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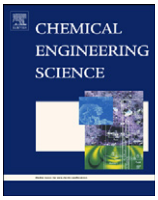

Extraction of ethane from natural gas at high pressure by adsorption on Na-ETS-10

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ABSTRACT

Methane/ethane separation was achieved using Na-ETS-10 as a packed-bed adsorbent over a pressure range of 450–5600 kPa at 298 K. At these pressures, pure methane gas raffinate streams were obtained prior to ethane breakthrough. The extract phase obtained following desorption from the packed-bed column was enriched in ethane. Extract phases containing up to 75% ethane were achieved following separations of a 93/7 methane/ethane feed mixture. Separation performance did not deteriorate as adsorption column pressures increased. Selective adsorption of a synthetic natural gas mixture using an Na-ETS-10 packed-bed column resulted in hydrocarbon outlet compositions ranging from pure methane (up to ~60 bed volumes at standard temperature and pressure) to ~93% methane, ~5% ethane and ~2% propane (~150 to ~850 bed volumes at standard temperature and pressure). In all cases, following desorption, the extract phase was highly enriched in the larger and more valuable hydrocarbons.

1. Introduction

Natural gas (NG) is one of the most important energy resources worldwide. Modern NG transport technologies ensure that large reserves of this high energy, clean burning fuel are available at a low overall cost. Since NG is a commodity, however, NG producers are constrained by the narrow operating margins between processing cost and market price.

NG must be conditioned before it is fed to pipelines for distribution; processing costs for treating NG are associated with both contaminant removal and liquid recovery (Tagliabue et al., 2009). Dehydration prevents corrosion, hydrate formation and freezing in the pipeline. Reducing the concentration of acid gases, including H_2S and CO_2, prevents corrosion and increases the NG energy content per unit volume. Removal of inert gases with no heating value (such as N_2) also increases energy density. Hydrocarbons heavier than methane, commonly known as natural gas liquids (NGL), can contribute to the energy content of NG, but heavier hydrocarbons generally have a higher product value when used as separate fuels or as chemical feedstocks, rather than as components of natural gas. For example, ethane (C2) is a key feedstock in industrial ethylene production (Ren et al., 2006) and, as such, efficient recovery of ethane (C2) from NGL can control operating costs for ethylene plants. In addition, heavy hydrocarbons (C3+) are commonly removed from NG to prevent fouling of downstream valves, pipes and other equipment.

NGL and C2 recoveries from NG, predominantly through cryogenic expansion, are both energy intensive processes (Pitman et al., 1998; Chebbi et al., 2010). A conventional cryogenic expansion process, also known as a turboexpander process, is outlined in Fig. 1. After pretreatment, the gas mixture is cooled by heat exchangers and partially condensed, followed by separation into liquid and vapour streams in a flash separator. The vapour stream, which contains the more volatile species, is expanded through a turboexpander into a distillation column (demethanizer), resulting in additional liquid condensation. The liquid stream is injected into the same column for recovery of the heavy hydrocarbon components. The bottom product, containing C2 and C3+ (NGL) species, can be further fractionated to produce feedstocks for polyethylene plants (C2) or incorporated into high heating value fuels such as Liquified Petroleum Gas (LPG). The top product of the demethanizer column (residue gas) must be recompressed from approximately 100–450 psi (700–3100 kPa) up to common pipeline pressures (800–1000 psi/5500–6800 kPa) in order to be delivered as sales gas.

Adsorptive separation based on cation-exchanged ETS-10-type adsorbents (Magnowski et al., 2011) has been proposed as a process that could decrease the energy consumption associated with ethane/methane separation and NGL recovery, reducing process costs and contributing to environmental sustainability. ETS-10 is a large-pored, mixed octahedral/tetrahedral titanium silicate with a framework composed of a three-dimensional

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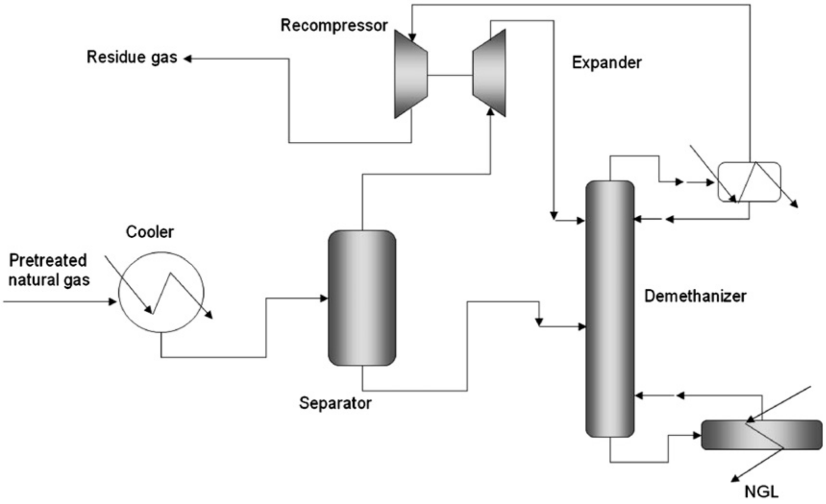

Fig. 1. Conventional NGL recovery process. Basic turboexpander process.

network of interconnecting channels and cavities (Kuznicki, 1991; Anderson et al., 1994), whose adsorption characteristics can be manipulated through cation exchange (Anson et al., 2008). When Na-ETS-10, Ba-ETS-10 and Ba/H-ETS-10 were applied to the separation of ethane from methane under low pressure conditions, Na-ETS-10 showed the most promising performance in terms of both adsorbent capacity and selectivity (Magnowski et al., 2011). It is important to note that, since the average kinetic diameter of molecules that can enter the pores of ETS-10 (8 Å) is much larger than either methane or ethane, this separation is likely achieved through equilibrium competitive adsorption (Kuznicki, 1991).

NG feedstocks for the NGL recovery process are generally high pressure streams, occasionally at pressures as high as 10^4 kPa. Hence, any potential adsorption process related to natural gas treatment should contemplate materials and engineering designs with efficient separation performance at higher pressures (Tagliabue et al., 2009). Working at high pressures would minimize the recompression work required before materials are introduced into the downstream pipeline. However, as is the case for previous studies of Na-ETS-10, adsorbent materials are generally evaluated at low pressures in the laboratory, far from the conditions found in natural gas pipelines. In fact, some previous work which examined the ethane/methane selectivity with as-synthesized (non-cation-exchanged) ETS-10 showed that for a given temperature, the selectivity of ethane/methane separation decreases as the pressure is increased, as is typical for molecular sieve separations (Al-Baghli and Loughlin, 2005, 2006). These results are silent, however, to ETS-10 performance at pressures above 500 kPa (72.5 psi) and to the effects of cation exchange on ETS-10 performance.

The use of a packed-bed column with Na-ETS-10 pellets for treating the NG feedstock at high pressures could be a promising alternative to strip paraffinic hydrocarbons from NG by selective adsorption, if the adsorbent is able to support efficient separation at high pressures. Similarly, a packed-bed column with Na-ETS-10 pellets could be used to extract the 1–2% ethane commonly present in the residue gas from demethanizer units in order to supply feedstock for ethylene plants. In both cases, adsorption at high pressure would minimize recompression work and address the difficulties associated with the separation of ethane as an intermediate between methane and propane. High pressure adsorptive separation could provide clear advantages relative to energy intensification in natural gas treatment processes.

The objective of the current study was to evaluate Na-ETS-10 as an adsorbent material capable of separating C1/C2 and C1/NGL at conditions approximating natural gas pipeline pressures. Adsorption isotherms were measured for methane and ethane at high pressures and used to estimate the mixture adsorption equilibrium on Na-ETS-10 crystals as a function of pressure. The separation performance of Na-ETS-10 within packed-bed columns was analyzed based on the raffinate and extract streams produced from C1/C2 and C1/NGL feed mixtures at room temperature and high pressures (up to 5600 kPa).

2. Experimental

2.1. Material synthesis

Hydrothermal synthesis of ETS-10 was carried out as previously described (Kuznicki, 1991). A mixture of 50 g of sodium silicate (28.8% SiO_2, 9.14% Na_2O, Fisher), 3.2 g of sodium hydroxide (97% NaOH, Fisher), 3.8 g of KF (anhydrous, Fisher), 4 g of HCl (1 M, Fisher) and 16.3 g of $TiCl_3$ solution (Fisher) was stirred in a blender for 1 h. The mixture was then transferred to a Teflon-lined autoclave and reacted for 64 h at 488 K. The product was washed with deionized water and dried at 373 K. Following drying, ETS-10 was reduced to a fine powder (<150 μm; 100 mesh). Samples to be used for breakthrough analysis were pelletized by mixing 2.5 g of Ludox HS-40 colloidal silica (Aldrich) with 6 g of dried ETS-10, homogenizing with mortar and pestle, and compressing in a pellet press. The resulting discs were ground and sieved to 20–50 mesh (297–841 μm).

2.2. Adsorption isotherms

The ethane and methane adsorption isotherms on Na-ETS-10 at high pressures (0–1800 kPa) were measured at 298, 323 and 373 K with an HPVA-100 High Pressure Volumetric Analyzer adsorption unit from VTI instruments (Hialeah, FL) using a static volumetric method. Low pressure isotherms (up to 10 kPa) were obtained at 298 K with an Autosorb-1MP volumetric system from Quantachrome Instruments (Boynton Beach, FL). Na-ETS-10 materials in crystalline powder form (with no added binders or diluents) were dried at 523 K for 12 h under a vacuum of greater than 10^{-4} Torr prior to adsorption tests.