by both micro- and mesopores. The calculated  $S_{\text{BET}}$  and  $V_{0.95}$  are 527  $\text{m}^2 \text{g}^{-1}$  and 0.489  $\text{cm}^3 \text{g}^{-1}$ , respectively.

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## ПРОИЗВОДСТВО НА АДСОРБЕНТИ ОТ ОТПАДНИ ГУМИ И ОХАРАКТЕРИЗИРАНЕ НА ТЯХНАТА ПОРИСТА СТРУКТУРА

Л. Гонсалвеш<sup>1\*</sup>, М. Димов<sup>2</sup>, С. Маринов<sup>3</sup>

<sup>1</sup> Централна научно-изследователска лаборатория, Университет "Проф. д-р Асен Златаров", Бургас 8000, България

<sup>2</sup> Катедра по физикохимия и органична химия, Университет "Проф. д-р Асен Златаров", Бургас 8000, България

<sup>3</sup> Институт по органична химия с Център по фитохимия, Българска академия на науките, София 1113, България

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(Резюме)

Фокусът на настоящото изследване е върху оползотворяването на отпадни гуми като адсорбенти, в т.ч. технически и активни въглини. Техническите въглини са получени чрез третиране на отпадни гуми с к.  $\text{HNO}_3$ , к.  $\text{HNO}_3 + \text{k. H}_3\text{PO}_4$  или к.  $\text{HNO}_3 + \text{C}_2\text{H}_4\text{Cl}_2$  и последваща сокслет екстракция с ацетон, докато активният въглен е получен чрез физическа активация на един от техническите въглини в поток на водна пара. Пористата структура на получените материали е охарактеризирана въз основа на  $\text{N}_2$  адсорбционни изотерми, снети чрез азотна физисорбция при  $-196^\circ\text{C}$  на апарат Surfer (Thermo Scientific). Установено бе, че получените технически въглини са мезопорести материали, характеризиращи се със слабо развита пориста структура и сравнително ниски стойности на  $S_{\text{ВЕТ}}$  и  $V_{0.95}$ , т.ч. до  $63 \text{ m}^2 \text{ g}^{-1}$  и  $0.205 \text{ cm}^3 \text{ g}^{-1}$ , съответно. Това налага прилагането на допълнителна обработка на техническите въглини, като физическо активиране с водна пара, с цел подобряване на тяхната пориста структура и техните качества като адсорбенти. Полученият активен въглен се характеризира с много по-добре развита пориста структура, представена от микро- и мезопори. Изчислените стойности на  $S_{\text{ВЕТ}}$  и  $V_{0.95}$  са  $527 \text{ m}^2 \text{ g}^{-1}$  и  $0.489 \text{ cm}^3 \text{ g}^{-1}$ .