

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
4 October 2007 (04.10.2007)

PCT

(10) International Publication Number  
**WO 2007/111738 A2**

(51) International Patent Classification:  
*F25J 3/08* (2006.01)

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(21) International Application Number:  
PCT/US2006/062038

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(22) International Filing Date:  
13 December 2006 (13.12.2006)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
60/752,451 21 December 2005 (21.12.2005) US

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

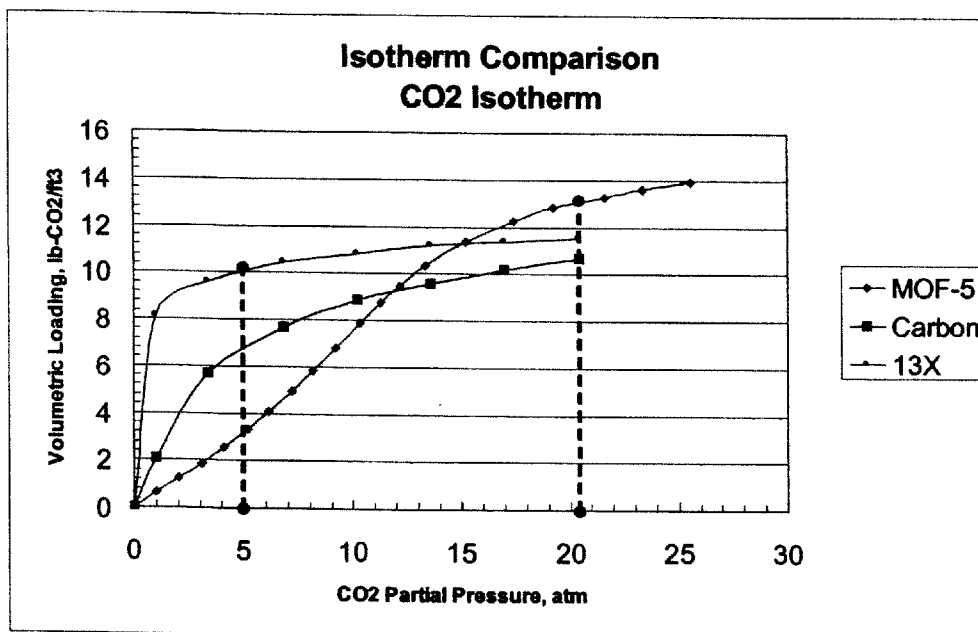
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(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT,

[Continued on next page]

(54) Title: THE USE OF MOFS IN PRESSURE SWING ADSORPTION



(57) Abstract: A pressure swing adsorption process using metal organic framework materials is presented for removal of carbon dioxide.



RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

**Published:**

— *without international search report and to be republished upon receipt of that report*

## THE USE OF MOFS IN PRESSURE SWING ADSORPTION

## BACKGROUND OF THE INVENTION

[0001] The present invention relates to adsorption processes, and more particularly to pressure swing adsorption processes. The process employs metal-organic framework materials having a high porosity and high surface areas, and are useful in the separation of carbon dioxide from hydrocarbon streams.

[0002] It is often necessary to separate one or more components from a gas mixture to generate a purified gas. This can be done for removing an impurity from a gas stream or for concentrating a component or components within a gas stream.

[0003] One technique for separation of one component in a gas from a mixture uses adsorption of one or more components from the mixture onto an adsorbent. This process is further enhanced through pressure swing adsorption (PSA). Pressure swing adsorption entails passing a feedstream over an adsorbent where one, or more, components of the feedstream are selectively adsorbed onto the adsorbent, and where the process of adsorption is performed at a relatively high pressure. The adsorbent is regenerated by reducing the pressure over the adsorbent, and a process of desorption is performed at the relatively low pressure. The desorption process can also be accompanied by the passing of a purge gas having a low concentration of the adsorbate to enhance desorption.

[0004] The separation of gases from a gas mixture through adsorption in a pressure swing adsorption process is controlled by the pressures used in the process and the capacity of the adsorbent for one, or more, of the components in the gas mixture. The process usually entails a tradeoff between the range in pressure, and the load capacity of the adsorbent for many of the materials used. It is desirable to be able to use materials that can overcome some of these tradeoffs.

## SUMMARY OF THE INVENTION

[0005] The invention is a pressure swing adsorption process for removing carbon dioxide from a hydrocarbon stream. The process passes the hydrocarbon stream over a metal organic framework material at a high adsorption pressure, generating an effluent stream with a reduced carbon dioxide content. The process then reduces the pressure over the metal organic

framework material and releases the carbon dioxide from the material, and generates a stream having carbon dioxide. The process steps are then repeated. In one embodiment, the process uses multiple adsorption beds comprising the metal organic framework material and cycles the pressures sequentially through the beds to produce a continuous process.

5 [0006] Additional objects, embodiments and details of this invention can be obtained from the following detailed description of the invention.

[0007] Figure 1 is the comparison of CO<sub>2</sub> adsorption on different materials;

[0008] Figure 2 is the comparison of CH<sub>4</sub> adsorption on carbon and MOF-5; and

[0009] Figure 3 is a comparison of CO<sub>2</sub> adsorption isotherms for a variety of MOFs and  
10 IRMOFs.

#### DETAILED DESCRIPTION OF THE INVENTION

[0010] The separation of gases from a gas mixture through adsorption in a pressure swing adsorption process is controlled by the difference between adsorption and desorption pressures and capacity of one of the components in the gas mixture. The process usually  
15 entails a tradeoff between the pressure differences and the capacity for many of the materials used. The capacity is the amount of material adsorbed by the adsorbent. It is desirable to be able to use materials that can overcome some of these tradeoffs.

[0011] In pressure swing adsorption, a gas made up of at least two constituents, is separated using the differences in selectivity of one of the constituents. Usually, the gas is  
20 purified by selectively removing an undesired constituent of the gas. The gas is typically fed into an adsorption unit at an elevated pressure, where one of the constituents is preferentially adsorbed onto an adsorbent. While one constituent is preferentially adsorbed, other constituents are also adsorbed, and it is desired to use adsorbents that have significant differences in the adsorption of the desired constituents.

25 [0012] The adsorbent is regenerated through reversing the adsorption process to desorb the constituents. This is done by changing the conditions of the adsorbent environment through reducing the pressure. At a defined time or conditions, the gas feed to the adsorption unit is stopped, and the adsorption unit is depressurized. Preferably, the gas feed is stopped when the adsorption unit is near or at capacity for the adsorbent with the desired constituent.

30 The adsorption unit is depressurized to a specified level where the adsorbed constituents

desorb generating a desorbent stream that is relatively rich in the constituent that is more strongly adsorbed onto the adsorbent. The desorption process can use an inert gas, or a non-hydrocarbon gas to facilitate the desorption process. The desorption gas is passed over the adsorbent to remove the adsorbed constituents as they desorb from the adsorbent. Preferably, the desorption gas is passed over the adsorbent in a direction opposite the direction of the feed gas to regenerate the adsorbent.

**[0013]** An aspect of a pressure swing adsorption system is the isotherm for adsorbing a component in a gas dictates the operating pressures and loading onto the adsorbent. Most materials have an isotherm, wherein the saturation limit is rapidly approached, and then there is a small incremental improvement in adsorption for a relatively large increase in pressure. The working capacity of an adsorbent is defined as difference in the amount of the adsorbed components on the adsorbent between the adsorption pressure and the desorption, or regeneration, pressure. Lowering the regeneration pressure can increase the capacity of the adsorbent for selectively removing a component from a gas, but the effluent stream from the regeneration step may need to be recompressed. However, a lower regeneration pressure increases the recompression costs.

**[0014]** In pressure swing adsorption, there are many classes of adsorbents that are suitable. The selection is dependent upon the feed gas constituents and other factors generally known to those skilled in the art. In general, suitable adsorbents include molecular sieves, silica gels, activated carbons, activated aluminas, and other porous metal oxides. When purifying methane containing streams, the methane is often adsorbed along with the impurities that one wishes to remove. The choice of adsorbent presents problems in selecting an adsorbent that has the greatest differential in adsorption between methane and selected impurities.

**[0015]** To overcome the tradeoffs and improve PSA, the search is for a high permeability material that also has a high capacity for use in a pressure swing adsorber. This means a material with a very high surface area and a high porosity as well as having a strong selectivity for carbon dioxide over methane. It is desired to increase the loading of the adsorbent, while minimizing recompression requirements. This translates to higher desorption pressures, or using an adsorbent that adsorbs carbon dioxide at a high pressure, and desorbs the carbon dioxide at an intermediate pressure.

**[0016]** One embodiment of the invention is a process using pressure swing adsorption for the removal of carbon dioxide from a hydrocarbon rich feedstream. The process comprises passing the hydrocarbon feedstream having carbon dioxide over an adsorbent in an adsorption zone, and at a temperature and pressure sufficient to adsorb a portion of the carbon dioxide.

5 The remaining gases in the feedstream become an effluent stream having a reduced carbon dioxide content. The adsorbent in the process is one of a series of materials known as metal organic framework (MOF) materials, and has a high surface area and high porosity. The surface area of the material is greater than 1500 m<sup>2</sup>/gm. The pressure in the adsorption zone is then reduced to a pressure for desorbing the carbon dioxide, and generates a desorption  
10 effluent stream having an enriched carbon dioxide content. The process during desorption can include passing a carbon dioxide lean purge gas over the adsorbent.

**[0017]** The process can be carried out by either passing the adsorbent bed through a high pressure adsorption zone, and then moving the adsorbent bed to a low pressure desorption zone, such as occurs with an adsorbent wheel in a rotating drum adsorber. The process can  
15 also be carried out by alternately pressurizing the adsorbent bed and passing the feedstream over the bed, and depressurizing the adsorbent bed and passing a purge gas over the bed.

**[0018]** These processes are improved and made continuous by using a sequence of at least two adsorbent beds, wherein the beds are cycled through the adsorption and desorption steps in a sequential manner to provide a continuous operation. The process of cycling the  
20 adsorbent beds comprises pressurizing a first adsorbent bed to an adsorption pressure and flowing the feedstream over the first adsorbent bed, while depressurizing a second adsorbent bed to a desorption pressure and flowing a purge stream over the second adsorbent bed. Switching the feedstream and the purge streams to the second adsorbent bed and first adsorbent bed respectively, and pressurizing the second adsorbent bed to the adsorption  
25 pressure and flowing the feedstream over the second adsorbent bed, while depressurizing the first adsorbent bed to the desorption pressure and flowing the purge stream over the first adsorbent bed. The process can be further smoothed with respect to pressure changes by additional beds, wherein intermediate beds are pressurized or depressurized before switching flows.

30 **[0019]** In the process for reducing carbon dioxide content in a methane feedstream, the feedstream is passed over the adsorbent, in a first adsorbent zone, at the highest pressure of

the process, with the carbon dioxide and some of the other constituents adsorbed, generating a carbon dioxide depleted methane stream. The carbon dioxide depleted methane discharges from the adsorption zone so that carbon dioxide adsorption fronts are formed in the zone at the methane feedstream inlet end and progressively move toward the outlet. Preferably, the adsorption zone is sized to produce a hydrocarbon gas product primarily comprising methane with a carbon dioxide concentration less than 1% by volume and preferably less than 0.1% by volume. The feedstream to the adsorbent unit is terminated when either the carbon dioxide adsorption front is at a predetermined point in the adsorption unit, or when there is an increase in the carbon dioxide in the CO<sub>2</sub> depleted methane stream to above a predetermined value. The feedstream is then terminated to the first adsorption zone, and directed to a second adsorption zone. The first adsorption zone is depressurized and a purge gas is passed through the first adsorption zone to regenerate the adsorbent in the first adsorption zone. The purge gas preferably flows in a counter current direction relative to the flow of the feedstream in the adsorption zones to remove the carbon dioxide in the reverse direction that it was adsorbed.

**[0020]** When the first zone has been regenerated, it is repressurized to the pressure level for the feedstream, the feedstream is switched to the first zone, and the second adsorption zone is depressurized and regenerated with a purge gas at regeneration conditions, and the process cycle is repeated.

**[0021]** The operating conditions for the pressure swing adsorption process include adsorption pressures from 2 MPa (20 atms.) to 5 MPa (50 atms.). The desorption pressure is in a range from 1 kPa (1 atm) to 1.5 MPa (15 atms.), with a preferred range from 500 kPa (5 atm) to 1 MPa (10 atms.). The desorption step is preferably operated at a pressure sufficient to minimize recompressing the desorption effluent stream. The adsorbent needs to be thermally stable for a range of temperatures, and operation is at temperatures between 0°C to 400°C.

**[0022]** New materials have been found to have good properties for adsorption separation. These materials are MOFs, or metal-organic framework materials. MOFs have very high surface areas per unit volumes, and have very high porosities. MOFs are a new generation of porous materials which have a crystalline structure comprising repeated units having a metal or metal oxide with a charge and organic units having a balancing counter charge. MOFs provide for pore sizes that can be controlled with the choice of organic structural unit, where

larger organic structural units can provide for larger pore sizes. The capacity and adsorption characteristics for a given gas is dependent on the materials in the MOF, as well as the size of the pores created. Structures and building units for MOFs can be found in US 2005/0192175 published on September 1, 2005 and PCT publication no. WO 2002/088148 published on  
5 November 7, 2002, both of which are incorporated by reference in their entireties.

**[0023]** The materials of use for this process include MOFs with a plurality of metal, metal oxide, metal cluster or metal oxide cluster building units, hereinafter referred to as metal building units, where the metal is selected from the transition metals in the periodic table, and beryllium. Preferred metals include zinc (Zn), cadmium (Cd), mercury (Hg), and beryllium  
10 (Be). The metal building units are linked by organic compounds to form a porous structure, where the organic compounds for linking the adjacent metal building units include 1,3,5-benzenetribenzoate (BTB); 1,4-benzenedicarboxylate (BDC); cyclobutyl 1,4-benzenedicarboxylate (CB BDC); 2-amino 1,4 benzenedicarboxylate (H<sub>2</sub>N BDC); tetrahydropyrene 2,7-dicarboxylate (HPDC); terphenyl dicarboxylate (TPDC); 2,6  
15 naphthalene dicarboxylate (2,6-NDC); pyrene 2,7-dicarboxylate (PDC); biphenyl dicarboxylate (BDC); or any dicarboxylate having phenyl compounds.

**[0024]** Specific materials that show improvement in adsorption properties have a three-dimensional extended porous structure and include: MOF-177, a material having a general formula of  $\text{Zn}_4\text{O}(\text{1,3,5-benzenetribenzoate})_2$ ; MOF-5, also known as IRMOF-1, a material  
20 having a general formula of  $\text{Zn}_4\text{O}(\text{1,4-benzenedicarboxylate})_3$ ; IRMOF-6, a material having a general formula of  $\text{Zn}_4\text{O}(\text{cyclobutyl 1,4-benzenedicarboxylate})$ ; IRMOF-3, a material having a general formula of  $\text{Zn}_4\text{O}(\text{2-amino 1,4 benzenedicarboxylate})_3$ ; and IRMOF-11, a material having a general formula of  $\text{Zn}_4\text{O}(\text{terphenyl dicarboxylate})_3$ , or  $\text{Zn}_4\text{O}(\text{tetrahydropyrene 2,7-dicarboxylate})_3$ ; and IRMOF-8, a material having a general formula of  $\text{Zn}_4\text{O}(\text{2,6 naphthalene dicarboxylate})_3$ .  
25

**[0025]** These materials have high capacities due to the high surface areas, and have favorable isotherms where the adsorbent releases a significant amount of the adsorbate, in this case carbon dioxide, at moderate pressures of around 5 atm. (0.5 MPa), as shown in Figure 3.



## EXAMPLE

[0026] The use of a metal organic framework material improves the characteristics of adsorption of carbon dioxide from a feedstream. As shown in Figure 1, the isotherms for carbon dioxide (CO<sub>2</sub>) adsorption is presented for a MOF, specifically MOF-5, and for two other adsorbents, 13X and activated carbon. The process was calculated based upon typical streams encountered in an Integrated Gasification Combined Cycle (IGCC). The calculations assume that the adsorption pressure is for a CO<sub>2</sub> partial pressure of 20 atm (2 MPa) and that the CO<sub>2</sub> removed from the feedstream will be recompressed. The adsorption isotherms are calculated as lbs of CO<sub>2</sub> per cubic foot of bed. For a desorption pressure of 5 atm (0.5 MPa), the capacities for 13X, activated carbon, and MOF-5 are 1.4, 3.5 and 9.8 lbs CO<sub>2</sub>/ft<sup>3</sup>, (or 22.4, 56.1 and 157 kg CO<sub>2</sub>/m<sup>3</sup>) respectively. This shows the MOF-5 is a superior adsorbent for carbon dioxide. The capacity can be increased by lowering the desorption pressure, and for activated carbon, with a desorption pressure at 1 atm, the capacity increases from 3.5 to 8.3 lbs CO<sub>2</sub>/ft<sup>3</sup> (133 kg CO<sub>2</sub>/m<sup>3</sup>). However, this comes at an expensive tradeoff in that recompression of the CO<sub>2</sub> from 1 atm to 20 atm would require 300% more horsepower when compared with compression from 5 atm to 20 atm.

[0027] When removing carbon dioxide from a methane rich stream, methane is also adsorbed onto the adsorbent. The methane is a co-adsorbate, and it is desirable to remove more carbon dioxide relative to the methane removed from the feedstream. The methane adsorption isotherm is shown in Figure 2 for MOF-5 and for activated carbon. The loadings for methane are 2.15 lbs-CH<sub>4</sub>/ft<sup>3</sup> and 1.05 lbs-CH<sub>4</sub>/ft<sup>3</sup> respectively. When comparing the loadings, the ratio of CO<sub>2</sub> to methane for MOF-5 is 4.56 and the ratio for activated carbon is 3.33. The MOF provides not only a greater loading, but a lower relative loss of methane from the methane stream for the same amount of carbon dioxide removed. This is an improvement in efficiency, and produces more of the product of natural gas by reducing methane losses.

[0028] A MOF-5 is a preferred material having zinc oxide cluster building units with the building units linked by a 1,4-benzenedicarboxylate organic compound. Another preferred material that is suitable for use in pressure swing adsorbers with high waste gas pressure include MOF-177, a material having zinc oxide cluster building units with the building units linked by a 1,3,5-benzenetribenzoate organic compound. Additional MOFs, as listed above, are also useful adsorbents for CO<sub>2</sub> removal.

[0029] One aspect of the invention is to have a material, or combination of materials, that changes the shape of the isotherm, such that the capacity-pressure curve does not taper off as pressure increases, but still retains significant capacity increases as the pressure is increased, as can be seen in Figures 1 and 2 with these materials for the normal pressure ranges for PSA.

5 [0030] While the invention has been described with what are presently considered the preferred embodiments, it is to be understood that the invention is not limited to the disclosed embodiments, but it is intended to cover various modifications and equivalent arrangements included within the scope of the appended claims.

## CLAIMS:

1. A pressure swing adsorption process for the removal of carbon dioxide from a hydrocarbon feedstream comprising:

(a) passing the feedstream comprising carbon dioxide and a hydrocarbon over an adsorbent, wherein the adsorbent comprises a metal organic framework (MOF) material, in an adsorption zone at a temperature and adsorption pressure sufficient to adsorb at least a portion of the carbon dioxide in the feedstream and thereby generating an effluent hydrocarbon stream having a reduced carbon dioxide content, continuing to pass the feedstream over the adsorbent for a time until the adsorbent has substantially reached its adsorption capacity;

(b) reducing the pressure in the adsorption zone to a desorption pressure and for time sufficient to desorb at least a portion of the carbon dioxide therefrom and withdrawing a desorption effluent stream having an enriched carbon dioxide content; and

repressurizing the adsorption zone to the adsorption pressure and repeating the steps (a) and (b).

2. The process of claim 1 further comprising passing a purge stream over the adsorbent during the desorbing step.

3. The process of claims 1 or 2 wherein the adsorption zone comprises a plurality of adsorbent beds comprising the adsorbent, and cycling the adsorbent beds through adsorption pressures, and desorption pressures in a sequential manner.

4. The process of claim 3 wherein the process of cycling the adsorbent beds comprises passing the adsorption beds through an adsorption zone and a desorption zone.

5. The process of claim 3 wherein the process of cycling the adsorbent beds comprises:

pressurizing a first bed to the adsorption pressure, while depressurizing a second bed to the desorption pressure;

switching flow streams from the first bed to the second bed, and from the second bed to the first bed; and

pressurizing the second bed to the adsorption pressure, while depressurizing the first bed to the desorption pressure.

6. The process of any of the claims 1-5 further comprising:

passing the effluent stream through a second adsorption zone at a temperature and pressure sufficient to adsorb at least a portion of the carbon dioxide in the effluent stream, wherein the adsorption zone has an adsorbent comprising a metal organic framework (MOF), and thereby generating a second effluent stream having a reduced carbon dioxide content; and

5       reducing the pressure in the adsorption zone to a desorption pressure sufficient to desorb at least a portion of the carbon dioxide therefrom and withdrawing a desorption effluent having an enriched carbon dioxide content.

7. The process of any of the claims 1-6 wherein the MOF material comprises a systematically formed metal-organic framework having a plurality of metal, metal oxide, metal cluster or  
10       metal oxide cluster building units, and an organic compound linking adjacent building units, wherein the linking compound comprises a linear dicarboxylate having at least one substituted phenyl group.

8. The process of any of the claims 1-7 wherein the MOFs are selected from the group consisting of MOF-5, a material having a general formula of  $Zn_4O(1,4$ -  
15       benzenedicarboxylate)<sub>3</sub>; IRMOF-6, a material having a general formula of  $Zn_4O(\text{cyclobutyl } 1,4\text{-benzenedicarboxylate})_3$ ; IRMOF-3, a material having a general formula of  $Zn_4O(2\text{-amino } 1,4 \text{ benzenedicarboxylate})_3$ ; and IRMOF-11, a material having a general formula of  $Zn_4O(\text{terphenyl dicarboxylate})_3$ , or  $Zn_4O(\text{tetrahydropyrene } 2,7\text{-dicarboxylate})_3$ ; IRMOF-8, a material having a general formula of  $Zn_4O(2,6 \text{ naphthalene dicarboxylate})_3$ ; MOF-177, a  
20       material having a general formula of  $Zn_4O(1,3,5\text{-benzenetribenzoate})_3$ , and mixtures thereof.

9. The process of any of the claims 1-8 wherein the temperature is operated from 0°C to 400°C, the adsorption pressure is from 2 MPa (20 atms.) to 5 MPa (50 atms.), and the desorption pressure is from 100 kPa (1 atm) to 1.5 MPa (15 atms.).

10. The process of any of the claims 1-9 further comprising recompressing the desorption  
25       effluent stream.

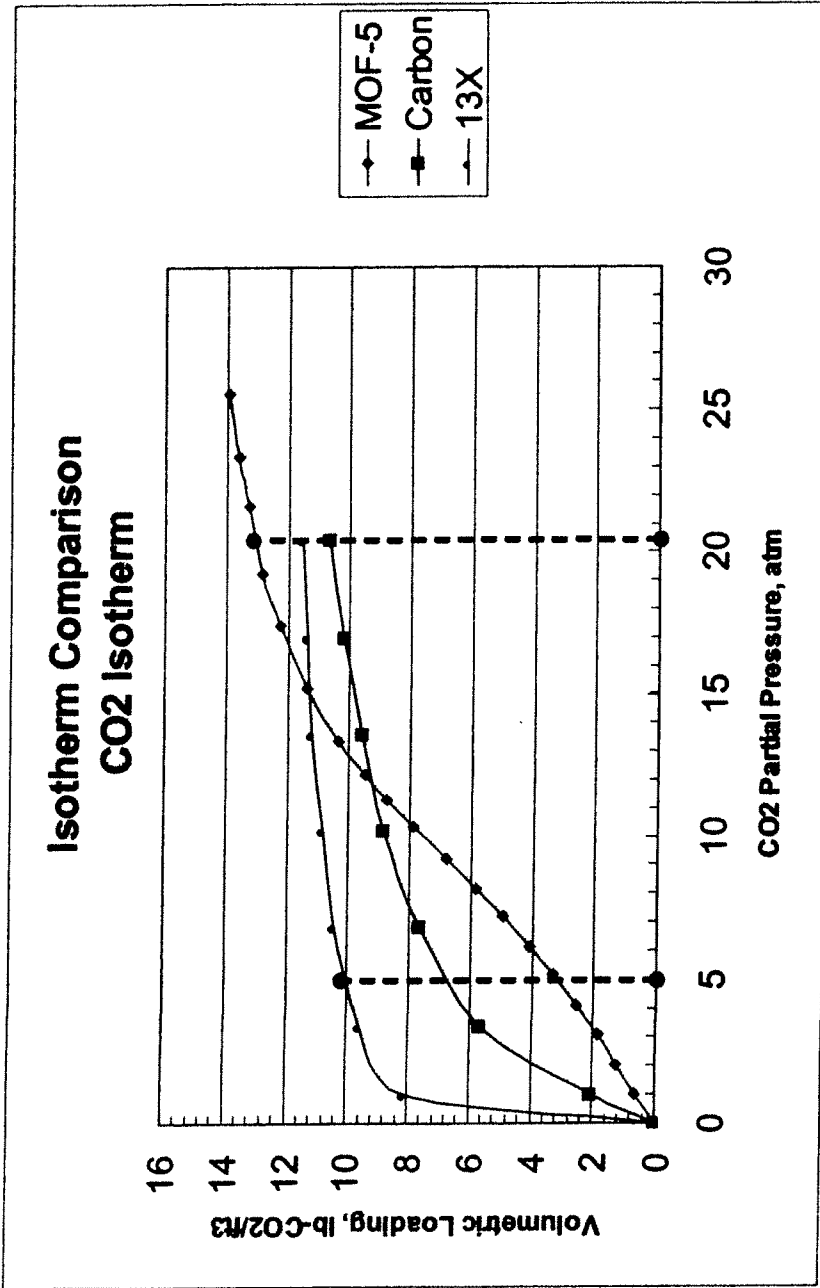


Figure 1

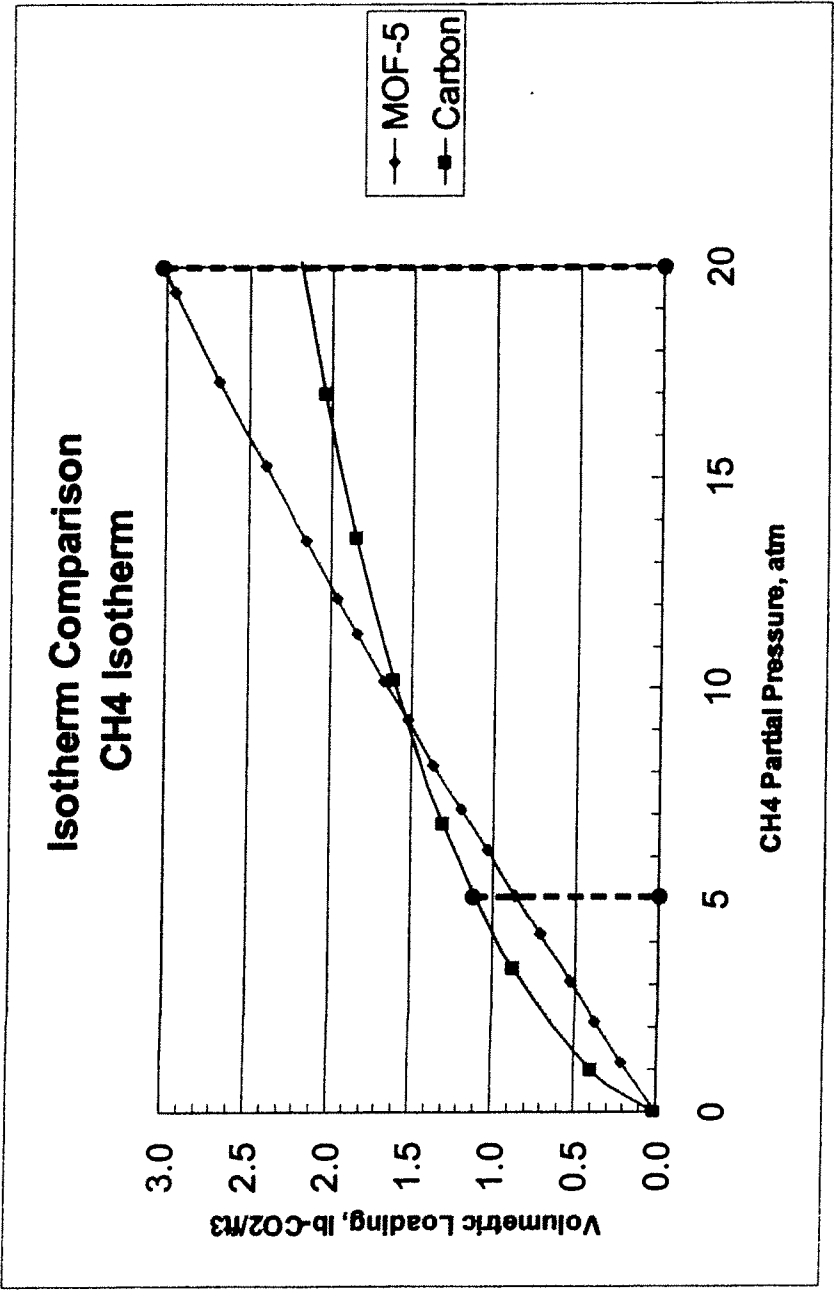


Figure 2

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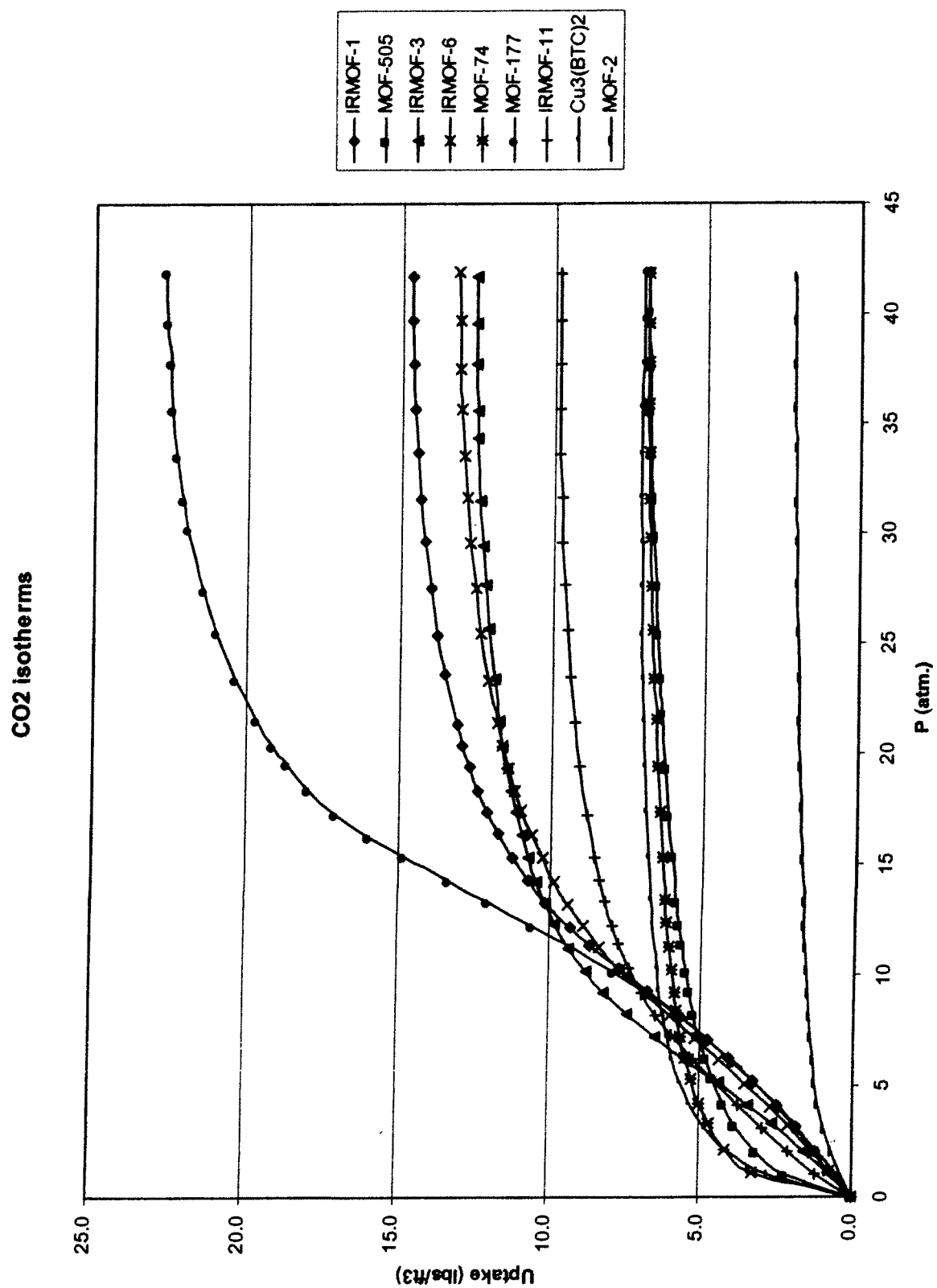


Figure 3