MODIFICATION OF PETROLEUM COKE BY IMPREGNATION WITH KRAFT BLACK LIQUEUR

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Abstract

With the goal of adding value to petroleum coke and studying the adsorbing potential of Kraft black liqueur, each a subproduct from the oil industry and paper industry respectively, the elaboration of an adsorbent from both residues was proposed for the removal of Nickel and Vanadium from aqueous solutions. To achieve this objective Venezuelan petroleum shot coke was selected and later impregnated with Kraft black liqueur. Different liqueur/coke proportions, temperatures and impregnating times were applied and studied. The adsorbing properties of the new material were evaluated through elemental and immediate analysis, TGA curves at different atmospheres, surface texture characterization and optical texture. The adsorbing potential was measured by the amount of Nickel and Vanadium removed from a solution contaminated with them. The results obtained show that: 1) the surface of the coke is significantly modified by the impregnation with the Kraft black liqueur, 2) there is a slight increase in the adsorption of Ni and V in the new materials in comparison to the original shot coke, 3) All the solid materials obtained possess a very low surface area, which indicates that the removal of Ni and V occurs through a different mechanism than that of activated carbon.

Key words
Petroleum Coke, Impregnation, Adsorbent

Introduction

Petroleum coke is a material that, under normal conditions, is chemically stable and non-reactive. It also has a high caloric value, insignificant surface area and low content of volatile material, like carbon oxides, sulphur and nitrogen (Siskin et al., 2006). Its use as an alternative in the plants of electric generation allows for a cost reduction of 30 to 45%, therefore the worldwide demand for coke by this sector is high. In the case of Venezuelan coke, the content of heteroatoms like sulphur, nitrogen, nickel and vanadium, restricts its use and promotes the use of other alternatives (Kräuter et al, 2003).

Generally, petroleum coke presents porosity, fissures and fragmentation on its surface. The quantification of the surface area of petroleum coke shows very low surface area values, so it will be absolutely necessary to increase these values if it's going to be used as an adsorbent. This is supported by the known fact that “the larger the surface area the larger the amount of adsorption sites available in the adsorbents surface”. Under the optic microscope, petroleum coke appears like a solid matrix with organic and inorganic inclusions, pores and micro fissures. Under polarized light the coke reveals small structural units, which may or may not vary in their orientation with respect to the lighting plane. Thus it is classified either as an anisotropic coke if the structures align with the lighting plane, or as an isotropic coke if the structures are not distinguishable to the polarized light. Given these characteristics, it is considered possible to improve the adsorption properties of the coke through carbonization and activation strategies which would increase the surface area. Such strategies would work by increasing the porosity while at the same time activating the surface, therefore making it suitable as an adsorbent. To achieve this objective, the coke was carbonized before it was impregnated with Kraft’s black liquor (a subproduct of the paper industry). In this way an added value would be given to these two subproducts by producing an adsorbent.

Kraft’s black liquor is a diluted solution of different chemical products (pH between 10 and 11) constituted by organic compounds that come from the solubilization of wood, and residues from inorganic compounds (mostly alkali and water), all of them used in the Kraft process for paper production (Rohella et al., 1996). Lignin is one of the main compounds in black liquor, and it is a cross-linked polyphenolic polymer without any ordered repeating units and has an elevated molecular weight. This compound is the result of combinatorial-like phenolic coupling reactions (Ralph et al., 2004), (Boerjan et al., 2003), and it was expected to react with the inorganic compounds of the black liquor under heat (Sharma et al., 2004), therefore increasing the surface area of petroleum coke and simultaneously activating it. In result it would produce an adsorbent appropriate for the removal of heavy metals like nickel and vanadium.

Experimental

Samples of delayed petroleum coke (CV) and black liquor (LN) from Caribbean pine and Gmelina were studied. Initial characterization of the CV showed and %C higher than 80%, %S lower than 5%, a %V of 6% approximately and a %Ni of 9% aprox. The LN contains approximately 70% of organic solids (cellulose, hemi cellulose and lignin), 30% of inorganic solids (NaOH) and 10% of total solids.

Two series of experiments we performed to impregnate petroleum coke with the black liquor. In the first series the LN used as it was received by the laboratory. For the second series, a litre of the LN was concentrated by evaporating it to %50 of its original volume, this solution was labelled "concentrated black liquor" distinguishing it with the initials LNc. This LNc was found to have a pH of 11.76.

To study the impregnation the following samples were prepared: CV/LN 75/25 and 50/50. The time for impregnation was 8 days, using constant manual agitation. Afterwards, the LN excess was evaporated and the samples were separated in portions of 105 gr for the corresponding activation treatment. The temperature applied was of 600^{o}C and the activation times studied were of 30 and 90 minutes (t_1 and t_2 respectively). As a reference the same activation process was applied to a CV sample without impregnation.

All CV samples attained were submitted to: *Immediate Analysis:* humidity, ashes and volatile matter percentages; *Elemental Analysis:* Carbon, Hydrogen and Sulphur percentages; thermal gravimetric analysis with a heating speed of 10ºC/min. and a maximum of 800ºC. Three types of atmosphere: O_2 (oxidizing atmosphere), N_2 (inert atmosphere) and H_2 (reductive atmosphere); *Micro and Macroscopic texture Analysis:* characterization and quantification of optic textures. For these analyses, tablets were made mixing epoxy-resin binder with 0.2 microns granulometry coke. The tablets were smoothed and polished previously to their observation in an Orthoplan model, Leitz optic microscope with polarized light, provided with oil immersion objectives of 32X and a total magnification of 320. The evaluation of the macroscopic textures comprehended the characterization and quantification of the superficial area, pore average diameter and pore volume. These tests were made by N_2 absorption with Micromeritics ASAP 2000 equipment. Finally we made an adsorption potential test for Ni y V.

Results and Discussion

The content of ashes and volatile material present in the coke was increased by the impregnation with black liquor, this been a negative aspect that could affect the adsorption properties of the samples (See Table 1). In general, the S content did not change significantly, whilst the C content increased and the H values decreased. In consequence, higher C/H values were attained, which indicates that the products obtained are more condensed and dense, as show by the density values. The surface area in all cases was very small, therefore the adsorption properties should be attributed to the surface groups from the coke and the ones added by the black liquor.

Table 1 Characterization of the Coke Impregnated.

Analysis	CV	CV/LN 75/25 t1	CV/LN 75/25 t2	CV/LN 50/50 t2	CV/NaOH 75/25 t2
% W	2,3	2,5	4,5	5,5	2,0
% VM	10,69	10,23	9,51	7,5	10,89
% Ash	0,68	1,04	2,25	5,86	0,75
%S	4,78	4,82	4,53	4,11	4,85
%C	82,00	81,59	79,11	86,51	88,17
%H	5,33	4,60	4,03	3,50	4,85
C/H	15,38	17,73	19,63	24,71	18,17
A (m^2/g)	5,3	3,84	2,8	1,85	5,00
d (g/ml)	1,76	1,90	2,08	2,41	1,89

Thermal Gravimetric Analysis (TGA)

The changes in the mass of the CV as a function of the temperature were studied. The oxidizing atmosphere with O_2 allows observing the mass loss by combustion. With the N_2 inert atmosphere the losses due to carbonization can be observed and with the reductive H_2 atmosphere the possible losses by reduction can be studied. (Figures 1 and 2).

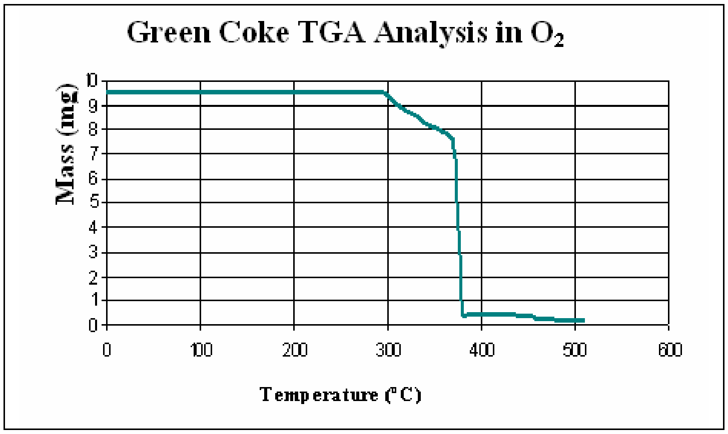

Figure 1. TGA of CV in O_2 Atmosphere.

In oxidizing atmosphere, a gradual mass loss was observed between 300°C and 350°C during which the sample lost 20% of its initial weight, from this point on the mass loss rate increases considerably and by 380°C, 95% of the sample had been consumed. In inert atmosphere, carbonization starts at 550°C, with a total mass loss of 8.2% when the analysis is finished at 800°C. In reductive atmosphere the same behavior is observed as in the inert atmosphere, however the mass loss begins at 510°C and by the end of the analysis the total loss is only a 12%. Such low values indicate a low reactivity on the surface of the CV without additives (Khezami et al., 2005), (Ferdous et al., 2002).

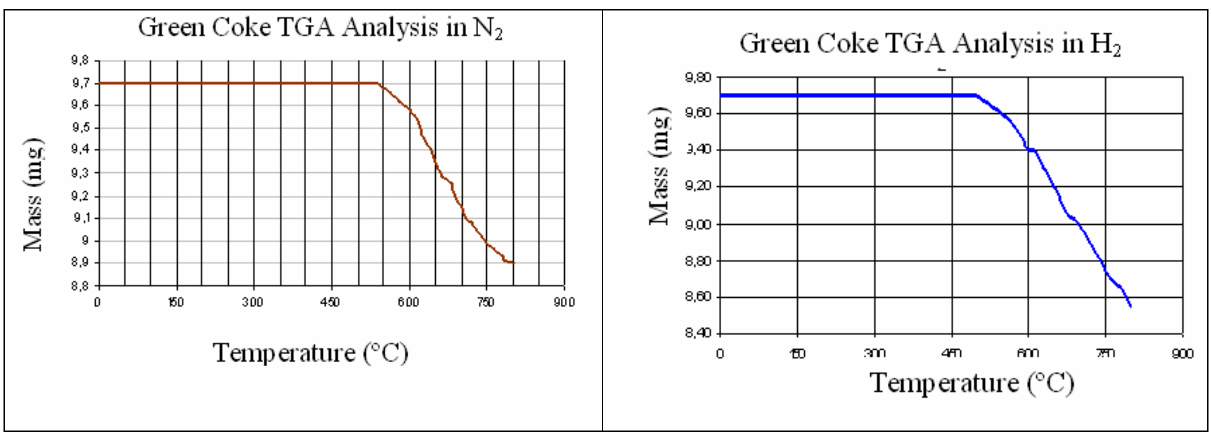

Figure 2. TGA of CV in N_2 and H_2 Atmospheres.

Optical Texture Analysis

The results presented in Table 2 show that the impregnation of the coke with the LN provokes a modification of the optic texture of the surface.

Table 2. Optic Texture of the Normal and Modified CV

SAMPLE	CGM	MGM	FGM	D	SD	SM	FMA	OTI
CV	0,460	0,006	0,005	0,045	0,479	0,000	0,006	14,20
CV/LN 50/50 t2	0,516	0,003	0,000	0,027	0,403	0,047	0,002	13,00
CV/LN 75/25 t1	0,555	0,015	0,001	0,006	0,407	0,015	0,001	12,40
CV/LN 75/25 t2	0,387	0,015	0,000	0,030	0,467	0,095	0,006	13,99
CV/NaOH 75/25 t2	0,305	0,009	0,001	0,013	0,372	0,274	0,026	12,92

The majority of the structures identified in the coke impregnated with LN or not, is Fine Grain Mosaics (FGM) and Small Domains (SD). However, in the samples that were impregnated a new texture was shown: Supra Mosaics (SM). Regarding the activation times, the samples that had a CV/LN ratio of 75/25 showed an increase of the most condensed textures Domains (D), Small Domains (SD), Supra Mosaics (SM) and Fluid Medium Anisotropy (FMA), with treatment time. Not withstanding, the most outstanding aspect of this study is the high values adsorption, for both Ni and V, of the coke sample impregnated with NaOH (See Table 3). As it's shown in Table 2 the sample possesses the highest values for SM and FMA optic textures. This could indicate that the chemical attack of the NaOH on the coke surface is stronger than that of the LN, causing the "emergence" of more mature textures. But it could also indicate that at the same time that there is a preferential activation of these textures, there is a preferential adsorption of the metallic ions over these textures.

Adsorption Properties

The adsorption capacity of the coke samples impregnated with LN and NaOH, present a slight enhancement when compared with the CV. Nevertheless, the results attained are not as significant as hoped. After revising the values in Table 1, it is concluded that this property does not change significantly after impregnation or treatment. Therefore the increase in the adsorption property of the coke must be caused by the action of the LN, which most likely involves a chemisorption mechanism rather than a physisorption, as corroborated by the small surface area. An interesting aspect observed was the fact that with the LN impregnations the hardness of the CV was qualitatively increased. Initially the coke exhibited a fragility that made it easy to crush, but after impregnation with LN the hardness of the coke increased proportionally to the concentration a quantity of LN used. It is possible that the LN when added to the coke, additionally to changing the surface in a macro and microscopic scale, it also acts as a cementing agent. This indicates that in order to increase the adsorption properties a more severe thermal treatment must be performed to increase activation. In all the samples analyzed, a preferential adsorption was observed for the V, the maximum been the CV impregnated with LNc. The only exception was the maximum adsorption of Ni by the CV impregnated with NaOH. The preference for the V over the Ni could be related to the smaller ionic radius and/or its high reactivity to oxygen and carbon.

Table 3. Adsorption Test for the Activated Products

SAMPLE	**ADSORBED CONTENT (%)**	
	V	**Ni**
CV	42,50	27,50
CV/LN 50/50 t2	46,00	33,50
CV/LN 75/25 t1	43,50	27,50
CV/LN 75/25 t2	44,50	30,00
CV/NaOH 75/25 t2	47,00	34,50
CV/LNc 50/50 t2	54,15	22,00

Conclusions

The internal surface as well as the external one of the coke is significantly modified by the impregnation with the Kraft black liqueur.

There is a slight increase in the adsorption of Ni and V in the new materials in comparison to the original shot coke.

It is possible that there is a preferential adsorption of the metals according to the optical texture of the coke.

The presence of the black liquor decreases the Sulphur content of the coke, enriching the carbon content of the collected solid.

All the solid materials obtained possess a very low surface area, which indicates that the removal of Ni and V occurs through a different mechanism than that of activated carbon.

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