

## CARBON DIOXIDE REMOVAL FROM NATURAL GAS USING AMINE SURFACE BONDED ADSORBENTS

Orlando Leal,\* Carmelo Bolivar,\* Cesar Ovalles,† Argelia Urbina,† Javier Revette† and Juan Jose Garcia†, \*Escuela de Química, Universidad Central de Venezuela and †INTEVEP, S. A., Apdo. Postal 76343, Caracas 1070A, Venezuela.

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### INTRODUCTION

The results of research on the greenhouse effect have shown, among other things, that the concentration of trace gases occurring in the atmosphere such as carbon dioxide, methane, nitrous oxide, ozone and halocarbons have grown significantly since the pre-industrial times. During this period, the CO<sub>2</sub> level has risen 30% to nearly 360 ppm from a pre-industrial era level of 280 ppm [1]. On the basis of a variety of evidence a consensus is emerging among researchers that humans beings, primarily through their burning of fossil fuels, are already perturbing Earth's climate [2]. All specialists agree that without drastic steps to curb greenhouse gas emissions, the average global temperature will increase 1 to 3.5 °C during the next century because effective level of carbon dioxide are expected to double sometime between the years 2050 to 2100 [3]. It may be that human-generated emissions of carbon dioxide will have to be reduced by as much as 50-80% to avoid major climate changes. Such a reduction in the CO<sub>2</sub> emissions rate probably cannot be accomplished without a massive switch to non-fossil energy sources. However, it has been proposed that emissions from fossil fuels can be moderated by three strategies: exploiting the fuels more efficiently, replacing coal by natural gas and by recovering and sequestering CO<sub>2</sub> emissions [4]. A rough analysis, based on the use of currently accepted values, shows that natural gas is preferable to other fossil fuels in consideration of the greenhouse effect [5] and improvements can be obtained if natural gas is upgrading by scrubbing the carbon dioxide out of it.

Removal of carbon dioxide from gaseous streams have been a current procedure in the chemical industry. The presence of tiny amounts of CO<sub>2</sub> can act as poison in catalytic processes such as ethylene polymerization or ammonia synthesis [6]. Therefore, several procedures have been devised to eliminate carbon dioxide from ammonia plants as well as natural gas and fuel gas power plants. Three different approaches have been used: adsorption on liquid amines [7], adsorption on solid materials [8], and membrane technology [9]. The former makes extensively use of alkanolamines in plants operating at low temperatures and high pressures. In this case inhibitors should be used to prevent the corrosion problem arising from the formation of highly reactive carbamates. A process commercially known as Selexol, uses a mixtures of polypropyleneglycoldimethyl ethers and CO<sub>2</sub> removal is based on physical adsorption in much heavier molecules [10].

The use of membranes to remove carbon dioxide and other acid gases was assessed by Bhide and Stein [9]. Aromatic polyimide separation membranes are particularly useful for CO<sub>2</sub> enrichment [11], because they are able to achieve high flow rates with good selectivity and relatively low temperatures. This procedure proved effective to removed carbon dioxide in concentration ranging between 5 and 40 mol %. However, membrane saturation might produce gas losses [11].

The removal of CO<sub>2</sub> from closed ambients, such as submarines, by solid adsorbents has been described elsewhere [12]. A solid matrix, usually an inorganic oxide, was chemically modified to obtain a material which reversibly adsorbed carbon dioxide from atmospheres containing about 1 % by volume of CO<sub>2</sub>. The adsorbent, which had a clay component as agglomerant, showed approximately a capacity of 20 l of wet carbon dioxide per kg of adsorbent. When silica gel was used as a solid, the modification of its surface could be accomplished by reaction with aminoalkoxysilanes such as 3-aminopropyltriethoxysilane, though condensation to the hydroxyl groups present on the silica gel surface. This process might involve the reaction of one, two or three hydroxyl groups at the surface per molecule of alkoxy silane. Therefore, the nature of the bonded species will depend upon the number and distribution of the hydroxyl groups at the surface of the silica gel. Previous studies indicated that annealed and rehydroxylated silica gel has a surface hydroxyl concentration of 4.6 -OH groups per square nanometer [13], of which 1.4 hydroxyl groups/nm<sup>2</sup> are interacting non-hydrogen bonded species and the remaining 3.2 hydroxyl/nm<sup>2</sup> are interacting groups arranged in pairs. All these groups can be involved in the reaction of the surface of the silica with polyalkoxysilanes. From C, N, H microanalysis studies, Burwell [14] concluded that this reaction gives a product with an average composition corresponding to the detachment of the silane to the surface, according to reaction (1).



that it is effective in either gas. A lower capacity was found when natural gas was used due to the residual carbon dioxide contained in it which remained in the reactor as the temperature was lowered from activation to room temperature. However this decrease is limited to less than 5%. Experiments performed at different space velocities showed that the adsorbed carbon dioxide started to be liberated by temperature programmed desorption (TPD) above 40°C and the process of release was maintained until above 100°C [12, 15]. The center of the peak is shifted to lower temperatures as the space velocity increases. At a space velocity of 2.4 h<sup>-1</sup> (1.2 l/h) the adsorption band is centered at 10°C and desorption is completed at 110°C whereas at a space velocity of 0.6 h<sup>-1</sup> (0.3 l/h) the desorption band is centered at 90°C and desorption is completed at 120°C. On the other hand if the desorption temperature was held at 140°C the adsorbent is regenerated in 2 h.

The influence of space velocity on the adsorption of carbon dioxide is shown in Fig. 2 where 100% corresponds to complete stripping of CO<sub>2</sub> from a natural gas containing 8.3% CO<sub>2</sub> and activation was undertaken under nitrogen as carrier. It is clear from this that as space velocity increases from 6 to 36 h<sup>-1</sup> (28 to 170 scf/h) the breakthrough time is reduced from 14 to 2.5 h, however the elution front remains clear-cut confirming the chemical nature of the surface adduct. The process also quantitatively subtracts carbon dioxide from the natural gas stream.

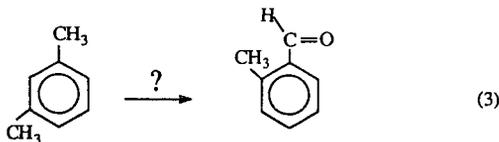
The influence of the pressure on the adsorption process is shown in Fig. 3. The capacity of the adsorbent before immediate breakthrough, when the system is operated at atmospheric pressure, is 14.0±0.7 liters of dry carbon dioxide per kilogram of adsorbent. At a pressure of 4 atm the obtained capacity is 13±2 l of CO<sub>2</sub>/Kg taken as average value at the different space velocities tested. Whereas at a pressure of 20 atm (300 psi) the adsorptive capacity has dropped to 8.3±0.2 l of CO<sub>2</sub>/Kg before immediate breakthrough. However a marked effect of the pressure is noticed here as the carbon dioxide seems to interact stronger with the adsorbent.

When carbon dioxide is saturated with water an increase of the capacity is observed, from 8.1 to 13.1 l of CO<sub>2</sub>/Kg at a space velocity of 170 scf/h (Fig. 4). Carbon dioxide scrubbing by the adsorbent leads to an enrichment of the natural gas as it is presented on Table 1.

The adsorbent used in all the above experiments was a modified silica/clay aggregate described before (Adsorbent I) [12]. Two new adsorbents were obtained: a) using an extrudated silica gel as matrix (Adsorbent II), b) using a silica gel Davison 923 with a surface area of 700 m<sup>2</sup>/g (Adsorbent III). The rest of the preparation procedure remained the same.

Adsorbent II showed a lower performance than adsorbent I and only at pressures higher than atmospheric carbon dioxide was adsorbed at room temperature. Adsorbent III resulted a better scrubber for carbon dioxide and there was an enhancement of the adsorptive capacity to a maximum of 28.5 liters of wet CO<sub>2</sub> per Kg of adsorbent at a pressure of 60 psi (4 atm).

When these materials are exposed to water vapor after being saturated their surface with carbon dioxide, production of small amounts of a substance with odor evoking an aldehyde compound is noticed. MS analysis revealed the presence of 2-methyl benzaldehyde. On the other hand, meta-xylene was detected on the solid NMR analysis as a residue from the preparation procedure. Thus, a reaction as the one shown below (eq. 3) conceivably had occurred:



This reaction and its mechanism is under investigation.

In summary, we have prepared an adsorbent which can be used to remove carbon dioxide from natural gas at pressures higher than atmospheric pressure. This removal is selective and reversible, and carbon dioxide is released by heating the adsorbent at about 110°C using nitrogen or the same natural gas as carrier. Improvements on the capacity of the adsorbents could be done by changing the solid matrix.



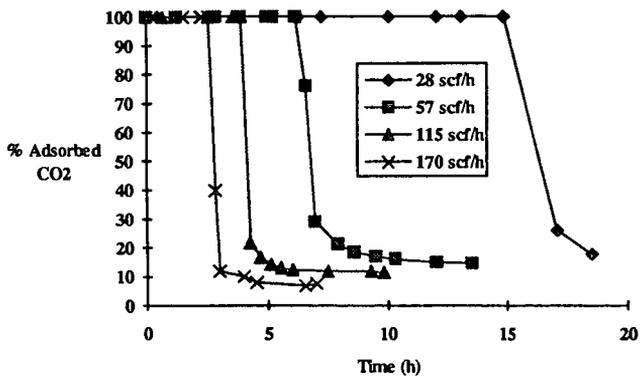


Fig. 2. Effect of space velocity on adsorption of CO<sub>2</sub> on adsorbent I from natural gas.

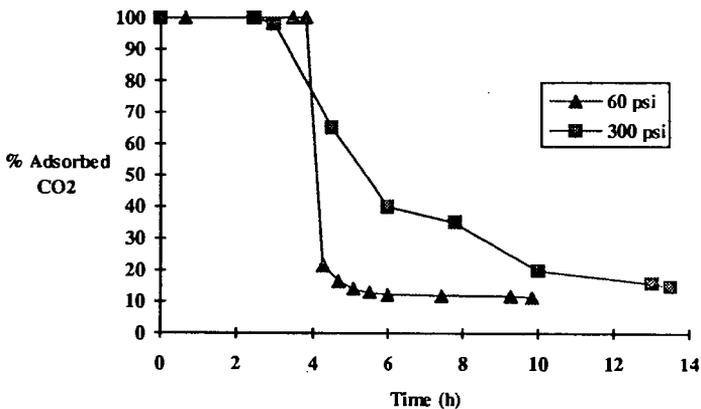


Fig. 3. Effect of pressure of operation on the removal of CO<sub>2</sub> on adsorbent I from natural gas.

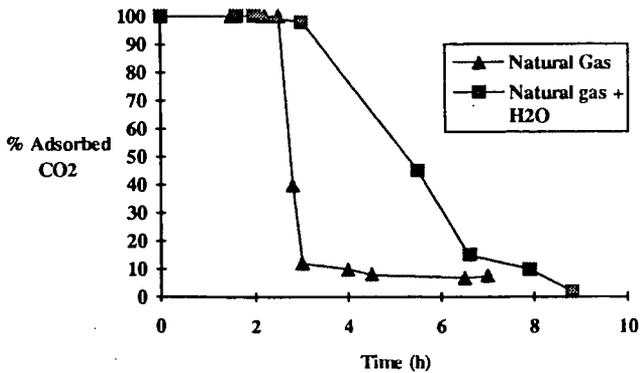


Fig. 4. Influence of water on the removal of CO<sub>2</sub> on adsorbent I from natural gas.