

LIGHT N-PARAFFINS SEPARATION BY INVERSE GAS CHROMATOGRAPHY WITH CUBAN VOLCANIC GLASS

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Abstract - In this work the applicability of a natural volcanic glass (technological type I material) from Cuba is investigated as adsorbent for separation of mixtures of C₁-(C₅; C₆; C₇; C₈; C₉) hydrocarbons by inverse gas chromatography under flow conditions in a temperature range of 328-343 K. The experimental results indicated that the material was mainly composed of silica and, in a lower proportion, of alumina, that provided surface Si-OH and Al-OH groups to favor the interaction and separation of the different components of paraffin mixtures. In fact, the calculated heats of adsorption were high enough to facilitate the separation procedure. The high availability and low cost of these materials make them potential and attractive candidates to be used in large scale applications.

Keywords: Adsorption; Separation; Linear paraffins; Glasses; Diffusion; Surface properties.

INTRODUCTION

The separation of individual components of paraffin mixtures is a key factor in the petrochemical industry. These products are one of the most important components of natural gas, fuel and lube oils due to their huge resources and relatively non-toxicity in comparison to other sources because the combustion of these products does not cause any formation of harmful products.

Several methods have been proposed to separate olefin/paraffin in industry (Brian, 2004). Among them, the common separation processes are absorption (Laredo et al., 2012; Gomes et al., 2014), cryogenic distillation (Torres-Ortega et al., 2013), and membranes (Merkel et al., 2013). Absorption is the most sustainable process to separate olefins and paraffins due to the

complexation of the double bond of the olefins with transition metals (Dewar, 1951; Eldridge, 1993). However, paraffins are exclusively formed by C-H bonds so the interactions required by the adsorption process must be non-specific. The fuel companies use molecular sieves such as carbons (Huang et al., 2011; Yahia and Ouederni, 2012) or zeolites (Rivera et al., 2011; Ferreira et al., 2013). Zeolites are molecular sieves with a well-defined microporous framework, which leads to efficient adsorbents and catalysts with high thermal stability (Beerdsen, et al., 2003); while activated carbons have also shown an excellent behavior in adsorption and separation processes. Nonetheless, the design and synthesis of these adsorbents raises the cost of the separation process, mainly in the case of activated carbons (He et al., 2012). In order to improve competitiveness, inexpensive adsorbents with high

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availability in the environment such as natural zeolites have been proposed (Rivera et al., 2011).

The aim of the present work is the search and development of alternative materials to separate these light paraffins. In this sense, a volcanic glass has been proposed as a potential material for this process due to its high availability and low cost. Volcanic glass is a natural glass, which results from the rapid cooling of lava. The physicochemical properties of these materials depend on the chemical composition of magma and its cooling rate (Friedman and Long, 1984). Volcanic glass has been used as starting material for the synthesis of zeolites (Yoshida and Inoue, 1986; Yoshida and Inoue, 1988) or smectites (Tomita et al., 1993), the adsorption of radioactive ions (Steinhauser and Bichler, 2008), arsenic (Ruggieri et al., 2008) or copper (Alkan and Dogan, 2001), the adsorption of dyes such as methylene blue (Dogan et al., 2004) methyl violet (Dogan and Alkan, 2003), victoria blue (Alkan and Dogan, 2003), the synthesis of composites with polyacrylamide (Tekin et al., 2010) and more recently in the separation of propane/propylene (Fernández-Hechevarría et al., 2015).

The adsorption and later separation of light alkane hydrocarbons using Inverse Gas Chromatography (IGC) has been widely reported in the literature. IGC is a highly selective and versatile gas phase technique to perform physicochemical characterization of different solids. It is based on injection of clearly identified molecules into a column packed with the material under investigation (Mohammadi-Jan and Waters, 2014). The interaction between adsorbate-adsorbent will determine the retention time and therefore the capacity to separate the mixture and will provide information on thermodynamics, surface energy, reaction kinetics, and textural parameters (such as specific surface area and porosity) (Lazarević et al., 2009). The surface energy of solid materials is an important property that controls many practical applications and is a direct manifestation of intermolecular forces. In the case of a *n*-paraffin mixture it would provide information about the differential adsorption heat as a function of the carbon number in the paraffins under study.

The most attractive aspect of the IGC is the effective application to a wide range of physicochemical characterization of non-volatile materials such as dispersive and specific parameters of surface free energy, diffusion coefficient, phase transitions and crystallinity (Voelkel et al., 2009; Mohammadi-Jan and Waters, 2014), which can yield vital information in the fields of polymer and coatings (Edelman and Fradet, 1989; Murakami et al., 1998; Abel et al., 2002), pharmaceuticals (Grimsey et al., 2002; Planinsek and Buckton, 2003; Mohammadi-Jan and Waters, 2014) fibers (Cantergiani and Benczédi, 2002; Heng et al., 2007) or nanomaterials (Batko and Voelkel, 2007;

Menzel et al., 2009). Basing on the physicochemical properties of the material introduced on the packed column, IGC can be used for the separation of paraffins, as was reported by Autié et al. in previous researches using porous hexacyanocobaltates (Autié-Castro et al., 2009), metal-organic framework (Cu-BTC and Fe-BTC) (Autié-Castro et al., 2015) or natural clinoptilolite (Rivera et al., 2011). In the present work, a packed column with inexpensive volcanic glass has been used to evaluate the separation capacity of this structure for C₅-C₉ paraffin mixtures as well as their adsorption heats by IGC.

MATERIALS AND METHODS

The material used for the separation of paraffins by IGC was a volcanic glass obtained from the Aji de la Caldera mine in Guantanamo (Cuba). The chemical composition of this volcanic glass was evaluated by wavelength disperse X-ray fluorescence (ARL ADVANTXP spectrometer) and UNIQANT software.

The crystalline phases were determined using a X'Pert PRO MPD Philips diffractometer with CuK_α (1.54Å) radiation.

FT-IR spectra were collected with a Varin 3100 FTIR spectrophotometer with a Harrick HVC-DRP cell. The analysis of the volcanic glass was carried out using about 30 mg of finely ground sample. The interferograms consisted of 120 scans and the spectrum was collected using a KBr spectrum as a background.

The textural properties of the volcanic glass were determined by N₂ adsorption-desorption at 77 K in a Micromeritics ASAP 2020 equipment. Prior to analysis, volcanic glass was outgassed at 673 K and 0.01 kPa for 12 h. The specific surface area was determined using the Brunauer-Emmett-Teller (BET) equation considering a N₂ molecule cross section of 16.2 Å² (Brunauer et al., 1938). The porosity of the volcanic glass was measured by Hg-Porosimetry using an AutoPore IV 9500 V1.07 equipment supplied by Micromeritics in a pressure range of 0.0034e224 MPa

The IGC data were recorded with Shimadzu equipment (model 14B) and a flame ionization detector (FID) in the 368-488 K temperature range. Helium was used as carrier gas at a flow rate of 12.8 cm³/min. Previously cleaned and weighed stainless steel columns (60cm long and 2.2mm inner diameter) were packed with 2.5 g of the material. The packed columns were outgassed overnight at 523 K under helium flow. *n*-Alkanes of analytical grade were used in all cases and injected as the smallest detectable amount of their vapor phases, extracted from the head space of their containers, to obtain data close to zero coverage.

To obtain the corrected retention time for the probes the relation ($t_R - t_0$) was used, where t_0 was the retention

time of methane, CH_4 (un-retained hydrocarbon), and t_R was the retention time of the probe. The corrected retention times were taken as the average number value among five injections. Mixtures of C_1 -(C_5 ;---; C_9) were prepared by introduction of a little quantity of CH_4 in the head space of each liquid alkane, and C_5 - C_9 net retention volumes, V_n , were calculated according to Eq. 1:

$$V_n = J \cdot V_f \cdot (t_R - t_0) \cdot \frac{T_c}{T_A} \cdot \frac{(P_0 - P_w)}{P_0} \quad (1)$$

where J is the James–Martin gas compressibility correction factor, V_f is the gas carrier flow rate at the flow meter temperature T_f ; T_c is the column temperature; T_A is the room temperature ($T_A = T_f$); P_0 is the outlet pressure; P_w is the vapor pressure of water at T_f .

The differential adsorption heat, Q_d , equal to the enthalpy for the standard adsorbed state ΔH_{d0} (within the Henry zone) was determined from the slope of a $\ln(V_n/A_s)$ versus $1/T_c$ plot according to equation (2):

$$Q_d = \Delta H_{d0} = -R \cdot \frac{d \left[\ln \left(\frac{V_n}{A_s} \right) \right]}{d \left(\frac{1}{T_c} \right)} \quad (2)$$

where R is the universal gas constant; and A_s is the product of the specific surface area (S), and the amount of sample (m) in the column.

RESULTS AND DISCUSSION

The chemical composition of the volcanic glass was estimated by X-ray fluorescence (XRFS) (Figure 1). These data reported that the material is mainly formed by SiO_2 (66.3 %) and Al_2O_3 (13.4 %). In addition, it is noteworthy the presence of other oxides such as, Fe_2O_3 , MgO , CaO , NaO or K_2O in minor proportions. Several authors have reported that basaltic magmas, which contain SiO_2 (< 50%) are very fluid and their lower viscosity favors the crystallization. However, the highly polymerized rhyolitic lavas that contain higher SiO_2 proportions (> 65%) are extremely viscous, yielding a layer of obsidian as much as meters to tens of meters thick (Friedman and Long, 1984). Considering this fact, the volcanic glass analyzed in this research should come from rhyolitic lavas that suffered a relatively slow cooling.

The XRD diffractogram of the volcanic glass showed a noisy profile (Figure 2), with a broad band from 20 - 30° attributed to the presence of an amorphous structure. Thus, it is noteworthy the presence of

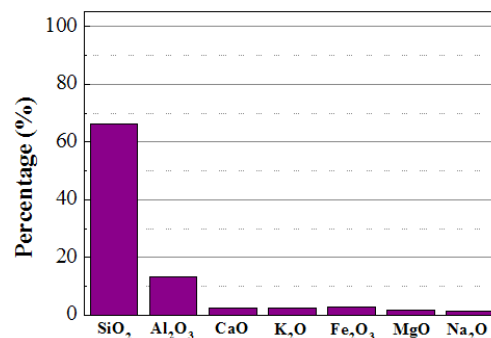


Figure 1. Chemical composition of the volcanic glass (estimated by XRFS).

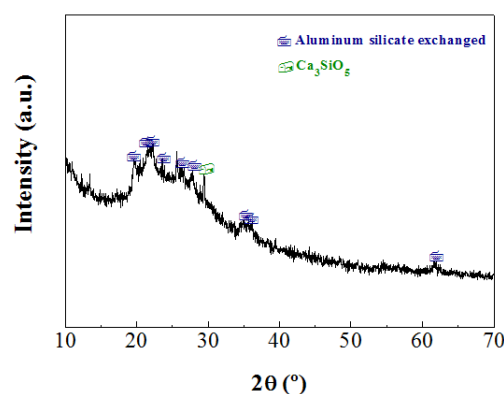


Figure 2. X-ray diffraction patterns of the volcanic glass.

small diffraction peaks, which are attributed to the substitution of silicon by aluminum in the quasi-amorphous aluminosilicates, leading to a charge deficiency that is counterbalanced by the presence of alkaline cations, such as Na^+ or K^+ . In addition, the diffraction peak located at about $2\theta = 22.9^\circ$, attributed to Ca_3SiO_5 , indicates the presence of another phase with higher crystallinity, although in low proportion. If this material is compared with another volcanic glass from Brazil (Andrade et al., 2018), the studied Volcanic glass was much less crystalline and also presented a different composition. Thus, the volcanic glass from Brazil presented labradorite, augite, quartz, cristobalite, sanidine, alumina, magnetite, pigeonite, enstatite and apatite. It is clear that both the composition and crystallinity depend on the origin of the volcanic glass, as expected.

Figure 3A shows the FT-IR spectrum of the volcanic glass between 4000 - 2750 cm^{-1} . The band located about 3600 cm^{-1} is attributed to the OH stretching modes of the structural OH groups (Franco et al., 2016), while the broad band close to 3430 cm^{-1} is attributed to the overlapping asymmetric and symmetric (H-O-H) stretching vibrations of H-bonded water (Madejová, 2003). The shoulder located about 3230 cm^{-1} is ascribed to an overtone of the bending mode of cation hydration water (Farmer, 1974). Figure 3B displays the FT-IR spectrum between 1800 - 750 cm^{-1} . The main

band located at about 1290 cm^{-1} is attributed to Si-O stretching of the amorphous aluminosilicate, while the band about 1160 cm^{-1} is assigned to the Si-O stretching mode typical of the clay minerals (Madejová, 2003). In this sense, previous researches have pointed out that volcanic glass can suffer an alteration process to form zeolites or smectites (Tomita et al., 1993). The band located about 980 cm^{-1} is attributed to the Si-O in-plane stretching vibrations, while the bands located about 900 cm^{-1} and 790 cm^{-1} are assigned to the Al-O-Si and Si-O-Si bending modes (Vilarrasa-García et al., 2017). The weak shoulder centered at about 1450 cm^{-1} is attributed to the presence of CO_3^{2-} species (Correia et al., 2015). Finally, the band with a maximum located at 1640 cm^{-1} is assigned to the H-O-H bending vibrations (Vilarrasa-García et al., 2017).

The textural properties were determined from the experimental adsorption isotherm of N_2 at 77 K (Figure 4). The isotherm is of type II according to the IUPAC classification, which is attributed to the presence of meso- and mainly macropores by the existence of interparticle voids (Thommes et al., 2015). The specific surface area was determined considering the linearity in the range of P/P_0 (0.10-0.25), which is ascribed to N_2 -adsorption on the monolayer, obtaining a value of $44\text{ m}^2/\text{g}$. This value is well below other porous materials, such as zeolites or activated carbon that can reach specific surface areas even more than $1000\text{ m}^2/\text{g}$. Previous researches have evaluated the textural properties of other volcanic glass coming from Turkey, obtaining S_{BET} values lower than $10\text{ m}^2/\text{g}$, probably due to the bigger particle size, which implies a decrease of the available surface (Dogan and Alkan, 2003; Dogan et al., 2004).

As was indicated previously, the N_2 -isotherm at 77 K revealed that the volcanic glass presented macroporosity, as observed from the sharp N_2 adsorption at high relative pressures, so the most appropriate technique to evaluate the porosity is Hg-porosimetry. It should be stated that Figure 5A reveals

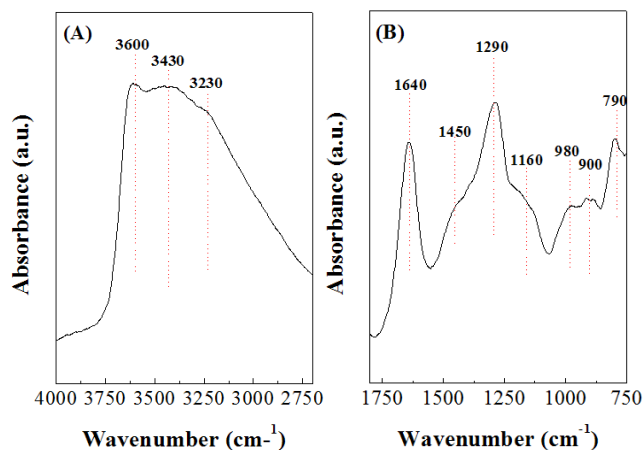


Figure 3. FTIR in the range of $4000\text{-}2700\text{ cm}^{-1}$ (A) and $1800\text{-}750\text{ cm}^{-1}$ (B) of the volcanic glass.

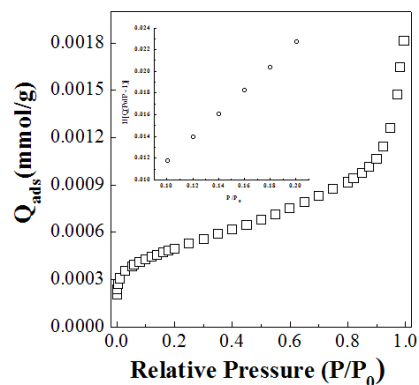


Figure 4. N_2 adsorption isotherm at 77K of the volcanic glass.

Hg-intrusion until 25 MPa characteristic of the filling of the voids between particles. From this pressure value, the volume barely changed, which indicates the absence of pores of small diameter. Figure 5B confirms this fact with about 90% of the pore volume inside of the macropore range, i.e., pore diameter higher than 50 nm, while only 10% can be considered as small macropores and mesopores.

Several experiments were carried out to understand the separation capability of paraffins in the volcanic glass. Figures 6-9 show the chromatographic profiles of several n-paraffin mixtures under different operational conditions. From these figures, it can be clearly observed that in all cases well-defined and symmetric elution peaks appeared. The adsorption process takes place following Henry's law where the interactions with neighboring molecules are non-specific and with scarce intensity. In all cases, it can be observed that an increase of the paraffin length favors its retention on the column. Considering that the volcanic glass is mainly macroporous, as indicated from the Hg-porosimetry, the existence of higher non-specific interaction between the longer carbon-chain paraffins and the volcanic glass is expected.

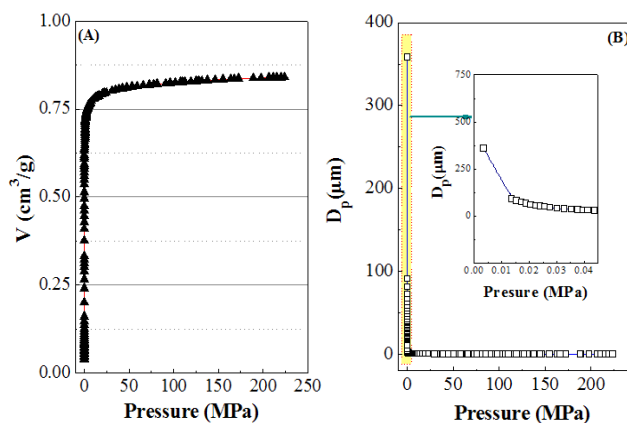


Figure 5. Hg-porosimetry profile (A) and pore diameter obtained from Hg-porosimetry as a function of the experimental pressure (B) for the volcanic glass.

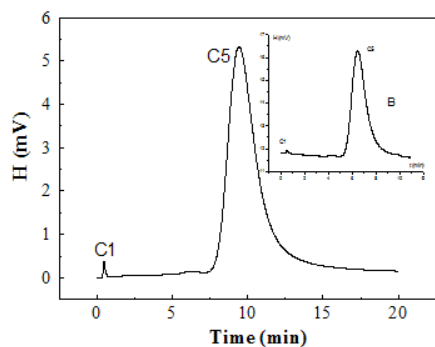


Figure 6. Chromatogram of C1+C5 at 368 K (A) and 378 K (B) in the volcanic glass.

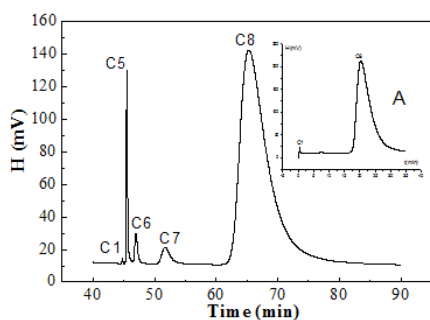


Figure 7. Chromatogram of C1+C8 (A) and mixture of C1+C5+C6+C7+C8 (B) at 448 K in the volcanic glass.

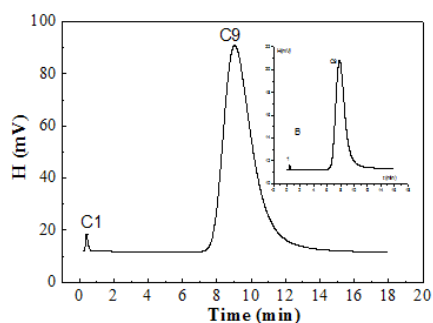
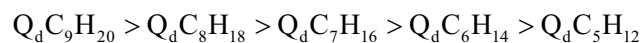


Figure 8. Chromatogram of C1+C9 at 473 K (A) and 478 K (B) in the volcanic glass.

The graphs of $\ln V_n$ vs. $1/T_c$ for every paraffin, represented in Figures 10 and 11, were a straight line in all cases with $R > 0.99$. The values of the differential heats of adsorption calculated from the slopes are included in Table 1.

From this table, it is observed that the heats of adsorption followed the order:



That is, it increased with the carbon number. If Q_d is represented vs the number of carbons of the paraffin molecule, a linear correlation was observed. The fitting was a straight line with $R > 0.99$ (Figures 10-11). This is explained by considering that n-paraffin interactions with the solid are of the van der Waals-type (i.e., non-

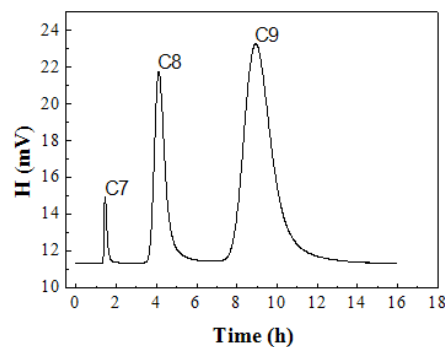


Figure 9. Chromatogram of C7+C8+C9 mixture at $T_c = 478$ K in the volcanic glass.

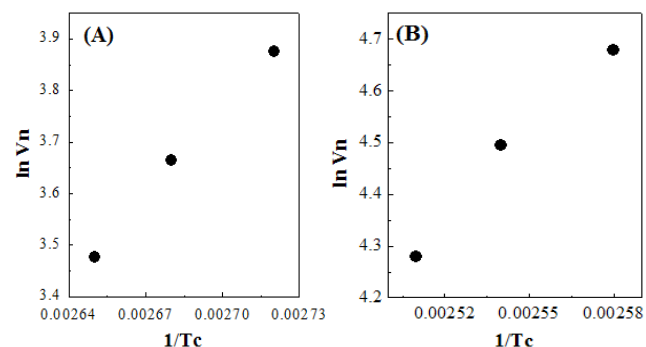


Figure 10. $\ln V_n$ vs. $1/T_c$ for C5 at 368-378 K (A) and for C6 at 388-398 K (B) in the volcanic glass.

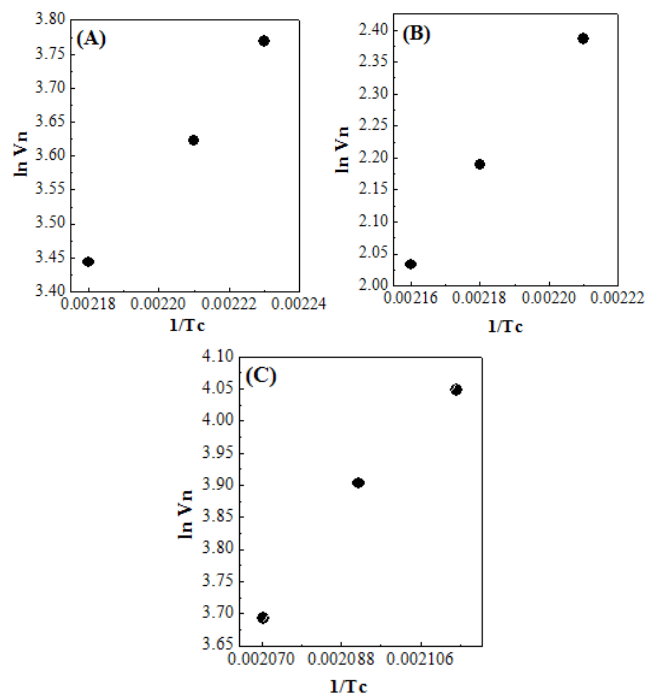


Figure 11. $\ln V_n$ vs $1/T_c$ corresponding to C7 at 448-458 K (A); C8 at 453-463 K (B) and C9 at 473-483 K in the volcanic glass.

specific type) and each CH_2 group contributes in the same way. This fact leads to a higher slope value for the longer carbon-chain paraffins, reaching the maximum

Table 1. n-Paraffin (HC) adsorptions heats in kJmol^{-1} (Q_{dif}), adsorption differences heats of two neighboring n-paraffin (ΔQ_{dif}) in kJmol^{-1} and their Bering-Serpinskii separation capacity $K_{\text{B-S}}$ in the volcanic glass.

HC	Q_{dif}	ΔQ_{dif}	$K_{\text{B-S}}$
C_5H_{12}	42.7	-----	-----
C_6H_{14}	51.3	8.6	2.1
C_7H_{16}	55.9	4.6	1.2
C_8H_{18}	61.5	5.6	1.4
C_9H_{20}	67.4	5.9	1.5

differential adsorption heat (67.4 kJ/mol) for C_9H_{20} , while C_5H_{12} only displays a differential adsorption heat of 42.7 kJ/mol . In addition, it was possible to know the contribution of each CH_2 of a paraffin group from the slope of the straight lines, obtaining a Q_{dif} around 5.3 kJ/mol . If the differences between these values are calculated (Table 1), all of them are much higher than 1, indicating that volcanic glass has excellent behavior in the separation of light paraffins.

On the other hand, Bering and Serpinski (Keltsev, 1984) pointed out that the separation criterion ($K_{\text{B-S}}$) is not determined by adsorption heat values, but by the difference between them. Thus, $\ln K_{\text{B-S}}$ values greater than 1 indicate that two neighboring components in the chromatogram could be completely separated. Greater values of $\ln K_{\text{B-S}}$ indicate that a better separation will be obtained. $\ln K_{\text{B-S}}$ was calculated from Equation 3.

$$\ln K_{\text{B-S}} = \frac{Q_{\text{Dif2}} - Q_{\text{Dif1}}}{RT} \quad (3)$$

Moreover, Figure 7 shows that, for a high temperature such as 448 K , the use of volcanic glass can resolve the $\text{C}_5\text{-C}_8$ mixture with well definite peaks. At 478 K the $\text{C}_7 + \text{C}_8 + \text{C}_9$ mixture is also well resolved (Figure 8). The Q_{dif} values suggested that the volcanic glass may separate a complex mixture of light n-paraffins $\text{C}_5\text{-C}_9$ with well defined peaks in adequate conditions of fluxes and temperatures as was shown experimentally in Figures 12-13.

When the adsorption heat values of n-paraffins in volcanic glass were compared with those obtained

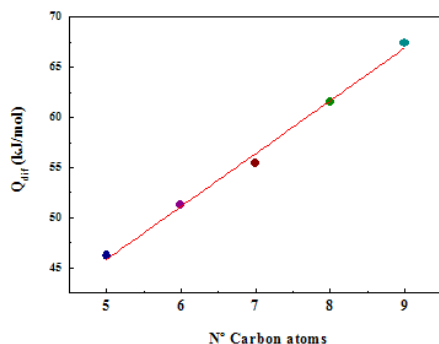


Figure 12. Q_{dif} vs. number of carbon atoms C5-C9 in the volcanic glass.

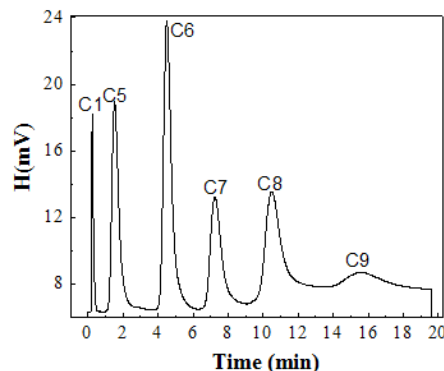


Figure 13. Chromatogram of $\text{CH}_4 + \text{C}_5\text{-C}_9$ mixture in the volcanic glass ($T_c = 400 \text{ K} + 5 \text{ K/min}$).

in other crystalline materials, it was observed that, although the studied volcanic glass is an amorphous mineral with macroporous and mesoporous surface, the n-paraffin-surface interactions were sufficiently strong to separate the components of a $\text{C}_5\text{-C}_9$ mixture (Table 2 and Figure 13). The data shown in this research are in the same range as those reported in the literature for MOFs (Autié-Castro et al., 2015) and natural zeolites (Rivera et al., 2011), previously. Table 2 results indicated that, in spite of the lower specific surface area, its capacity to separate paraffins was similar to material presenting higher surface area. It must be considered that volcanic glass is highly available in the mines.

As was indicated previously, the volcanic glasses are formed by a disordered and quasi-amorphous structure where a proportion of Si^{4+} are replaced by Fe^{3+} and Mg^{2+} species, which causes a charge deficiency that is neutralized by Ca^{2+} , Na^+ or K^+ . These cations could be substituted by ionic exchange so volcanic glasses could be used as adsorbent of cations. A previous research has reported that volcanic glasses are efficient materials for ethane-ethylene separation (Fernández-Hechevarría et al., 2015), since the higher electronic density generated by the double bond of the ethylene molecule favors a stronger interaction with the volcanic glass in comparison to the C-C bond. In the case of the paraffins, the exclusive presence of C-C and C-H bonds implies that the interactions must be non-specific. Nonetheless, it is well known that the

Table 2. n-Paraffin (HC) adsorption heat in kJmol^{-1} (Q_{dif}) in VVN and in other materials reported in different works.

HC	Q_{dif}	$Q_{\text{dif(B)}}$	$Q_{\text{FeBTC(C)}}$	$Q_{\text{dif(D)}}$
C_5H_{12}	42.7	57	49.9	33.4
C_6H_{14}	51.3	63.9	51.1	38.8
C_7H_{16}	55.9	70.2	52.5	43.7
C_8H_{18}	61.5	76.9	53.8	48.3
C_9H_{20}	67.4	83.5	55.2	51.6

(B): Cu-BTC metal-organic frameworks (Autié-Castro, G., 2015); (C): Fe-BTC metal-organic frameworks (Autié-Castro, G., 2015); (D): Cliptonite (Rivera A., 2011).

increase of the hydrocarbon chain causes an increase of the van der Waals and London interactions. These interactions must be related with the textural properties of the volcanic glass. Considering the low ordering and low surface area value, it seems clear that the interactions volcanic glass-olefin must take place on the surface of the material, discarding the presence of an ordered nanostructure such as zeolite-A, zeolite-X or zeolite-Y, that can act as molecular sieves. The obtained data reveal how the paraffins with longer chains appear at higher retention time, which is ascribed to stronger non-specific interaction (London and van der Waals) with the surface of the amorphous volcanic glass.

CONCLUSIONS

A natural volcanic glass has been used as stationary phase to separate complex mixtures of light hydrocarbons $C_5+C_6+C_7+C_8+C_9$ at programmed temperature conditions by inverse gas chromatography. The volcanic glass showed similar adsorption heats and separation capacity to those reported in the literature for crystalline materials. Moreover, the non-specific interactions between the surface and n-alkanes C_1 --- C_9 , give rise to a sufficiently high heat of adsorption to separate these light n-paraffins. The low cost of these materials makes it a promising material to be used on larger scale to separate great volumes of mixtures and obtain pure components of C_5 --- C_9 paraffins.

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