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Cryogenic CO_2 Capture in Natural Gas

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Abstract

Increasing world energy demand and pricing trends have encouraged oil and gas companies to look at developing contaminated natural gas fields previously deemed uneconomic. At the same time, world wide perceptions on climate change are pressuring energy companies to adopt global best practices to reduce carbon emissions. Developing currently unviable contaminated natural gas fields requires developing new technologies for high CO_2 gas treatment. Current technologies available in the market for natural gas treating may not be ideally suitable for treating highly contaminated natural gas where CO_2 geo-sequestration is required. Use of physical and chemical absorption solvents have been the most popular method for treating natural gas with high CO_2, and to a lesser extent, membranes and adsorption methods. These technologies remove CO_2 at near ambient pressures thus requiring substantial amount of compression to levels needed for geo-sequestration. Cryogenic CO_2 removal methods can capture CO_2 in a liquid form thus making it relatively easy to pump underground for storage or send for enhanced oil recovery. This new cryogenic CO_2 removal method has been researched and tested in a demonstration plant and is soon to be implemented in commercial field applications. This paper intends to share recent field experience and test results from Cool Energy's CryoCell® demonstration plant in Western Australia. The CryoCell® process was developed by Cool Energy Ltd and tested in collaboration with other industrial partners including Shell Global Solutions. This presentation will also discuss and compare existing CO_2 treatment technologies for developing high CO_2 natural gas fields requiring CO_2 geo-sequestration with the CryoCell® CO_2 capture process. Basic economic comparisons between the CryoCell® process and an amine based process including CO_2 geo-sequestration will be presented.

Keywords: Carbon dioxide, Cryogenic, Capture, Natural Gas

1. Introduction

Natural gas consists of various impurities that must be removed prior to the gas being transported in pipelines to end users. Carbon dioxide is one of the main components of natural gas that must be removed to an acceptable level by the gas producer prior to export. Conventional CO_2 removal technologies remove CO_2 from natural gas at low pressure and release it to the atmosphere. This article looks at an alternative method, CryoCell® technology, for

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removing CO_2 from natural gas in a liquid form whereby it can be readily pumped to the required pressure for geological storage.

Chemical and physical solvent processes are the most widely used conventional CO_2 removal methods while membranes are also applicable in certain cases. Chemical solvents (eg: alkanolamines, alkaline salts) remove CO_2 via a chemical reaction at kinetically favored conditions. Physical solvents (eg: methanol) absorb by dissolving CO_2 in the liquid phase. Both solvent processes involve regeneration and circulation of solvents. Membranes on the other hand, rely on the relative permeation rate of CO_2 compared to the other components of natural gas. Detailed descriptions of these conventional CO_2 removal technologies and their relative merits and drawbacks are described in several open literature sources including the GPSA Data Book[1]. The CryoCell® technology uses a cryogenic process to remove CO_2 from the natural gas, while avoiding the shortcomings of the conventional acid gas treatment processes. The CryoCell® technology eliminates water consumption, usage of chemicals, and corrosion related issues. Physical scale up rates of solvent process is linear with feed gas CO_2 concentrations as they depend on solvent circulation rates. The CryoCell® process on the other hand, shows a non-linear scale up rate with feed gas CO_2 content.

2. Technology Description

Carbon dioxide, in its pure form, possesses unique and distinct thermodynamic properties compared to light hydrocarbons in natural gas. Conventional CO_2 separation technologies are based on exploiting one or more of those unique physical or chemical properties of CO_2. CryoCell® technology uses the distinctive solidification property of CO_2 as the basis of separation of CO_2 from the other light natural gas components.

Pure CO_2 has a sublimation point (at atmospheric pressure CO_2 does not exist as a liquid) of -78.5^o C compared to the melting point of –182^o C for methane, which is the major constituent of natural gas. A natural gas mixture consisting of light hydrocarbons and CO_2 will 'split' into vapour, liquid and solid phases when subjected to thermodynamic equilibrium at certain pressure and temperature conditions. The solid phase produced will be pure CO_2, while the liquid and vapour phases will consist of both CO_2 and hydrocarbons.

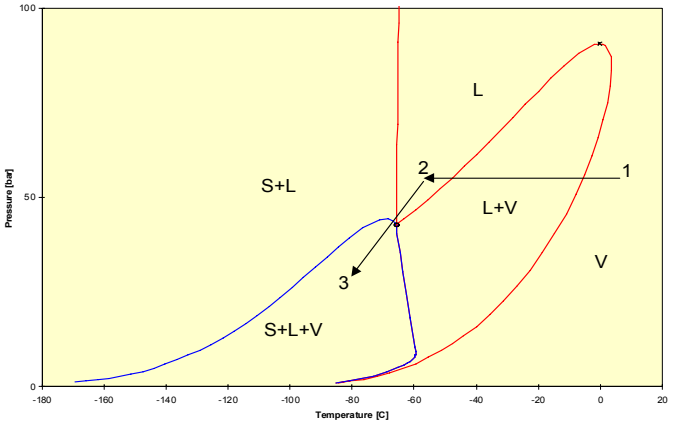

Figure 1 : Phase Envelope of a lean natural gas-CO_2 gas mixture

The above thermodynamic behaviour can be illustrated in a phase envelope of a gas mixture containing 50 mole % CO_2, 40 mole % Methane and the remainder light hydrocarbons (See Figure 1). The three phase regions (V-vapour, L-liquid, S-solid) are shown in the phase envelope, the red curves indicate equilibrium between two phases and the blue curves indicate equilibrium between three phases.

A typical thermodynamic operating path of the CryoCell® process is shown by the black arrows. The vapour mixture at intermediate pressure and ambient temperature (point '1') is cooled to a temperature just above the CO_2

freeze point whereby some or all of the stream condenses to a liquid phase (point '2'). The liquid is then flashed across a Joule-Thomson valve, creating an isenthalpic flash, such that the fluid is split into vapour, liquid and solid (point '3'). From a process point of view, the pre-cooling temperature (point '2') and the isenthalpic flash pressure (point '3') are selected such that the vapour phase CO_2 composition is minimal and the liquid phase methane composition is minimal. The physical separation of the light phase and the dense phases are achieved in a separator vessel, such that the vapour phase has sufficiently low CO_2 to be suitable for export while the dense phase is rich in CO_2 and can be sent for disposal. The solid CO_2 collected in the bottom of the vessel is melted, using an external heat source, such that it mixes with the liquid phase to be removed from the vessel. As the CryoCell® separator liquids are directed to disposal it is essential that the hydrocarbon concentration is minimal within the liquid CO_2 and as the CryoCell® separator vapour is directed to sales it is also critical to maintain the sales gas specifications for CO_2 content. Therefore the CryoCell® separator feed gas is pre-conditioned to have certain CO_2 and ethane plus composition specifications. These concentrations are obtained from extensive field trials and in-house thermodynamic models.

Based on the above operating principles several CryoCell® flow schemes were developed to treat a varying range of gas composition in feed streams. The process schemes were based on, (a) CO_2 content (high: >20 mole% or low: <20 mole%), (b) NGL content (lean or rich). Lean gas here is defined as streams where the recovery of natural gas liquids (NGLs) is considered uneconomical and rich gas is defined as streams where the recovery of NGLs is considered economical.

A process configuration for a low CO_2-lean gas is shown in Figure 2. The feed gas is initially dehydrated to low water specifications (5 ppm) to handle downstream cryogenic operations. The gas is then heat exchanged with treated gas and cold CO_2 prior to cooling to a temperature just above the CO_2 freeze point. The liquid is then expanded across a Joule-Thomson valve entering the CryoCell® separator as a three-phase mixture. The solid CO_2 collected in the bottom of the separator is melted by a heater and separated with the liquids. The gas is compressed to sales gas specifications and the liquid pumped to the required disposal pressure. This process configuration is considered as the base case design for the CryoCell® process and subsequent modifications are discussed below.

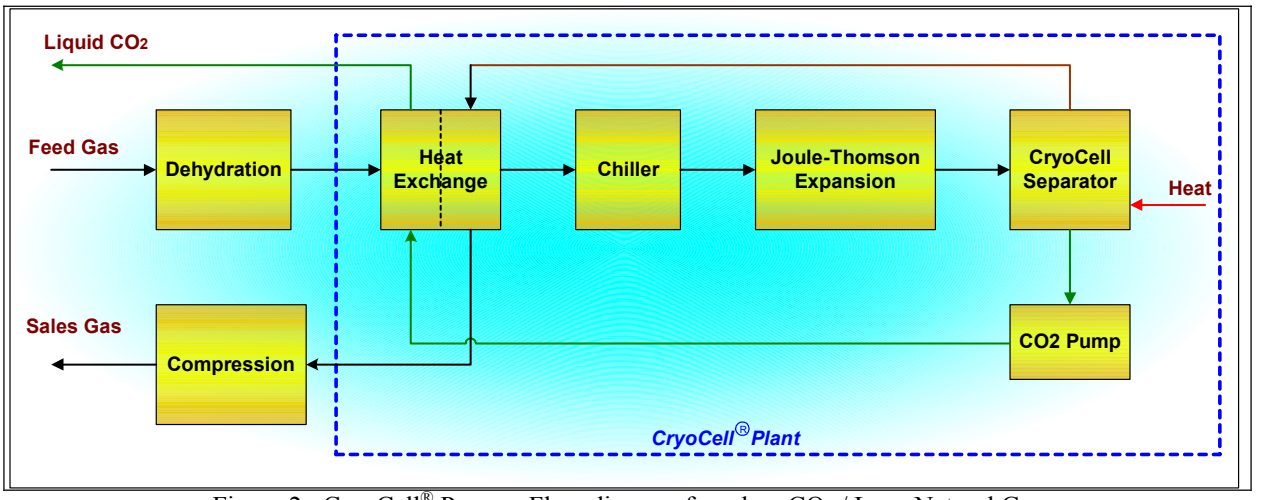

Figure 2 : CryoCell® Process Flow diagram for a low CO_2 / Lean Natural Gas

The process configuration for a low CO2-rich gas is shown in Figure 3. The base case process configuration is modified by adding a natural gas liquids (NGL) recovery column.

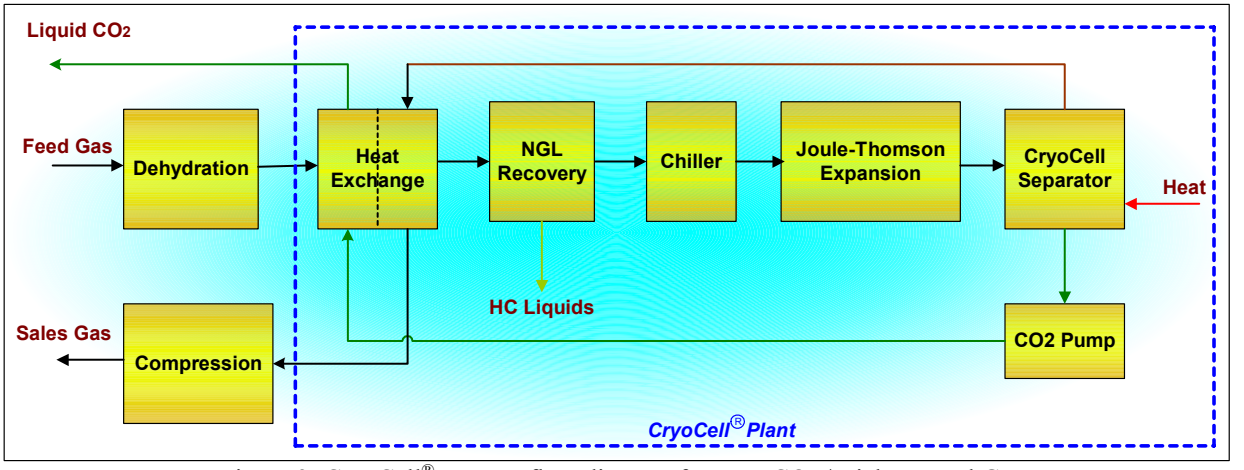

Figure 3: CryoCell® process flow diagram for Low CO_2 / Rich Natural Gas

The process configuration for a high CO_2 – lean gas is shown in Figure 4. The base case is modified to add a column for bulk CO_2 removal in the liquid form and the CryoCell® feed consists of around 20 mole % CO_2.

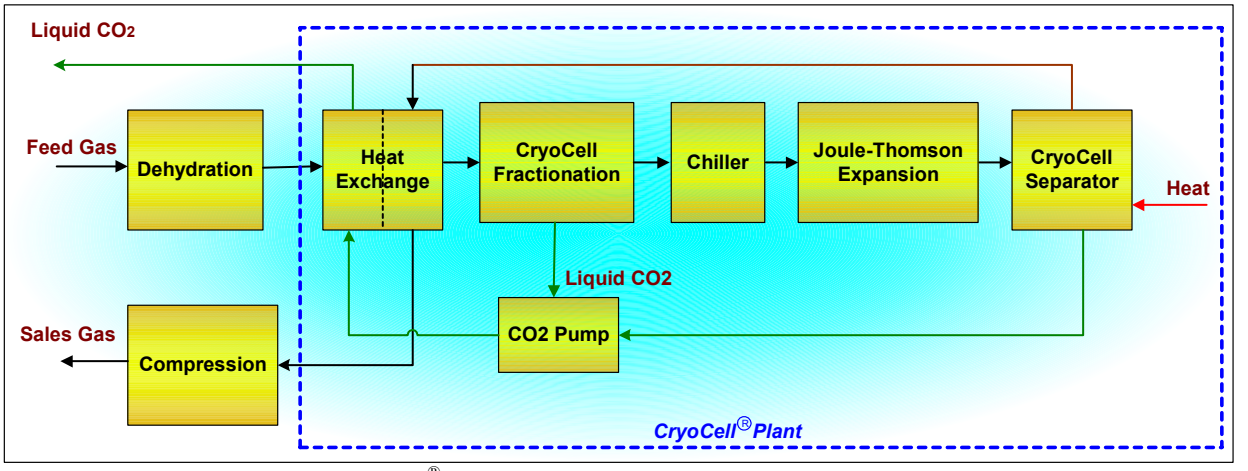

Figure 4: CryoCell® process flow diagram for high CO_2 / Lean Natural gas

An alternative configuration for high CO_2 – lean gas, combines two CryoCell® separators in series as shown in Figure 5. The CO_2 concentration in the feed gas is reduced to around 20 mole% in the first CryoCell® separator and recompressed prior to processing in the second CryoCell® separator.

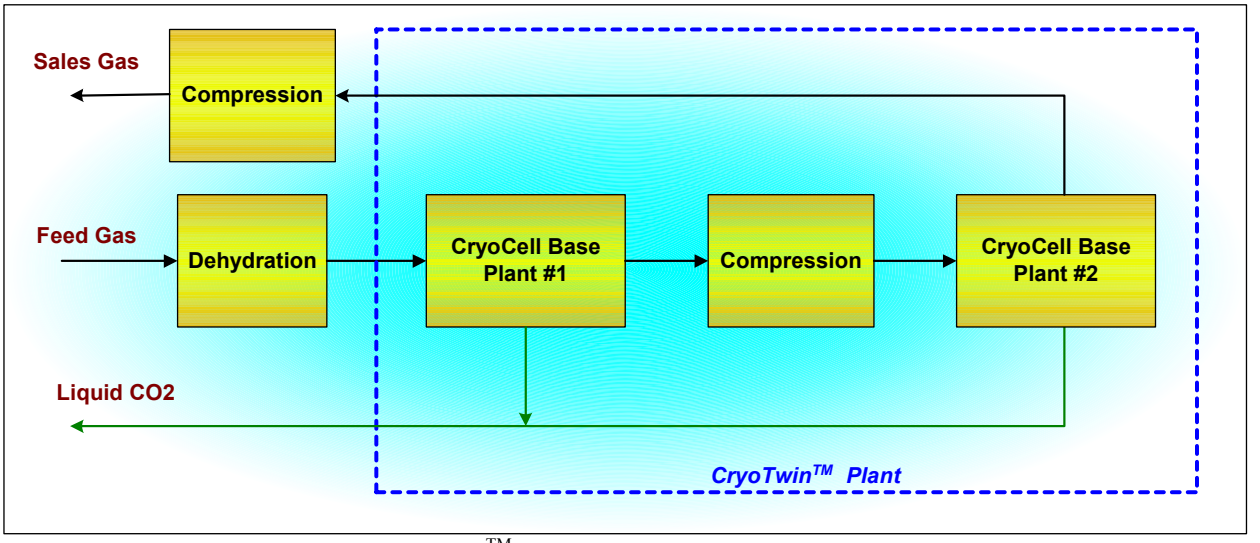

Figure 5 : CryoTwin™ process flow diagram for high CO_2 / Lean Gas

The process configuration for a high CO_2 – rich gas is shown in Figure 6. This process configuration has an added NGL recovery column along with the bulk CO_2 removal column.

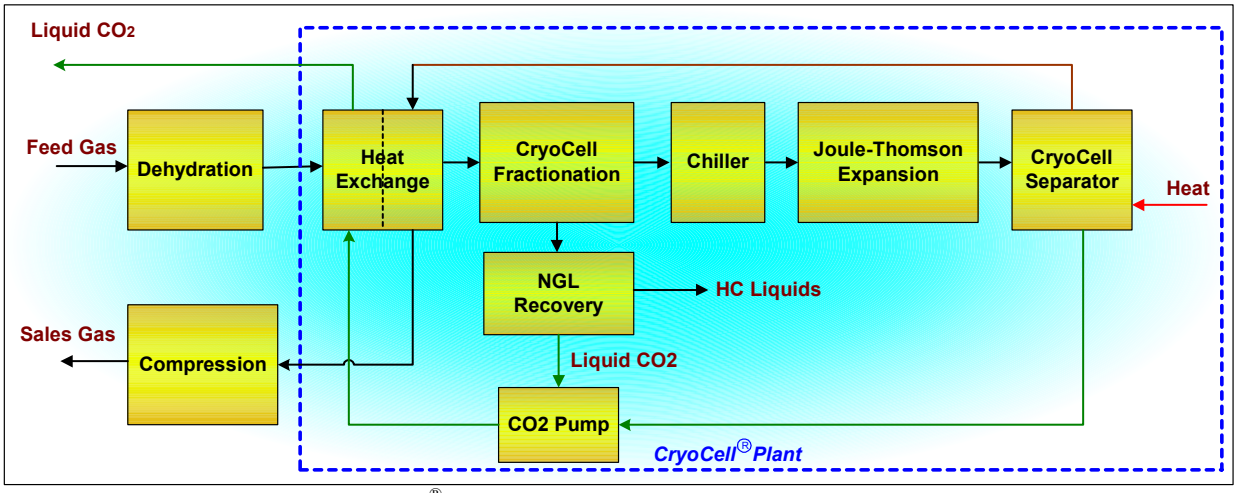

Figure 6: CryoCell® process flow diagram for high CO_2 / Rich Natural gas

Note that the block diagrams do not show all the heat integration steps and are intended only to identify the key steps of the CryoCell® process.

3. Process Modeling

The CryoCell® CO_2 separation process has been developed with a clear understanding of the vapour-liquid-solid thermodynamic equilibrium (VLSE) of the CO_2-light hydrocarbon system. State-of-the-art commercial process simulators (such as Aspen HYSYS®) are programmed to handle vapour-liquid equilibrium (VLE) and do not have VLSE flash calculation capabilities. Proprietary multiphase flash prediction software such as STFlash®, developed by Shell Research and Technology Centre, can be used for predicting solid CO_2 formation, post isenthalpic expansion temperatures and phase compositions for given CO_2 – natural gas mixtures at various conditions. Although STFlash® served as a critical tool in understanding the VLSE process – it is not a process simulator.

Therefore there was a need to be able to predict the three-phase isenthalpic expansion temperature and phase compositions within a two-phase process simulator. CryoFlash®, an in-house algorithm, was developed to meet this need by incorporating solid CO_2 properties into HYSYS® and using existing HYSYS® process components. The CryoFlash® algorithm was used to model and simulate the CryoCell® separator along with the bottom heater. The CryoFlash® predictions were compared with STFlash® predictions and found to show good agreement. The field trial data were also compared with CryoFlash® predictions, details of which are discussed below.

4. Field Trials

As part of commercializing the CryoCell® technology, a demonstration plant was designed and built by Cool Energy Ltd in the Perth basin, Western Australia. The demonstration plant design was based on the CryoCell® process flow scheme for low CO_2 – lean gas as shown in Figure 2, above. The 2 mmscf/d (million std. cubic feet per day) plant was built in ARC Energy's Xyris gas field near Dongara, 370 km north of Perth. A slip stream from the Xyris wellhead gas was taken as the feed source and processed in the demonstration plant and returned to be blended with ARC Energy treated gas prior to export. The lean gas has a composition of 3.5% CO_2, 92% C1 and 2% C2 as main components. The plant design allowed the CO_2 concentration in the feed gas to be artificially increased to desired test conditions by injecting liquid CO_2. The low CO_2 concentration of the Xyris gas (already meeting pipeline specification) allowed the trials to be conducted with various higher CO_2 concentrations and with minimal impact on ARC Energy gas sales. A schematic diagram of the Xyris test site along with ARC Energy operations are shown in Figure 7.

The demonstration plant features a sophisticated data acquisition, monitoring and control system to acquire and store process data from the field. A Siemen's state-of-the-art multi-channel gas chromatograph (Maxum II®) was used to analyse and report up to 12 process stream compositions in real time.

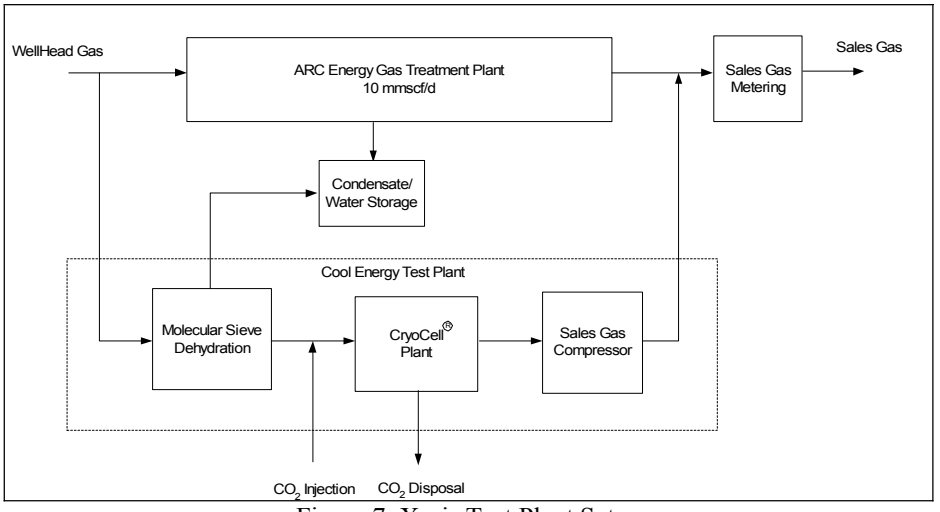

Figure 7: Xyris Test Plant Setup

The field trials were conducted between May 2006 and December 2007 by staff from Cool Energy in collaboration with ARC Energy operations at Xyris. Representatives from Shell Global Solutions were also present during some of the trials.

5. Field Results

The field results were obtained after establishing steady-state operating periods at each test condition. The most vital set of results were the CryoCell® vessel temperature and the treated gas vapour composition. The set of field results plotted in Figure 8 was obtained for various feed gas CO_2 compositions and pre-expansion temperatures at fixed

vessel pressure. From Figure 8 it can be seen that there is an excellent match between the CryoFlash® model predictions and the field data. Tests were also carried out with higher CO_2 where it was shown that CryoCell® technology can remove CO_2 from a natural gas containing 60 mole% down to 26 mole%, from 40 mole% to 14 mole%, from 21 mole% down to 4 mole% and from 13 mole% to 3 mole% at the selected three CryoCell® operating pressures.

The tests were carried out at inlet feed gas temperatures ranging from -50 °C to -65 °C at a feed gas pressure of 5500 to 6500 kPag, while the CryoCell® vessel heater was maintained between -50 °C to -60 °C during the tests. The feed gas flow rate was set at 600 to 1300 kg/hr, depending on the desired feed gas composition and resulting feed gas / injection CO_2 mixture.

A series of plant tests were also witnessed by Dr. D-Y. Peng, co-author of the Peng-Robinson equation of state[2] and the test results were independently assessed using rigorous thermodynamic calculations. The results from Dr. Peng's model predictions were also successfully matched with the CryoFlash® model predictions[3].

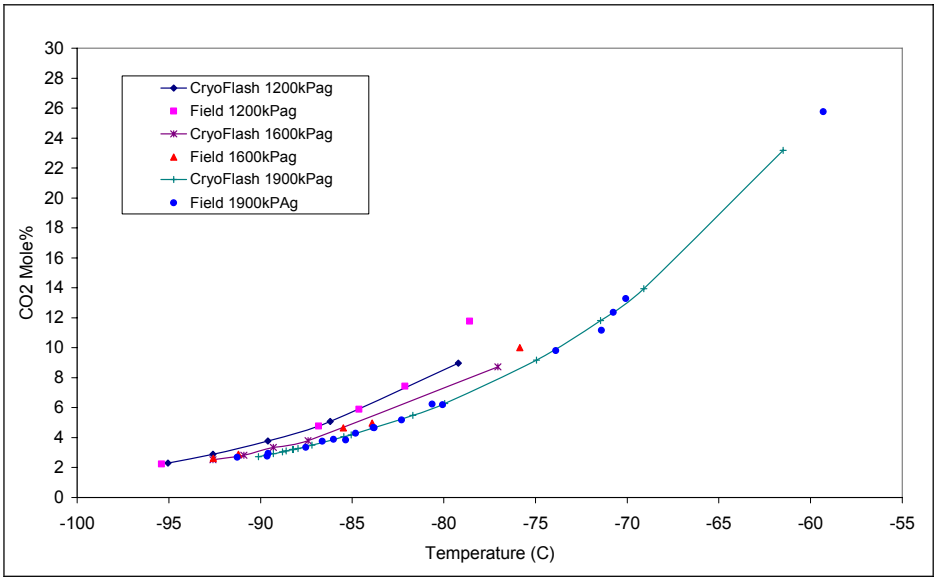

Figure 8: CryoCell® performance at various operating pressures

6. CryoCell® and Amine Plant Comparison

A comparison was carried out to benchmark the CryoCell® process against an amine based process for 50 mmscf/d, 20 mole% and 35 mole % CO_2 feed gas plants. A lean feed gas composition with negligible amount of H_2S and no exportable NGLs was used for this exercise as shown in Table 1. The feed gas was assumed to be water saturated at a plant inlet pressure of 80 barg and 40° C. The export gas was specified at 75 barg with a CO_2 content of maximum 3 mole %. It was assumed that CO_2 would be sent to geological storage at a pressure of 138 barg.

Composition	20 Mol%	35 Mole%
Carbon Dioxide	20.0	34.9
Methane	75.6	61.4
Ethane	2.1	1.7
Propane plus	2.4	2.0

Table 1: Plant feed gas compositions (water free basis)

Since the plant configurations and supporting utility requirements are distinctly different between the two processes, for completeness the comparison was conducted for a complete plant from inlet to outlet, including all utilities, and using consistent parameters for all comparisons.

The process models for the amine and CryoCell® plants were simulated using Aspen HYSYS®, as well as the Cool Energy's proprietary CryoFlash® model that was used for the CryoCell® plant designs. The simulation results for the four cases are summarized in Table 2 as plant performance data.

	Amine		CryoCell	
	20 Mole%	35 Mole%	20 Mole%	35 Mole%
Sales Gas Rate (MMscf/d)	37.7	27.8	38.2	29.6
Fuel Gas Rate (MMscf/d)	2.8	5.1	1.3	2.0
CO_2 for Storage (t/d)	460	859	460	859
Compression Power (MW)	1.9	3.8	4.3	7.0
Electrical Load (MW)	1.3	2.2	0.2	0.3
Process Heating (MW)	19	35	<0.1	<0.1
Hydrocarbon Efficiency* (%)	91	85	91	88

Table 2: Process Performance Comparison

* Hydrocarbon Efficiency = $\frac{\text{Heating Value of Feed Gas – Heating Value of Fuel and Losses}}{\text{Heating Value of Feed Gas}}$

The process results indicate that the CryoCell® plant and an Amine plant have similar hydrocarbon efficiencies for a 20 mole% case, where as the hydrocarbon efficiency for a CryoCell® plant improves with increasing CO_2 content. The CryoCell® process has higher compression power requirements while the Amine plants have higher electrical load and heating requirements.

Cost estimates for each process were prepared by sizing the major equipment items, then estimating the equipment cost using in-house unit cost data taken from third-party cost estimate studies. Major equipment costs for process and utilities were factored to estimate shop fabricated package prices, and the total equipment package price was factored to arrive at a total installed cost for the process plant. Allowances were added for engineering and project management costs, and other indirect costs such as license fees and initial solvent charge were also included. Although the accuracy of the cost estimates are expected to be ± 30%, the relative differences between estimates will be more accurate since the estimates are generated from consistent unit costs and factors based on equipment size.

The cost estimates are shown in Table 3 for the four cases. The estimates indicate a significant cost advantage for a CryoCell® based process for both the 20 mole% and 35 mole% cases. The major savings in a CryoCell® plant are clearly associated with the gas treatment, CO_2 disposal and plant utilities sections. Utility cost savings result from a significant reduction in electricity consumption by eliminating solvent pumping and by eliminating process heat requirement for amine reboiler duty. A portion of the CryoCell® savings is offset by the cost of sales gas compression and process refrigeration.

	Amine		CryoCell®	
	20 Mole%	**35 Mole%**	**20 Mole%**	**35 Mole%**
Plant Inlet	632	632	1,602	1,267
CO_2 Removal and Dehydration	22,585	41,711	14,004	22,064
CO_2 Disposal	14,207	22,831	1,044	1,508
Sales Gas Export	2,160	1,080	14,540	8,856
Refrigeration	0	0	3,974	15,577
Utilities	12,375	21,451	2,540	3,542
Total Direct Costs	51,959	87,705	37,705	52,816
Indirect Costs	12,400	21,072	11,172	14,648
Total Installed Plant Costs	**64,359**	**108,777**	**48,877**	**67,464**

Table 3 : CryoCell® and amine plant cost comparison (AUD thousands)

A qualitative comparison of the operating costs and complexity of the two processes indicates significant advantages for the CryoCell® process including:

- No process makeup water supply and treatment are required
- No process heating system required
- No chemicals are required by the process, hence no consumable costs
- Water is removed immediately downstream of the inlet separator so there is no corrosion potential and associated corrosion monitoring and mitigation costs
- No winterization requirements for cold climates
- No foaming potential

Some of the operating cost savings will be offset by higher rotating equipment maintenance costs for a CryoCell® plant.

7. Discussion and Conclusion

The CryoCell® CO_2 removal technology has been successfully demonstrated in a field trial, where the laboratory concepts of cryogenic CO_2 removal from high CO_2 natural gas using solid CO_2 formation have been effectively scaled up into a small field application. Several important insights relating to heat integration of the process, designing of the CryoCell® heater and level control in the CryoCell® vessel were gained during the plant trials.

The field trial data were used to verify and fine tune an in-house thermodynamic model (CryoFlash®) developed for simulating the CryoCell® process. The model has been subjected to a rigorous thermodynamic review by an independent expert.

The field test program has demonstrated the technical viability of solid phase CO_2 separation and cost comparison studies indicate improved economic viability for high CO_2 gas field developments. Using the tuned CryoFlash® models several field application studies have been carried out for potential customers from various part of the world with plant capacities ranging from 50 -200 mmscf/d of plant feed.

Cool Energy expects to undertake the first commercial application of this new technology in the near future and has recently completed the first phase of a Front End Engineering and Design (FEED) study for DrillSearch Energy Ltd for a 60 mmscf/d CryoCell® plant with geological storage of CO_2 in the Cooper Basin, in South Australia. The project partners have undertaken a drilling program and will arrive at a final investment decision after analysing the drilling results during the later part of the year.

In addition, multiple projects are in various stages of proposal for development of high CO_2 reserves in Indonesia, which has been identified as a major market due to the large number of underground high CO_2 discoveries.

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