

Unburnt carbon from coal fly ashes as a precursor of activated carbon for nitric oxide removal

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Abstract

The aim of this work is to evaluate the characteristics of an activated carbon obtained from unburnt carbon in coal fly ashes to be used in the removal of NO. Carbon-rich fraction was obtained by mechanical sieving of fly ashes. The mineral matter was removed by conventional HCl and HF demineralization procedure. Activation was carried out with steam at 900 °C in order to develop porosity onto the sample. Characterization of samples was performed by several techniques with a main objective: to follow the mineral matter content, composition and distribution on the samples in order to better understand how to remove it from unburnt carbon in fly ashes. To study the use of this unburnt carbon as a precursor for the preparation of activated carbons for gas cleaning, the NO removal by ammonia using activated carbon as a catalyst at low temperature was performed. Results show a good performance of activated carbon in this reaction that is in relationship with BET surface area.

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1. Introduction

Coal combustion products (CCPs) are a waste residue from the burning of coal in thermoelectric power stations. In the European Union (EU 15) approximately 65 million tonnes of coal combustion products (CCPs) were produced in 2003 [1]. Fly ash (FA), which is obtained by electrostatic or mechanical precipitation of dust like particles from the flue gas, represents the greatest proportion of total CCP production (approximately 44 million tonnes). Within the EU, the utilization for FA in the construction industry is currently around 47%, about 42% are used as a replacement for naturally occurring resources and the rest is disposed.

FAs consist mainly of oxides of silica, aluminium, iron and calcium. Some unburnt or partially burnt carbon residue is collected with the FA in the precipitators [2]. Over more recent years increasingly stringent environmental requirements have required slightly lower furnace temperatures and the progressive injection of air to reduce the degree of nitrogen oxidation,

the so-called low NO_x burner. The drawback of this technology is the higher LOI (loss on ignition, a measure of the unburnt carbon) in the resulting FA. Carbon has some unfortunate effects on the use of FA for concrete industry decreasing the marketability of some FAs.

An interesting possibility might be to make them a low-cost adsorbent for gas and water treatment [3]. The results obtained are encouraging for the removal of heavy metals and organics from industrial wastewater. However, some research can be found in the literature concerning gas cleaning. Dry flue gas desulphurization has been tested under different types of fly ash treated with calcium hydroxide [4–6] and the results have been shown to be promising. FAs have been also proposed to be used as adsorbents for NO_x removal from flue gases [7]. The authors found that the unburnt carbon remaining in the FAs particles contributed the main surface area and adsorption.

So, this carbon presents in FAs can be a precursor of activated carbons since it has gone through a devolatilization during the combustion in the furnace of the power station and, therefore, it only requires a process of activation [8]. Recently the adsorption of NO_x, mercury, CO₂ and SO₂ onto activated carbons from FAs have been reported [9–12]. In the case of NO_x adsorption [9] the

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Table 1
Carbon distribution in recovered sieved fractions

	<125 μm	125–200 μm	200–320 μm	320–500 μm	>500 μm
Weight (%)	82.10	15.40	1.69	0.67	0.14
C (%)	1.17	5.84	25.84	37.60	26.30

results have shown poor performance for NO_x capture of carbons from FAs.

This investigation was undertaken to determine and evaluate the NO abatement capacity of activated carbons obtained from fly ash carbon-rich fractions and its further demineralization and activation.

2. Experimental

2.1. Materials

Coal fly ashes (FAs) from a power plant at Escucha, Teruel (ENDESA Company) were chosen as starting material (named CVESC-AR) to obtain an enriched carbon fraction. This fly ash is produced in full-scale boiler under what can be considered typical utility operating conditions. Approximately 50 kg of FAs were fractionated by standard dry-sieving techniques. Sieves specified as openings of 125, 200, 320 and 500 μm were used to mechanically separate FAs. Each collected fraction was weighed.

Table 1 shows weight distribution and carbon content of each fraction. Richer carbon fraction is 320–500 μm but weight percentage is very low. So the three fractions with carbon content higher than 25% were mixed to obtain a fraction with particle size higher than 200 μm , called CVESC-EN. The fraction with particle size lower than 200 μm was called CVESC-RJ.

Carbon-enriched fraction, CVESC-EN, was demineralized with HCl and HF following the procedure described in [13]. Sample was initially treated with HCl 5N at 55 °C during 45 min; after this period of time, the sample was filtered and water washed to eliminate all chloride. After drying, the sample was treated with HF 5N at 55 °C during 45 min; after this step, the cake was treated with concentrate HCl (38% wt.) at 55 °C during 45 min. Finally, the sample was filtered, water washed and dried. This demineralized sample was named as CVESC-EN-DM.

Demineralized sample was activated with steam in a fluidized bed at 900 °C, during 2 h. After this period of time, steam flow was cut off and switched by nitrogen flow until room temperature was reached. Activated sample was named CVESC-EN-DM-ACT.

2.2. Characterization

Proximate analysis of samples was carried out according to standards ISO-589-1981 for moisture content, ISO-1171-1976 for ash content and ISO-562-1974 for volatile content. Ultimate analysis was carried out in an apparatus CARLO ERBA 1108 to determine C, H, N and S contents.

Mineral matter characterization of samples was carried out by X-ray diffraction (XRD) and inductively coupled plasma (ICP-

AES). The identification of mineral composition of samples was carried out by XRD in an apparatus BRUCKER D-8. XRD profiles were obtained by using Cu $K\alpha$ radiation, using a range of 2-theta from 3° to 80°, a step of 0.05° and a step time of 5 s. In order to improve clarity when profiles of different samples are compared, X-axis was presented from 20° to 40°. The composition of ash was determined by ICP-AES in an apparatus JY 2000 ULTRATRACE on a dissolution coming from the digestion by LiB_4 and further HCl attack of samples.

The morphology of samples was examined by scanning electronic microscopy (SEM) in a JEOL SM6400 apparatus. Samples were coated with a layer of gold. The images were obtained by backscattered electrons detection (except in two cases, further indicated).

Textural characterization was performed by mercury porosimetry and N_2 adsorption. Mercury porosimetry was carried out in an apparatus Poremaster from Quantachrome. Nitrogen adsorption/desorption isotherms at –196 °C were obtained in an apparatus AS-1 from Quantachrome. Prior to the analysis, samples were outgassed at 250 °C up to a vacuum of 10^{-5} mm Hg. BET equation was used to determine surface area of samples.

2.3. NO experiments

An experimental installation described elsewhere [14] was used to test NO removal capacity of samples in conditions of selective catalytic reduction (SCR) reaction using ammonia as a reducing agent. The installation consists of a fixed bed reactor, devices for the preparation of gas mixtures, temperature control and on-line analysis of the concentration of the gas stream. A flow of 1000 ml/min of gas containing 1000 ppmv of NO, 6% (v/v) O_2 , 1200 ppmv NH_3 and N_2 as balance is passed through a bed of 15 g of sample at 150 °C of temperature. The reactor was provided with a bypass which allows the measurement of the NO concentration before each experiment. The NO analyzer is a non-dispersive infrared photometer (NDIR). The reaction results are described in terms of NO conversion as:

$$\% \text{NO conversion} = \frac{\text{NO}_{\text{in}} - \text{NO}_{\text{out}}}{\text{NO}_{\text{in}}} \times 100$$

3. Results and discussion

Results corresponding to proximate and ultimate analysis are shown in Table 2. Hydrogen content is very low, indicating a high degree of condensation. Enrichment in carbon by physical separation has occurred. However, ash content of carbon-enriched sample is too high to consider steam activation because it will lead to an increase of ash content because the degree of burn-off achieved. So, chemical demineralization procedure was applied to sample CVESC-EN. After this treatment, ash content decreases considerably as well as carbon content increases. Activation step lead to the gasification of the sample, increasing ash content with respect demineralized sample and decreasing carbon content, as expected.

Table 2
Proximate and ultimate analysis of the studied samples (wt.%)

	Moisture	Ash	Volatile	C	H	N	S
CVESC-AR	0.21	95.10	1.59	2.35	0.02	0.02	0.54
CVESC-RJ	0.19	97.95	1.18	1.88	0.04	0.00	0.54
CVESC-EN	0.47	75.71	1.77	24.32	0.08	0.68	0.54
CVESC-EN-DM	1.31	26.36	1.68	70.43	0.19	0.94	0.47
CVESC-EN-DM-ACT	1.09	27.43	1.66	66.54	0.18	0.78	0.42

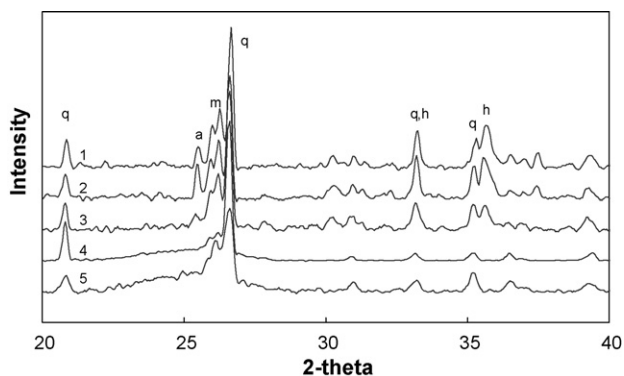


Fig. 1. XRD profiles of samples: (1) CVESC-AR; (2) CVESC-RJ; (3) CVESC-EN; (4) CVESC-EN-DM; (5) CVESC-EN-DM-ACT. Quartz (q); mullite (m); hematite (h); anhydrite (a).

Main mineral phases in raw FA, sample CVESC-AR, were: quartz, mullite, hematite and anhydrite as can be seen in XRD profiles depicted in Fig. 1. These mineral phases can also be found in sieved fractions, CVESC-EN and CVESC-RJ, but in different proportion from CVESC-AR. Hematite and anhydrite phases disappeared after demineralization. Semi-quantitative analysis is performed on base of the patterns' (from JCP2 data

Table 3
Semi-quantitative phase analysis (%)

	Quartz	Mullite	Hematite	Anhydrite
CVESC-AR	32.0	49.0	8.7	10.0
CVESC-RJ	27.6	48.7	8.5	15.2
CVESC-EN	34.4	48.6	6.2	10.7
CVESC-EN-DM	63.4	36.6		
CVESC-EN-DM-ACT	43.7	56.3		

base) relative heights and of their III_{cor} (cell parameter) values. These results are presented in Table 3. The sieving of FA into two fractions has lead to some segregation of the mineral species.

The composition of ash of each sample, expressed as main oxides of metals, is shown in Table 4. It can be seen a high Fe content because the coal burned was lignite with a high pyrite content. The composition obtained confirms the results obtained by XRD regarding the segregation of the mineral matter into the sieved fractions.

From SEM images obtained at high magnification, it can be observed that samples are composed of spheres, spheroids and agglomerates (Fig. 2a, secondary electrons). Backscattered elec-

Table 4
Ash composition (expressed as main oxides of metals, %)

	Al ₂ O ₃	CaO	Fe ₂ O ₃	K ₂ O	MgO	Na ₂ O	SiO ₂	TiO ₂
CVESC-AR	26.22	7.59	16.17	1.43	1.36	0.13	44.91	0.88
CVESC-RJ	26.55	7.54	15.61	1.44	1.36	0.20	45.72	0.86
CVESC-EN	26.69	6.32	13.72	1.37	1.21	0.10	45.00	0.78
CVESC-EN-DM	38.85	0.31	2.72	0.21	0.31	0.03	57.35	1.21
CVESC-EN-DM-ACT	45.36	0.46	4.50	0.23	0.33	0.03	46.66	1.58

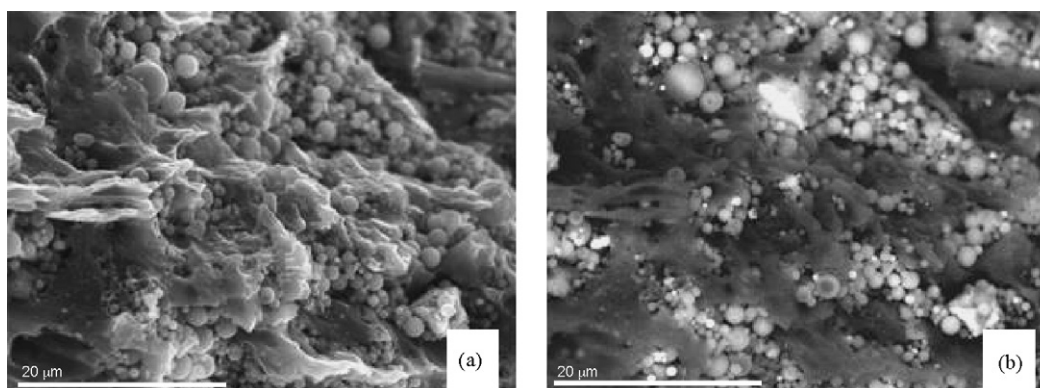


Fig. 2. SEM microphotographs of sample CVESC-EN (at the same magnification, bars represent 20 μm): (a) secondary electrons and (b) back-scattered electrons.

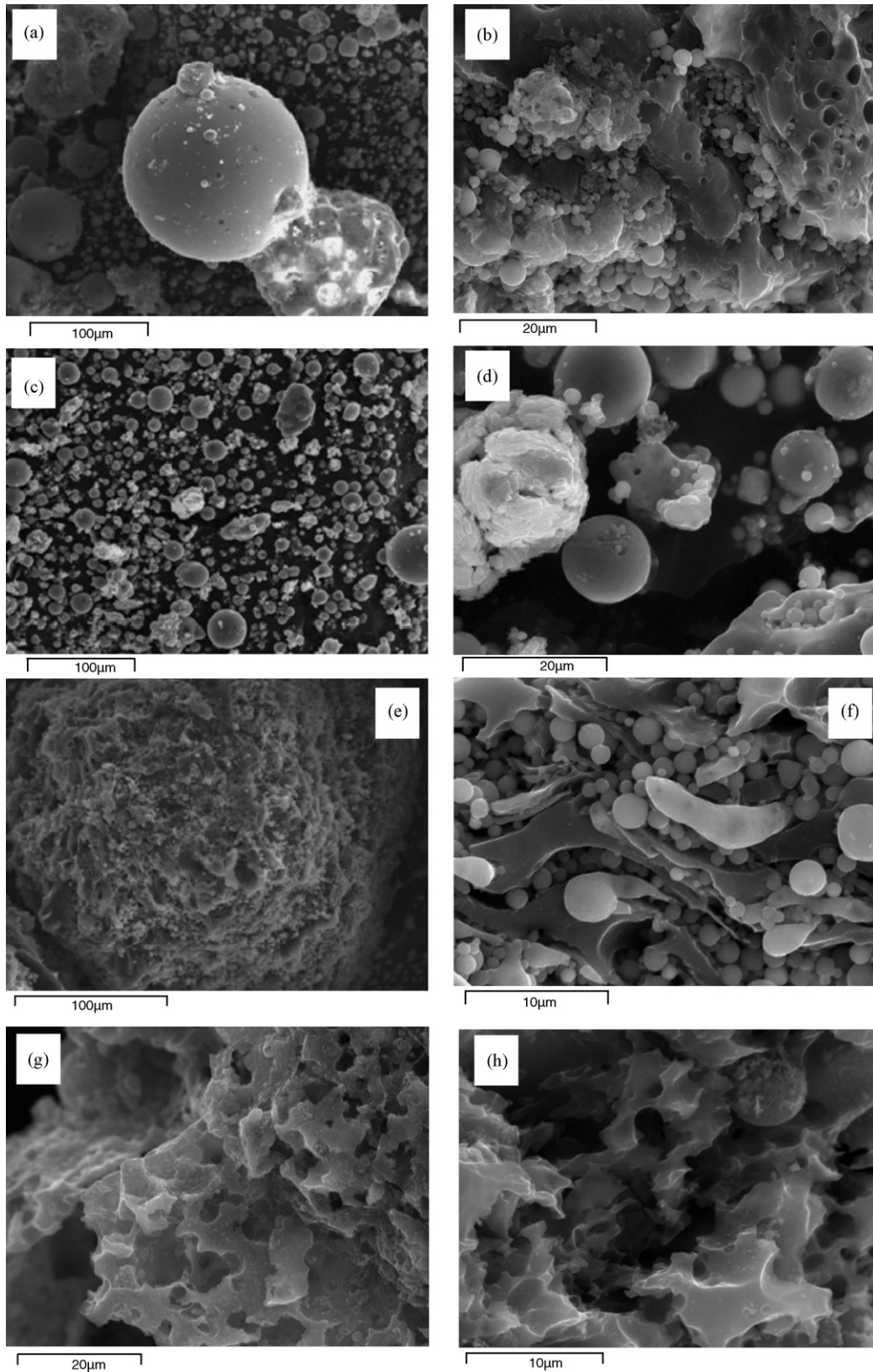


Fig. 3. SEM microphotographs of samples (back-scattered electrons): (a) CVESC-AR (bar represents 100 μm); (b) CVESC-AR (bar represents 20 μm); (c) CVESC-RJ (bar represents 100 μm); (d) CVESC-RJ (bar represents 20 μm); (e) CVESC-EN (bar represents 100 μm); (f) CVESC-EN (bar represents 10 μm); (g) CVESC-EN-DM (bar represents 20 μm); (h) CVESC-EN-DM-ACT (bar represents 10 μm).

trons detection in the same zone (Fig. 2b) shows that dark areas are composed of carbon structures, whereas the small spheres of inorganic matter (higher intensity) indicate an advanced fusion stage of mineral matter due to high temperatures reached during combustion.

Fig. 3 shows the micrographs of samples studied. Their comparison at the same magnification (Fig. 3a and c, 400×; Fig. 3b and d, 2000×) indicates the high degree of heterogeneity of particle size in the sample as received (CVESC-AR), and how the rejected fraction (CVESC-RJ) is mainly comprised of the small inorganic spherical particles of homogeneous diameter. The enriched fraction, sample CVESC-EN, is comprised of large particles (Fig. 3e) of carbonaceous material. Inside the big pores, small glassy spheres can be found (Fig. 3f), indicating the difficulty of inorganic matter removal by physical methods. Microphotographs corresponding to demineralised sample are depicted in Fig. 3g and h. Chemical treatment with HCl/HF had a direct effect on the removal of mineral matter spheres from unburnt particles. Most of them have been removed and it can be found small spheres in the inner part of the big pores of these particles. These observations are consistent with the decrease of ash content and the increase of carbon content observed in sample CVESC-EN-DM.

Nitrogen isotherms of sieved samples and demineralized sample are type II according to the BBDT classification [15], typical for non-porous or macroporous materials. Accordingly, BET surface areas shown are low (the reported values are not corrected for their mineral matter content). The inorganic fraction made a relatively constant contribution of roughly 0.7–0.8 m²/g in any ash [16]. However, values of surface area in Table 5 were not corrected for the inorganic contribution because the samples are further used as they obtained and characterized and this type of correction would not reflect the real properties of the whole material. Isotherm of steam activated sample is type I, with some hysteresis during desorption indicating the presence of some mesoporosity. Surface area of this sample is higher than demineralized one despite of both samples have similar ash and carbon content, indicating that the physical activation has created porosity responsible of the increase of the surface area reported in Table 5.

Bulk density and intraparticle porosity obtained from mercury porosimetry are given in Table 5. The value of density is lower for carbon-enriched sample in relation with CVESC-AR and CVESC-RJ samples, as expected, but this value is high compared to those reported for activated carbons. The high ash content is the responsible of this value (density of mineral matter has an accepted value of 2.1 g/cm³).

Table 5
Data from N₂ adsorption and mercury porosimetry

	S_{BET} (m ² /g)	d_p (g/cm ³)	Porosity (%)
CVESC-AR	3	1.44	41.4
CVESC-RJ	2	1.44	40.1
CVESC-EN	14	1.19	43.6
CVESC-EN-DM	43	0.76	61.0
CVESC-EN-DM-ACT	122	0.82	58.8

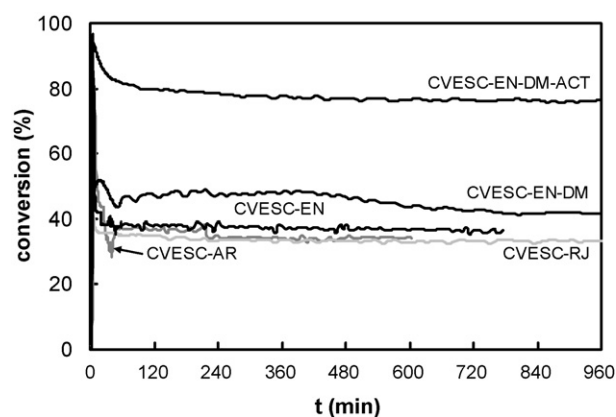


Fig. 4. NO conversion curves for studied samples at 150 °C.

In order to investigate the potential use of this activated carbon obtained from FAs in gas cleaning applications, the removal capacity of NO was tested in conditions of SCR reaction. During the SCR process, NO, in the presence of an excess of O₂ is selectively reduced by NH₃ to N₂ and H₂O over a catalyst at temperatures of 300–400 °C. Two great disadvantages of this SCR control unit are the high cost of the catalysts used (mainly based on titania-supported V₂O₅) and the need to reheat the gases to the optimum temperature for catalysts operation. Activated carbons can operate at lower temperatures (100–200 °C) with high De-NO_x activity [14,17–20] and can be cheaper than catalysts if an appropriate precursor is selected.

The NO conversion curves versus time for samples CVESC-AR, CVESC-RJ, CVESC-EN, CVESC-EN-DM and CVESC-EN-DM-ACT are depicted in Fig. 4.

The conversion curves of NO on the samples reached steady state quickly and are maintained 10 h after. Low de-NO_x activities are achieved by only sieved samples, but they cannot be explained only in terms of carbon adsorption/reduction. Pasel et al. [21] attributed some NO catalytic activity to mineral matter present in carbon catalytic supports. Sample CVESC-RJ show an ash content of 98% but it exhibit a NO conversion value near 30%. In this case, the NO removal capacity cannot be only attributed to mineral matter itself because some part of the mineral matter is located inside the pores of organic matter. Enriched-carbon sample exhibit the highest NO abatement capacity among sieved samples in direct relationship with carbon content of this sample. The increase of conversion reached by the demineralized sample can be attributed to both increase of carbon content and surface area. However, the performance of activated sample cannot be correlated neither with the decrease of ash content nor with the increase of carbon content as the rest of the samples studied, as can be seen in Fig. 5a and b. The increase of the surface area is the direct responsible of the increase of NO conversion, as can be seen in Fig. 5c. However, carbon content and the development of porosity are connected, because activation only affects to carbon in samples, because mineral matter has no contribution to surface area, at it has been described previously in this paper. So, the increase in carbon content of the precursor would allow obtaining a high performance active carbon after proper activation.

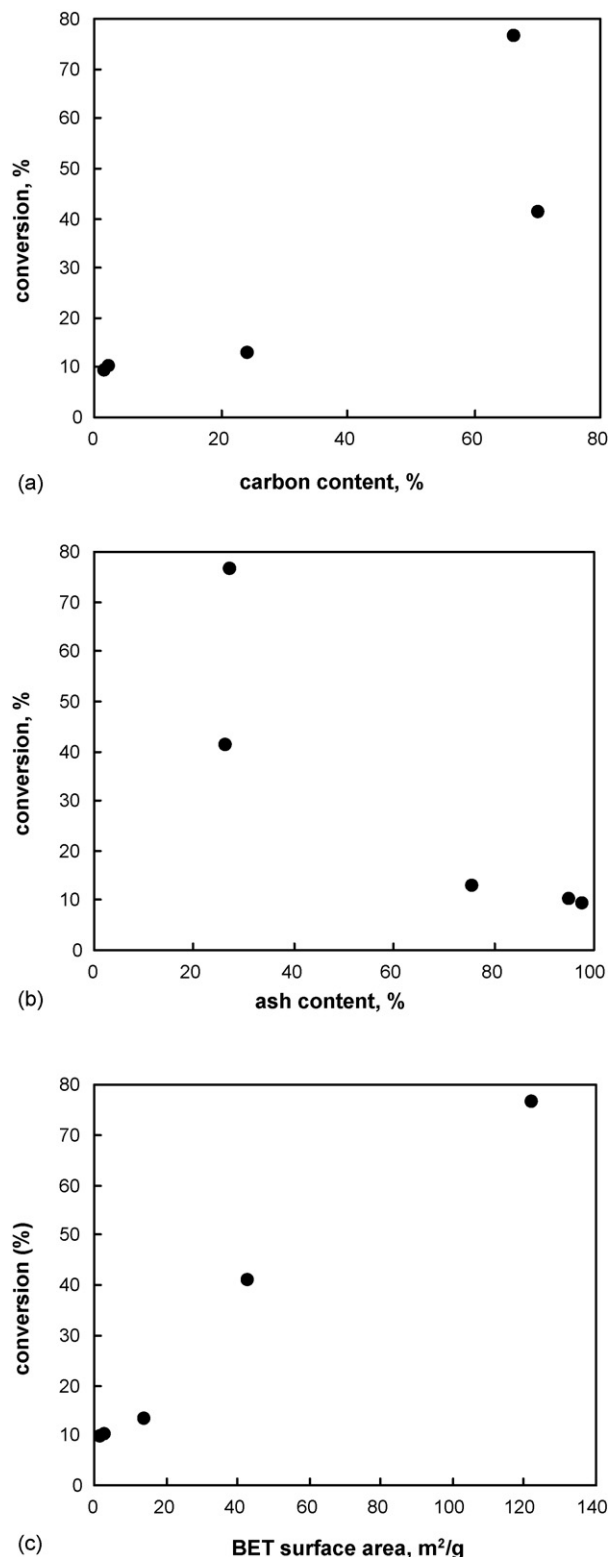


Fig. 5. Relationship of NO conversion with (a) carbon content; (b) ash content; (c) BET surface area.

Thus, in order to obtain a more suitable activated carbon for environmental applications in gas phase from FAs mineral matter must be removed efficiently from unburnt carbon before activation. Results presented in this work show that this carbon

has characteristics that makes it an attractive precursor for the preparation of activated carbons. So, further work will be carried out in the way to improve mineral matter removal as well as to study the best activation conditions to optimize surface area.

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