Energy Conversion and Management xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Energy Conversion and Management

journal homepage: www.elsevier.com/locate/enconman

Natural gas dehydration by molecular sieve in offshore plants: Impact of increasing carbon dioxide content

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ARTICLE INFO

Article history:
Received 9 December 2016
Received in revised form 28 February 2017
Accepted 2 March 2017
Available online xxxx

Keywords:
Natural gas
Dehydration
Adsorption
Temperature swing adsorption
Zeolite molecular sieve
Carbon dioxide

ABSTRACT

Dehydration is a critical operation in natural gas conditioning as it reduces the potential for corrosion, hydrate formation and freezing in process equipment and transportation pipelines. Water dew point adjustment is particularly challenging in the remote ultra-deepwater natural gas reserves of the Brazilian Pre-Salt fields due to their very high carbon dioxide contents – from 30% up to 90% in raw natural gas – which is a consequence from the carbonaceous rock of the reservoir structure and long term elevation of carbon dioxide content due to its injection for early enhanced oil recovery. Under this scenario, the study evaluates the impact of the carbon dioxide content of the natural gas on the performance of water dew point via water adsorption on 4 Å Zeolite molecular sieve beds. Process simulation with adsorption simulator Adsim (Aspen Technology, Inc), at varying operation pressures and carbon dioxide contents in raw natural gas, indicated that, although adsorption meets water removal specification in a condensation free operation, the high fugacity of carbon dioxide penalizes the dehydration performance due to probably two facts: (i) higher carbon dioxide fugacity in the humid natural gas imply higher saturation water content in the gas phase, which increases the service of dehydration units; and (ii) higher carbon dioxide fugacity in the humid natural gas establishes a discreet adsorption competition with water resulting in 6.5% increase of adsorbent bed volume for operating pressures of 35 bar or higher.

1. Introduction

Natural gas (NG) is the cleanest and the most hydrogen-rich among all fossil energy sources with high efficiencies for power generation [22]. A strong growth in NG electricity generation is expected, with a 2.5-fold increase in NG demand by 2050 [19]. Although the long-term (2050) role of NG electricity generation depends on the required level of reduction of carbon dioxide (CO_2) emissions, it is expected that the costs of carbon capture and storage decrease with time. This magnifies the potential of fossil fuels to play a more durable role in low-carbon grid, supporting NG as a "bridge fuel" for the electric sector [7].

The forecasted expansion on the NG demand is supported by the expansion of proved USA reserves of shale gas [7] and associated gas in deepwater oil-gas fields. The majority of ultra-deepwater oil and NG production occurs in four countries: Brazil, USA, Angola, and Norway, with USA and Brazil accounting for more than 90% of global ultra-deepwater (UDW) production, which is expected to increase in both countries [8]. In the UDW of the Brazilian Pre-Salt fields, extracting oil with associated gas at high gas-to-oil ratio (GOR) and high CO_2 contents is a technological barrier to surpass. Several challenges associated to Exploration & Production (E&P) in the Pre-Salt fields are inexorably connected with the extreme sea depth > 2000 m, the large volume of associated NG due to GOR > 500 Nm^3/m^3 oil, the NG logistics issues due the long distance from coast at high depth – also entailing flow assurance issues where Water Dew Point Adjustment (WDPA) is critical – and, last but not least, the technological gaps to be surpassed

Abbreviations: AASATI, Adsim Adsorption Simulator from Aspen Technology, Inc; AZ, active zone; BIP, binary interaction parameter; CAPEX, capital expenditures; CCS, Carbon Capture and Storage; CH_4, methane; CO_2, carbon dioxide; EOR, enhanced oil recovery; EOS, equation of state; E&P, Exploration & Production; FPSO, floating production storage & offloading; GOR, gas-oil ratio (Nm^3/m^3 oil); GRG, generalized reduced gradient optimization method; H_2O, water; H_2S, hydrogen sulphide; HC, hydrocarbon; HCDP, hydrocarbon dew point; HCDPA, hydrocarbon dew point adjustment; MS, molecular sieve; MTZ, mass transfer zone; NG, natural gas; NZ, non-utilized zone; PFD, process flowsheet diagram; PR, Peng-Robinson; PR-EOS, Peng-Robinson Equation of State; PSA, Pressure Swing Adsorption; TEG, triethylene glycol; TSA, Temperature Swing Adsorption; TSA-MS, Temperature Swing Adsorption with Molecular Sieves; VLE, vapor-liquid equilibrium; WDP, water dew point; WDPA, Water Dew Point Adjustment.

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http://dx.doi.org/10.1016/j.enconman.2017.03.005
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Nomenclature

D	bed diameter (m)	P_k	partial pressure of species k (bar)
IP	ADSIM isotherm parameter	T	temperature (K)
L	bed height (m)	$Tsat$	bed saturation time (h)
P	pressure (bar)	W_k	loading of species k (kmol/kg)

related to new cost-effective technologies for processing of huge flow rates of NG with extra high CO_2 content (79–90%) and its evident interconnections with the destination of immense inventories of CO_2 [11].

The UDW fields and the destination logistics of the huge CO_2 inventories separated from the raw NG, led Brazilian E&P to adopt early CO_2 Enhanced Oil Recovery (CO_2-EOR). It is worth noting that CO_2-EOR was traditionally used after a decline in reservoir pressure due to fluid extraction, typically after 35–45% of the original oil-in-place has been recovered [33]. Nowadays, CO_2-EOR is important because it aids to extract approximately 30–60% more oil from the reservoir [17]. Applying CO_2-EOR early in the life of UDW large fields improves economic viability (higher volumes of oil recovered) besides accelerating capacity of CO_2 storage [20]. In CO_2-EOR operation, more than 50% of injected CO_2 returns to the surface with the extracted oil and gas [17]. Consequently, CO_2 content in the associated NG increases continuously with time.

NG with high CO_2 content leads to significant water content in the gas phase after the gas-oil-water high pressure separators [2], requiring gas dehydration as a critical operation for WDPA in the NG conditioning process. Water removal is particularly important when CO_2 is present in the NG at high pressures [5]. Processing CO_2 rich NG requires WDPA[1] and hydrocarbon dew-point adjustment (HCDPA), besides removal of CO_2. This demands large gas plants on the topside of Floating Production, Storage and Offloading (FPSO), which hold weight and area limitations [26]. Furthermore, the offshore produced NG is transported by subsea pipelines under cold water, entailing high pressures and low temperatures, which under high water contents results in blockage by accumulation of gas hydrates [25], considered a relevant challenge in Brazilian Pre-Salt UDW [9]. Among the contaminants of NG, water is the most undesirable one. Besides provoking hydrate formation, water causes corrosion, pressure drop and losses in gas transmission efficiency [15]. Equally relevant is the risk of hydrates in CO_2-EOR transport systems [31], requiring also WDPA.

There are several methods for high capacity dehydration of high pressure NG. Glycol absorption of water and adsorption dehydration are the most employed [5]. NG dehydration using triethylene glycol (TEG) as dehumidifying agent is the conventional first option for WDPA [22], with TEG Coldfinger technology being recognized as one of the promising processing alternatives [28]. In a typical TEG unit, raw NG contacts lean TEG in countercurrent flow, so that dry NG leaves the contactor as top product. Water rich TEG is sent to a regeneration stripper, where lean TEG is recovered as bottom product, returning to the contactor after heat exchange with rich TEG feed. The main design variable for WDPA with TEG is the degree of TEG re-concentration, i.e. the TEG purity at the bottom of the regenerating stripper [2]. Deep WDPA demands high TEG purity, resulting in high reboiler temperature, potentially thermally degrading TEG [13].

The second option NG dehydration is adsorption dehydration with molecular sieves (MS). Adsorption dehydration is used when the WDPA target in dry NG is beyond the achievable WDPA via TEG [17]. In the context of adsorption dehydration, the required WDPA is only attainable by employing Temperature Swing Adsorption (TSA) and/or Pressure Swing Adsorption (PSA). These alternatives are essential when the NG is being processed or liquefied at low temperatures, with final WDP as low as −160 °C [23].

NG drying via TSA with zeolite MS, or TSA-MS, [23] is primarily utilized to meet deep WDPA not achievable with TEG systems. In spite of being more capital intensive than TEG systems, TSA-MS is low energy-intensive, becoming an attractive option in recent years [24]. A compromise lower cost solution, when processing stringent WDPA targets at high NG capacities, is to locate the costly TSA-MS units as a polishing step downstream of a TEG unit [1].

High pressure TSA-MS is widely used for high capacity NG dehydration services with 4 Å Zeolite [12]. The adsorption step is kept contacting raw NG until the MS is nearly water saturated, when thermal desorption is initiated for bed regeneration. Thus, TSA-MS cycles between two states, adsorption and desorption, each one with characteristic temperature [24]. At low temperature (T) adsorption is much more favored than desorption, while at high T desorption prevails (Fig. 1).

However, there are questions to be answered before the adoption of TSA-MS units in UDW FPSOs can be recommended. These questions are related to the large services of humid gas (high GOR) to dehydrate; the high water content boosted by high CO_2 content; and the constantly increasing high CO_2 content from early CO_2-EOR. Additionally, TSA-MS units have large sizes which have to face the reduced availability of topside area in view of the massive machinery for CO_2 and NG compression [4]. Moreover, the precise design of TSA-MS is a challenging task, particularly because several operating parameters that affect it are subjected to changes along the campaign like the long term changing NG composition by continuous CO_2-EOR and the consequent changes of NG variables such as water content, flow rate, temperature, pressure and bed residence time. These design issues can only be tackled by using appropriate simulators capable to handle TSA-MS with correct calibration in terms of adsorption isotherms and mass transfer.

This paper fills the literature gap on technical analysis of TSA-MS for large scale NG dehydration with high CO_2 contents

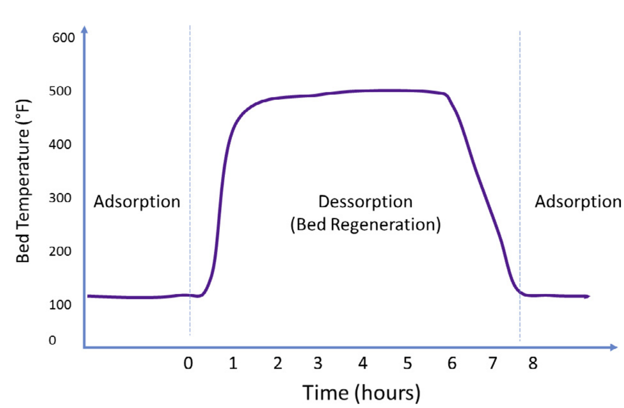

Fig. 1. Temperature swing adsorption in molecular sieve unit (TSA-MS): typical times and bed temperatures in adsorption-desorption cycles.

[1] The water dew-point (WDP) is defined as the temperature at which liquid water and gas phase water are in phase equilibrium at a given pressure. WDP is related to the pressure and water fraction in the gas [21].

Please cite this article in press as: Santos MGRS et al. Natural gas dehydration by molecular sieve in offshore plants: Impact of increasing carbon dioxide content. Energy Convers Manage (2017), http://dx.doi.org/10.1016/j.enconman.2017.03.005