

## PROCESSING OF CARBON DIOXIDE RICH GAS

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### Abstract

Efforts to commercialise high carbon dioxide content natural gas have traditionally been unsuccessful due to high processing costs. However, increased demand for natural gas can make development of marginal, high carbon dioxide content gas fields an attractive proposition despite the high carbon dioxide disposal costs, usually to underground storage, so as to avoid emissions to atmosphere.

In processing high carbon dioxide content natural gas, to ultimately inject the produced carbon dioxide into underground storage, having product carbon dioxide at high pressure and in the liquid phase is very important so as to reduce the power consumption for carbon dioxide pressure boosting, reduce machinery cost and reduce both overall investment cost and operating cost. Conventional process technologies for carbon dioxide removal, based on chemical or physical solvents and/or semi-permeable membranes, suffer in this regard due to the product carbon dioxide being gaseous and at low pressure. In contrast, low temperature fractionation offers important advantages in being able to upgrade natural gas whilst producing high purity carbon dioxide as a liquid at high pressure.

This paper reviews low temperature fractionation technologies for processing carbon dioxide rich natural gas. It then considers the merits of using the extracted carbon dioxide for enhanced oil recovery (EOR), to obtain revenues, and the processing of the carbon dioxide rich associated gas that arises from injected carbon dioxide ultimately ~~breaking through~~ with the associated gas. Processing this gas also requires extraction of NGL and handling of increasing carbon dioxide levels and the effect of these requirements on process technology selection is discussed. Finally, process technology developments are discussed that look to optimise the processing of associated gas from carbon dioxide EOR projects so as to minimise costs and increase project viability.

### Introduction

In much of the world the commercial production of natural gas is threatened by marginal economics. This is particularly true with raw gas containing a high concentration of contaminants that are expensive to remove. Even countries with significant gas reserves are turning to importing liquefied natural gas (LNG) with its attendant geopolitical concerns over certainty of supply and cost. Or even increasing their use of high carbon (but low cost) fossil fuels for power generation. So efficiently maximising the use of indigenous natural gas has to be a priority to ensure security of supply at reasonable cost to the consumer and to offset the use of high carbon producing fossil fuels that contribute to climate change.

Monetisation of high carbon dioxide content natural gas becomes increasingly viable with higher natural gas costs and, especially as far as gas processors are concerned, if technology developments can reduce gas processing cost. However, natural gas processing plants that produce very large quantities of carbon dioxide will have to consider disposal of the carbon dioxide to underground storage which inevitably requires high pressure dense phase carbon dioxide (typically at a pressure over 140 bar). Clearly such disposal adds significant cost. So can carbon dioxide rich natural gas be processed economically whilst sequestering the carbon dioxide? And if so what process technologies are appropriate?

### Process Technology Options

Several established process technologies, including chemical solvent, physical solvent and semi-permeable membranes, are used to upgrade high carbon dioxide content gas to meet natural gas sales specifications [1]. However, all have relatively high capital and operating costs that can prohibit commercial development, even if the produced carbon dioxide is only emitted to the atmosphere. Investment costs increase to the power of 0.6-0.7 with feed gas carbon dioxide level (and closer to 1.0 for semi-permeable membranes). Physical solvents are more appropriate than chemical solvents at high carbon dioxide partial pressure but suffer due to pick-up of heavier hydrocarbons in the solvent. This increases processing cost and causes loss of valuable natural gas liquids (NGL) revenues. Semi-permeable membranes can suffer from hydrocarbon condensation (and require expensive upstream processing), loss of NGLs and relatively frequent membrane change-out.

### Cryogenic Fractionation for High Pressure Carbon Dioxide

#### Benefits

In processing high carbon dioxide content natural gas to ultimately inject the produced carbon dioxide into underground storage, producing the carbon dioxide as liquid (and preferably at high pressure) minimises the cost to boost to injection pressure and is therefore critical in reducing overall power consumption, machinery cost, transportation cost and both overall investment cost and operating cost. The carbon dioxide also needs to be dry to avoid corrosion in the transportation pipeline. The very large volumes of carbon dioxide and the need for dry high pressure carbon dioxide product means that processes based on physical or chemical solvents and/or semi-permeable membranes are prohibitively expensive due to the sheer quantity of carbon dioxide to be extracted, compressed from low pressure and transported.

In contrast to the process technologies above, the efficiency and performance of cryogenic fractionation actually increases as feed gas carbon dioxide level increases. Low temperature

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processing has been reported as especially attractive for removing carbon dioxide from natural gas containing over 20 mol. % carbon dioxide [2]. Costain has developed cryogenic fractionation technology to remove carbon dioxide from hydrogen-rich synthesis gas on gasification based power plants and from oxyfuel fired flue gas and this technology uses similar principles as for natural gas processing.

The large difference in the boiling points of methane and carbon dioxide makes separation by distillation relatively easy. Fractionation products can usually be of high purity with high product recoveries. Fractionation also produces liquid carbon dioxide from the base of the demethaniser at a pressure of up to about 35 bar. This can be pumped to high pressure for storage and provides another compelling advantage over alternative technologies.

Clearly, if cryogenic processing was suitable for natural gas containing over 20 mol. % carbon dioxide thirty years ago it is suitable for even lower carbon dioxide content gas today when the costs of carbon dioxide disposal are considered. Cryogenic technology should thus be considered in any evaluation of process technologies, especially for sequestration of carbon dioxide.

There is nothing new in the use of low temperature fractionation to produce carbon dioxide. High purity carbon dioxide has been produced commercially by cryogenic fractionation of carbon dioxide rich gas streams for many years - such as from amine regenerator overheads. Mechanical refrigeration is needed to meet the overall heat balance to produce liquid carbon dioxide but operates at no lower than  $-40^{\circ}\text{C}$ . These plants employ well-proven, reliable and robust refrigeration systems and conventional equipment.

Low temperature fractionation of carbon dioxide rich natural gas avoids hydrocarbon losses into the carbon dioxide (that diminish the performance of other processes) and thereby maximises both sales gas production and carbon dioxide purity. The latter is important as sequestered carbon dioxide normally requires low contaminant levels.

### Benefits of Cryogenic Fractionation

- High Methane/Carbon Dioxide Relative Volatility
- High Product Recoveries
- High Carbon Dioxide Purity
- High Pressure Carbon Dioxide

### Sales Gas Purity

The one reservation with low temperature fractionation of carbon dioxide rich natural gas is that it cannot achieve typical sales gas specifications of about 4 mol. % carbon dioxide or less. This is because the operating pressure for fractionation must be lower than the critical pressure of the column overheads stream (at which relative volatilities are unity). For a high purity methane stream the operating pressure must be below the critical pressure of methane (46 bar a). In practice (to ensure the relative volatility of methane to carbon dioxide is well above unity and separation is viable) the demethaniser maximum operating pressure would be limited to about 36 bar a. However, the operating temperature in the upper part of the demethaniser would then be below  $-60^{\circ}\text{C}$  so carbon dioxide would freeze. To ensure demethaniser operating temperatures high enough to avoid carbon dioxide freezing the carbon dioxide content of the overhead methane rich stream must be no less than 15 mol. %, with 20 mol. % a pragmatic value for design purposes. At this overheads composition the critical pressure locus of the methane-carbon dioxide binary is well above 46 bar a and the demethaniser can be operated at about 40 bar a whilst achieving high relative volatility.

### “Ryan Holmes” Cryogenic Fractionation

Carbon dioxide solidification in the cryogenic demethaniser and the inability to produce sales gas quality methane can be resolved by extractive distillation, by adding ethane and heavier hydrocarbons at the top of the column. This increases the solubility of carbon dioxide in the liquid phase, increases operating temperatures and raises the critical pressure locus so as to increase relative volatility and make separation easier. As a result a sufficiently pure methane product, containing 4 mol. % carbon dioxide or less, can be obtained and no further sales gas processing is needed [3]. This technique was developed by Koch Process Systems and is named “Ryan Holmes” technology. The carbon dioxide rich demethaniser bottoms product is contaminated with hydrocarbon solvent so further fractionation is then needed to remove it. As a result the process can incur high refrigeration duties and high power consumption. Refrigeration may be needed at lower temperatures than propane can achieve (-40°C) unless solvent flows are increased [4], otherwise some carbon dioxide needs to be evaporated to avoid needing ethane or ethylene refrigerant. Solvent regeneration consumes a lot of heat.

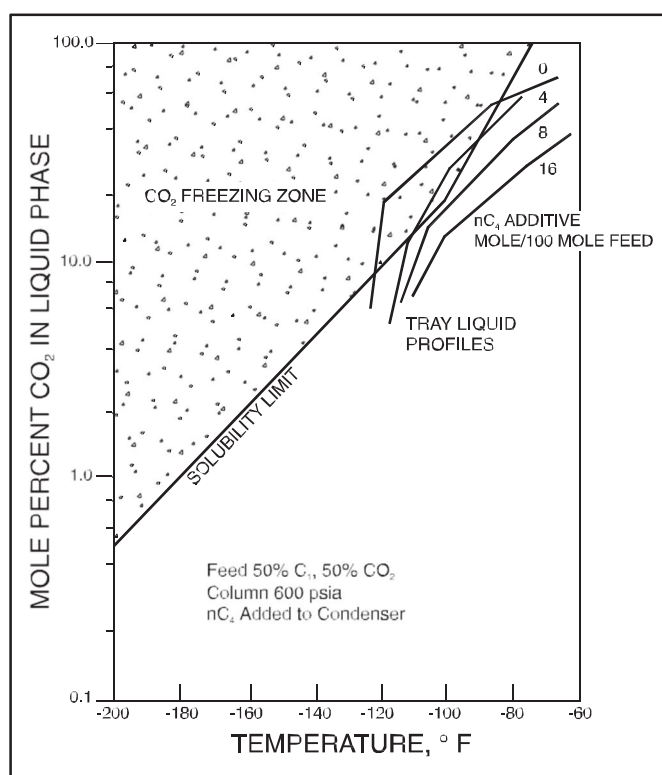
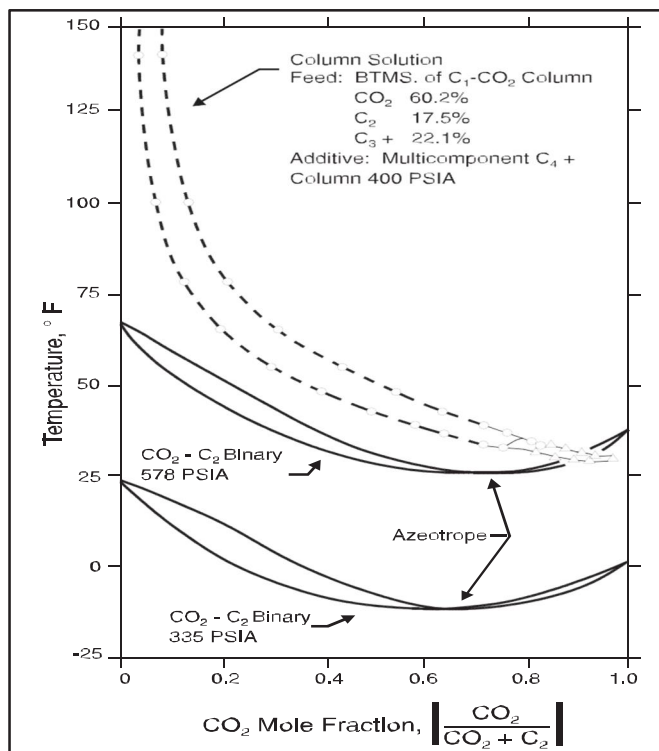


Figure 1 Distillation Profile C1/CO<sub>2</sub> Binary with nC<sub>4</sub> Additive [5, 6]

Ryan and Holmes also developed a technique for the distillation of carbon dioxide and ethane, which is limited by an azeotrope of about two thirds carbon dioxide and one third ethane at essentially any pressure (so carbon dioxide is the more volatile for carbon dioxide to ethane ratios of up to about two) as shown in Figure 2. To obtain pure carbon dioxide and pure ethane requires the addition of butane or heavier hydrocarbon which reverses the volatility so that carbon dioxide is the more volatile for all compositions [7].

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**Figure 2** Vapour . Liquid Equilibrium CO<sub>2</sub> . C<sub>2</sub>H<sub>6</sub> [6]

Ryan Holmes technology has been used for approximately 12 plants in the US. A 170 MMscfd plant was operated by Amerada Hess at Seminole, Texas and 140 MMscfd and 110 MMscfd plants by Shell, Wasson, Denver [8]. After a spate of projects in the 1980s, depressed gas prices restricted the installation of new facilities.

### Other Cryogenic Fractionation Processes

Ross and Cuellar [9] discuss a cryogenic fractionation process at the Sandridge Energy owned Century Plant, Fort Stockton, Texas to process 65 mol. % carbon dioxide content feed gas. The overhead gas from the cryogenic demethaniser (21 mol. % carbon dioxide) is passed to a Selexol<sup>®</sup> physical solvent process for further carbon dioxide removal to meet sales gas specifications. The carbon dioxide level in the demethaniser overhead gas is dictated by approach to freezing conditions, as discussed above. Whilst the bulk removal of carbon dioxide by fractionation minimises the duty on the Selexol<sup>®</sup> process, the low pressure carbon dioxide from the Selexol<sup>®</sup> regeneration system requires significant recompression to boost it to storage pressure. This combination of two process technologies makes good use of the attributes of each but the production of low pressure carbon dioxide makes it unlikely to be optimal for many potential applications.

Cryogenic fractionation processes to remove carbon dioxide from natural gas by freezing and subsequent thawing have been proposed and are at various stages of technology development and demonstration. These are ExxonMobil CFZi<sup>®</sup>, CryoCell<sup>®</sup> and Sprex<sup>®</sup>. Of these CFZi<sup>®</sup> is by far the most advanced [10].

Controlled Freeze Zone<sup>®</sup>, CFZi<sup>®</sup> technology removes acid gas components by permitting them to freeze in a specially designed section of a fractionation column to then be melted and fractionated to

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strip light hydrocarbons so as to produce liquid carbon dioxide product at elevated pressure. The sweet natural gas product meets gas quality specifications.

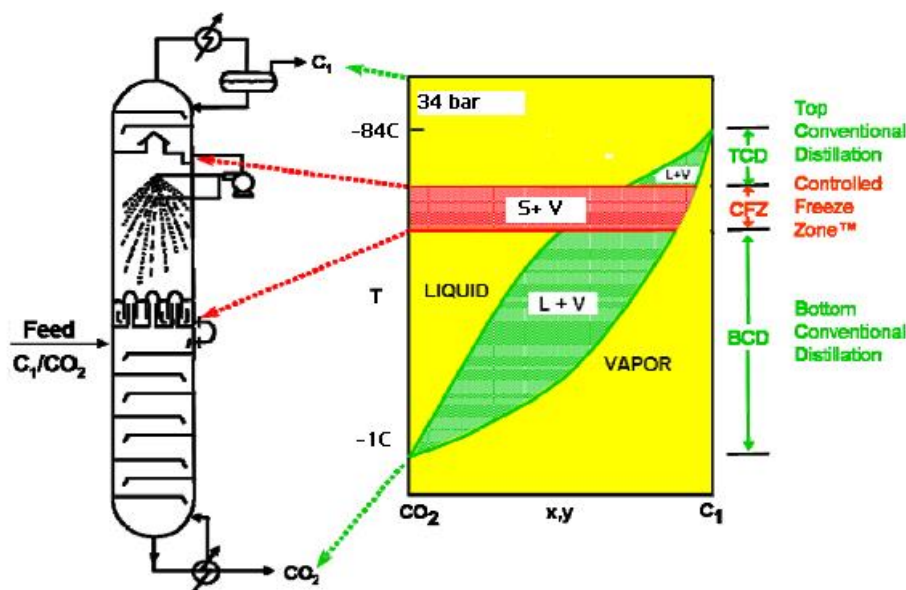


Figure 3 CFZi Principles of Operation [11]

CFZi was developed in the early 1980s and first demonstrated at a pilot plant in Clear Lake, near Houston in 1986. This facility could produce natural gas containing only 300 ppm of carbon dioxide and a carbon dioxide product containing only 0.5 mol. % methane. ExxonMobil has now completed a demonstration plant at its Shute Creek Treatment Facility in La Barge, Wyoming [10]. This was used during 2012 and 2013 to assess CFZi performance over a wide range of gas compositions to provide data to facilitate scale-up to fully commercial plant sizes (1 BSCFD).

ExxonMobil has identified capital cost, operating cost and efficiency improvements (for production of carbon dioxide at high pressure for storage) over both Ryan Holmes technology and cryogenic bulk fractionation with Selexoli though just as with these processes refrigeration requirements are high. CFZi can require more low level refrigeration (at below  $-40^{\circ}\text{C}$ ). CFZi is proposed as a good technology choice for processing raw gas containing as little as 8 mol. % carbon dioxide. As noted earlier this is not surprising and highlights how carbon dioxide sequestration has increased the commercial importance of cryogenic fractionation.

CFZi is not readily appropriate for feed gases of moderate to high ethane content. If not removed upstream then ethane will appear in the carbon dioxide bottoms stream and downstream separation may require breaking of the carbon dioxide and ethane azeotrope, depending on the level of propane plus components.

CryoCell® was developed by Cool Energy Ltd. and tested in a demonstration plant by Shell Global Solutions and others in Western Australia [12]. Feed gas is cooled and partially condensed at elevated pressure and the resulting liquid is let-down via a Joule-Thomson valve into a CryoCell® separator. This is then heated to melt the solid carbon dioxide and the resultant liquid is pumped away as product carbon dioxide. Field demonstrations showed that carbon dioxide content could be reduced from 60 mol. % to 26 mol. % and from 40 mol. % to 14 mol. % as limited by the vapour-liquid-solid equilibrium.

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Little recent information has been made available about CryoCell® to enable any technical assessment to be made against Ryan Holmes or CFZi .

A further cryogenic technology (which uses fractionation) is Sprex®CO<sub>2</sub> (Special pre-extraction method), owned by Total, IFP Energies Nouvelles and Prosernat and a development of hydrogen sulfide removal technology for over 40 mol. % carbon dioxide content feed gas. The fractionator uses a condenser at -30°C and produces all carbon dioxide as liquid. As discussed, such cryogenic fractionation systems are appropriate for the bulk removal of carbon dioxide but need further processing of the natural gas product to meet sales gas specifications. Sprex®CO<sub>2</sub> technology has been demonstrated in a pilot facility at Lacq, France but little recent information is available.

In conclusion, the similarities between established Ryan Holmes technology and emerging CFZi suggest both are candidates for processing carbon dioxide rich gas (of about 10 mol. % carbon dioxide or more). CFZi requires less processing steps and less equipment but until the technology is used and proven commercially there will be inevitable doubts over it due to the very unusual approach of removing a component from natural gas by freezing. Any cost savings with CFZi may be eroded for highly carbon dioxide rich feed gas and/or NGL rich feeds. At present there is insufficient knowledge and experience to effectively screen out one technology or the other without plant design and costing being performed on a case specific basis.

## Carbon Dioxide Assisted Enhanced Oil Recovery (EOR)

### Commercial Justification

The discussion to date has highlighted that cryogenic process technology can treat high carbon dioxide natural gas to produce pure carbon dioxide at high pressure for storage. But the most likely commercial use of the technology may be not for naturally occurring carbon dioxide rich gas but to process that arising from enhanced oil recovery (EOR).

Carbon dioxide has been used extensively in the US to increase recovery from depleted oil fields, based on the availability of naturally occurring carbon dioxide [13]. Carbon dioxide is miscible with the crude oil and increases production by lowering viscosity and swelling the oil to drive it from the reservoir, especially for light oil and/or shallow formations. Oil recovery can be increased to 70% of oil in place. Between 3 and 15 Mscf of carbon dioxide is required per barrel of recovered oil. The use of carbon dioxide captured from flue gas has also been practiced, notably at Weyburn, Canada where carbon dioxide produced from coal gasification at a power plant in North Dakota is used for EOR and carbon sequestration.

In the US, 300,000 barrels of oil per day (bopd) or about 6% of national oil production is currently obtained via injection of 68 million tonnes per year of carbon dioxide in 136 projects [14].

With high global oil prices being sustained, declining production from existing oil fields and difficulties in replacing oil reserves, carbon dioxide injection for EOR is projected to grow.

EOR via carbon dioxide injection is particularly appropriate for oil fields with low recovery rates which are located close to the source of carbon dioxide (to minimise carbon transportation costs) and where carbon dioxide emissions to atmosphere incur a significant cost penalty [15]. Joint work between ADNOC and Masdar to develop large scale carbon capture and storage (CCS) is targeting 70% oil recovery [16]. Studies in Kuwait have been promising [17]. It is expected that carbon dioxide injection will dominate EOR in the Middle East, maybe as soon as 2020.

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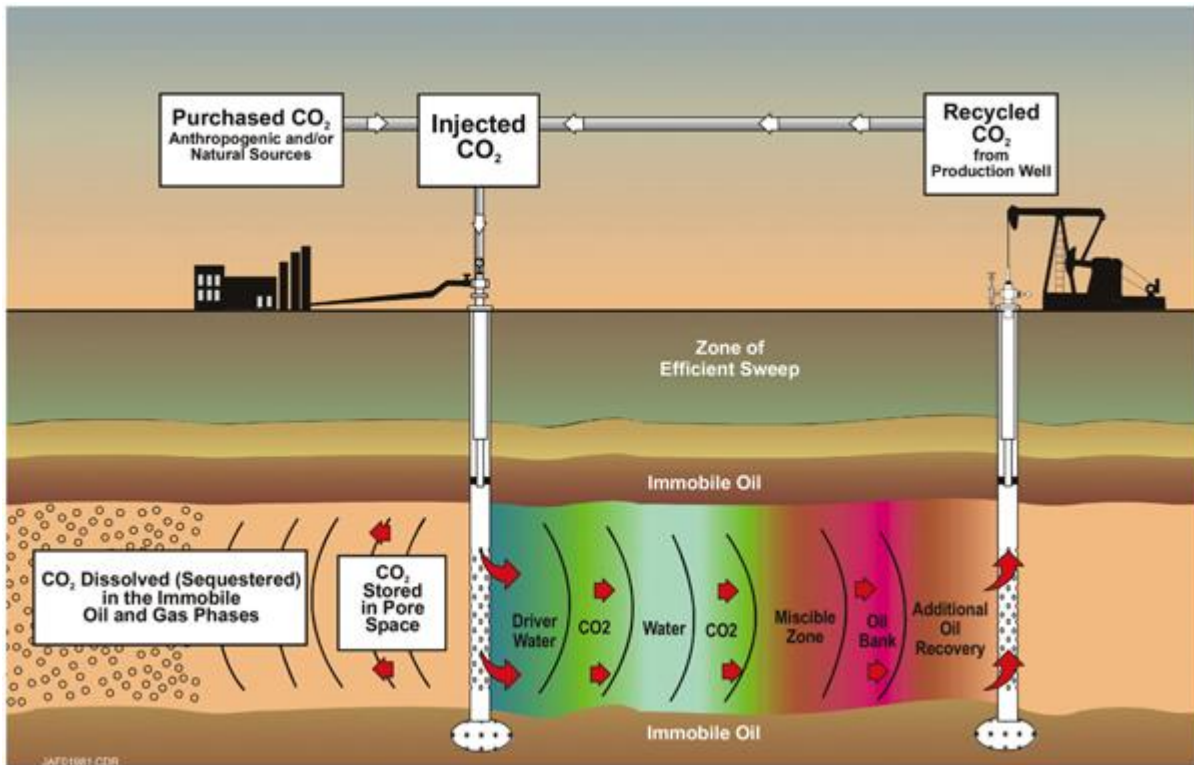


Figure 4 Carbon Dioxide EOR [18]

Initial evaluations (based on a nominal 5% additional recovery) indicate that carbon dioxide EOR in the North Sea could recover up to 3 billion barrels of oil. The potential to both increase oil revenues and reduce carbon dioxide emissions to atmosphere is naturally gaining attention.

### Cryogenic Fractionation for Carbon Dioxide EOR

The injected carbon dioxide ultimately breaks through with the produced oil and associated gas and it needs to be extracted, along with NGL, from the associated gas. Clearly the carbon dioxide is recycled back to the oil reservoir for EOR and sequestration so obtaining intermediate or high pressure carbon dioxide from the gas processing plant is important to reduce power consumption and cost. The justifications for low temperature fractionation that apply for high carbon dioxide content natural gas clearly apply to EOR processing too and should make it the technology of choice.

Low temperature fractionation requires that feed gas water content is reduced to about 1 ppmv by either molecular sieve technology or enhanced tri-ethylene glycol (TEG) such as Drizoï (licensed by Prosernat) to avoid freezing and blockage. However dehydration is required for any process technology producing carbon dioxide for sequestration as the carbon dioxide must be dry. Therefore one of the often raised arguments against cryogenic processing . dehydration cost . does not apply.

An EOR gas processing plant needs to process low pressure feed gas to give three primary products. The first is sales gas which meets natural gas transmission, hydrocarbon dewpoint and heating value specifications. The level of carbon dioxide thus needs to be less than about 4 mol. %, lower if nitrogen is present. The second product is carbon dioxide. Recycled carbon dioxide purity specifications are dictated by the need to exceed the minimum miscibility pressure (MMP) of the oilfield and they should also be within agreed transportation limits. A typical specification is 3 mol. % maximum of total



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nitrogen, methane and ethane as these components increase MMP [19]. Other light hydrocarbons decrease MMP. If hydrogen sulfide is present this will also require removal. Contaminants in the carbon dioxide can influence reservoir dynamics as well as phase behavior and should be minimised. Specifying the optimal contaminants level may require evaluation and techno-economic optimisation of the overall system. The third primary product is NGL.

In a typical EOR production profile [5, 20] the carbon dioxide content of the gas starts at only a few percent but can eventually reach 90 mol. % as the gas volume increases. The NGL content of the gas also increases with time as the lighter hydrocarbons are stripped from the oil.

### Suitability of Ryan Holmes Fractionation

As noted earlier, cryogenic fractionation is optimal for processing natural gas with very high levels of carbon dioxide and is the only technology worth considering for gas of 90 mol. % carbon dioxide, as encountered with EOR. It was noted earlier that Ryan Holmes technology, CFZi and bulk fractionation with downstream physical solvent are appropriate for high carbon dioxide content streams.

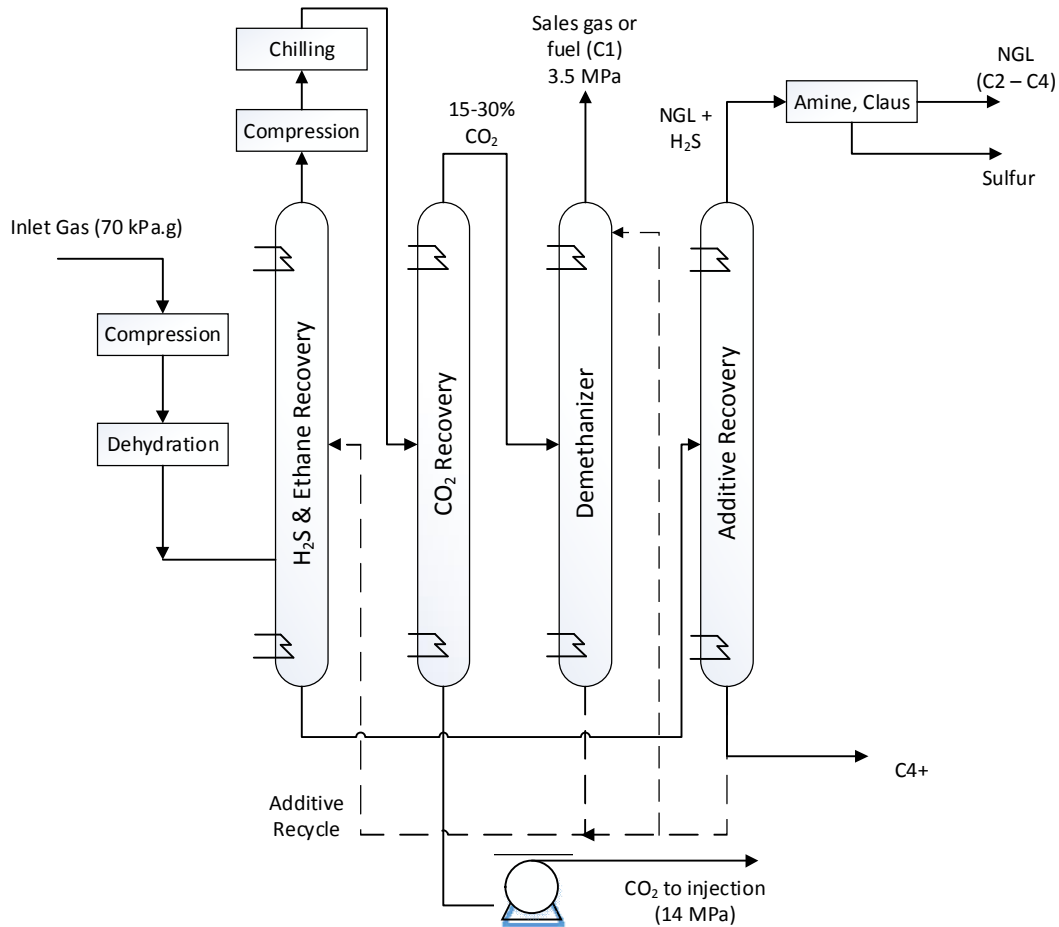
Amongst the cryogenic fractionation schemes for EOR, Ryan Holmes technology must be the leading candidate as the others are either not suitable or non-optimal for processing feed gas of significant NGL content. Ryan Holmes technology uses the NGL content of the feed gas as an inherent aspect of the carbon dioxide removal process and was originally developed and established to recover NGL from high carbon dioxide content gas [21].

#### Ryan Holmes vs. CFZi

- Proven Technology
- Handles NGL rich feed
- No Hydrogen Sulfide in CO<sub>2</sub>
- Conventional Equipment
- Similar Refrigeration Duties
- *But More Process Equipment & More Operating Variables*

The Ryan Holmes configuration considered most representative for EOR is shown as Figure 5 [5, 22] as used at Seminole, Texas. In a four column flowsheet NGL is removed (from carbon dioxide) in the first column as bottoms product. This separation is performed at a pressure of about 24 bar using -20°C propane refrigeration for the provision of reflux. Recycled butane or heavier solvent is added to overcome the carbon dioxide-ethane azeotrope so that ethane and heavier are removed as column bottoms with carbon dioxide leaving in the overheads. The ethane and heavier stream also contains all the hydrogen sulfide contained in the feed gas. This avoids contamination of the carbon dioxide destined for EOR injection and is an important differentiation from CFZi (in which hydrogen sulfide is present in the carbon dioxide product).

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**Figure 5** Four Column Ryan Holmes Process

The overheads stream is compressed to about 40 bar and further fractionated in a second column for bulk carbon dioxide removal. A bottoms stream of pure carbon dioxide is produced. The overheads stream is about 30 mol. % carbon dioxide, which is as low as feasible with -40°C propane refrigeration in the column condenser. The liquid carbon dioxide product is suitable for reinjection for EOR.

Ethane or ethylene refrigeration could optionally be used in the condenser. This increases the complexity of the refrigeration system but reduces the carbon dioxide level in the overheads to as low as is feasible (about 15 mol. %), minimises hydrocarbon solvent flow to the demethaniser, reduces recycle from the demethaniser to the first column and reduces refrigeration duty.

The overheads stream from bulk carbon dioxide removal is fractionated to produce low carbon dioxide content methane overheads by addition of hydrocarbon solvent to avoid solidification, as per Ryan Holmes. The hydrocarbon additive leaves in the bottoms product with carbon dioxide and is recycled to the first fractionation column for separation.

The bottoms stream from the first column is processed in the additive recovery column. The hydrocarbon solvent, typically butane, leaves this column as bottoms product (for recycle) with light hydrocarbons leaving as overheads.

### Robustness in Plant Design

The increase in both carbon dioxide content and paraffinic hydrocarbon content with time on EOR projects can be quite dramatic. This has to be considered carefully and catered for in process design and process system control. Early years, peak levels and later years operation all have to be assessed for equipment and plant design. For the majority of a plant's life it will be operating at very high carbon dioxide levels but needs to be flexible and robust for low carbon dioxide and NGL levels during early years. Declining feed gas pressure and declining gas flow need to be considered for later operation [8].

Clearly modern day process simulators can offer improved thermodynamic property prediction and quicker evaluation of multiple design alternatives than with early Ryan Holmes designs but the need for robustness to all reasonably feasible feed gas conditions means plants cannot be overly integrated in the way modern NGL extraction plants are (with extensive use of multistream heat exchangers for instance). The relative amounts of carbon dioxide and NGL components in the feed gas are uncertain. Energy integration would cause uncertainty as to how the plant would contend with a wide range of feed gas conditions, especially as in early years most feed gas will leave the processing plant as product gas whereas in later years the vast majority will leave as liquid carbon dioxide or NGL.

High carbon dioxide content feed gas leads to high energy consumption for both the reboiling of fractionation columns and for process refrigeration. Clearly this adds to capital cost. Process concepts and configurations to reduce energy consumption have been proposed including locating semi-permeable membranes upstream of Ryan Holmes fractionation. Semi-permeable membranes can effectively reduce the feed gas carbon dioxide content prior to cryogenic fractionation but do not provide liquid carbon dioxide at elevated pressure as needed for EOR.

## Process Technology Development

### Pure Carbon Dioxide Product

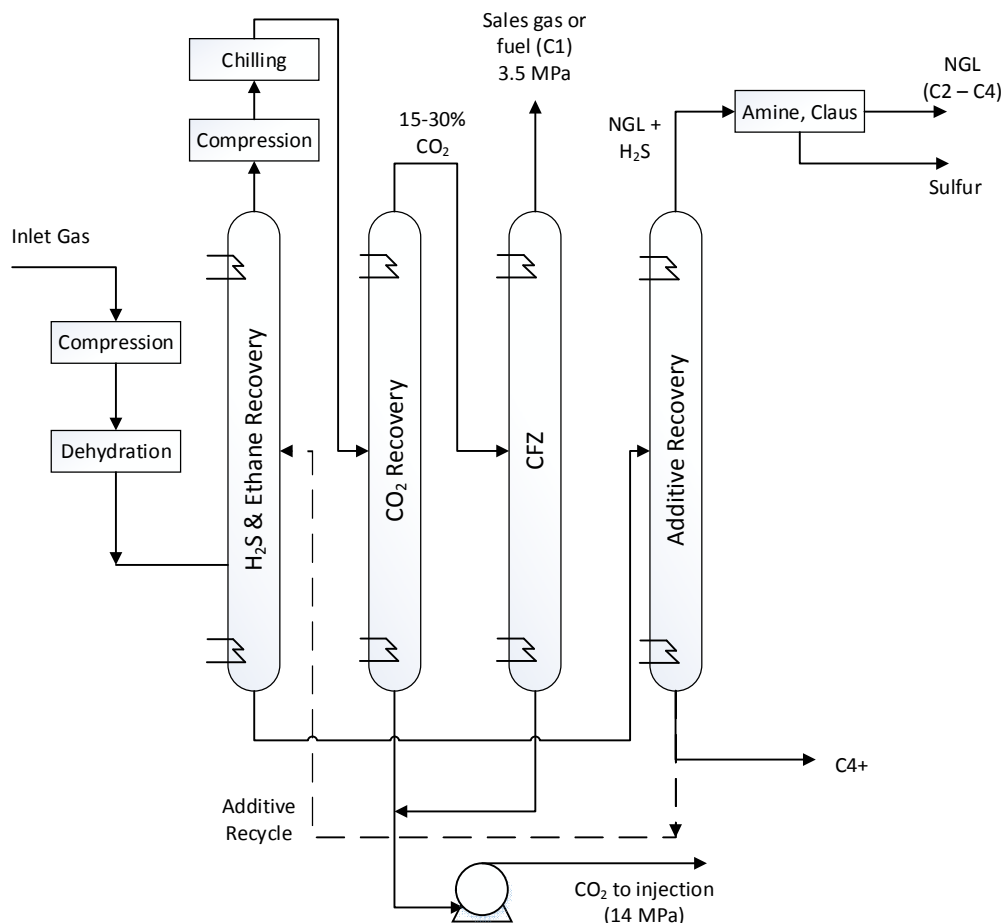
It will be apparent that reducing the high processing costs is very important in ensuring carbon dioxide EOR projects can be commercially viable.

Ryan Holmes technology has been discussed with a focus on the demethaniser operation. The upstream ethane recovery column uses Ryan Holmes technology to break the carbon dioxide and ethane azeotrope prior to bulk carbon dioxide removal to provide demethaniser feed. This process system could just as well produce feed to a CFZi column instead of the Ryan Holmes demethaniser. This would avoid carbon dioxide recycle (and thus the need for its separation) as shown in Figure 6.

In this event the CFZi column is fed by a methane-carbon dioxide stream of about 30 mol. % carbon dioxide as noted earlier. The CFZi column produces a sales gas quality methane overheads product and pure liquid carbon dioxide as bottoms product. Unlike the Ryan Holmes demethaniser which requires hydrocarbon solvent to avoid solidification (and therefore produces a bottoms stream containing hydrocarbon solvent) the CFZi bottoms can be blended with the pure carbon dioxide leaving the upstream bulk carbon dioxide recovery column to be pumped to EOR injection pressure.

Just as with the Ryan Holmes flowsheet (Figure 5), the bottoms from the ethane recovery column are sent to the additive recovery column for separation into NGL as overheads and butane and heavier as bottoms. Hydrogen sulfide leaves in the overhead for further processing, typically in an amine solvent process followed by a Claus plant to produce elemental sulfur.

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**Figure 6** Three Column Ryan Holmes Integrated with CFZi

The only recycle flow is the hydrocarbon solvent for breaking of the carbon-dioxide and ethane azeotrope in the first column. The hydrocarbon and carbon dioxide recycle from the Ryan Holmes demethaniser is completely avoided.

This combined Ryan Holmes and CFZi configuration could potentially provide considerable savings in refrigeration, power consumption, machinery cost and equipment cost and therefore substantially lower gas processing costs.

### Propane Recovery

The process configuration could be simplified if ethane can be tolerated in the product carbon dioxide. This may not be ideal in the context of the minimum miscibility pressure discussed earlier but unless ethane product is specifically required for downstream use, typically for ethylene production, it would reduce overall capital cost.

The first column removes a moderate level of propane and does not require Ryan Holmes distillation to break the carbon dioxide and ethane azeotrope as ethane now goes overhead. This process configuration has no recycle flows at all. Hydrogen sulfide has to be removed upstream in a selective amine process and sent to a Claus plant to avoid it otherwise contaminating the carbon dioxide product.

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The overheads from the propane recovery column is compressed and sent to the bulk carbon dioxide recovery column and CFZi column as in Figure 7. The additive recovery column is not required.

The bottoms from the carbon dioxide recovery column contains ethane and the propane not recovered from the feed gas and is blended with the CFZi column bottoms for injection for EOR.

By avoiding all recycle this flowsheet would demonstrate further savings in refrigeration, power consumption, machinery cost and equipment cost. The pressure required for carbon dioxide injection is elevated slightly to offset the presence of the ethane.

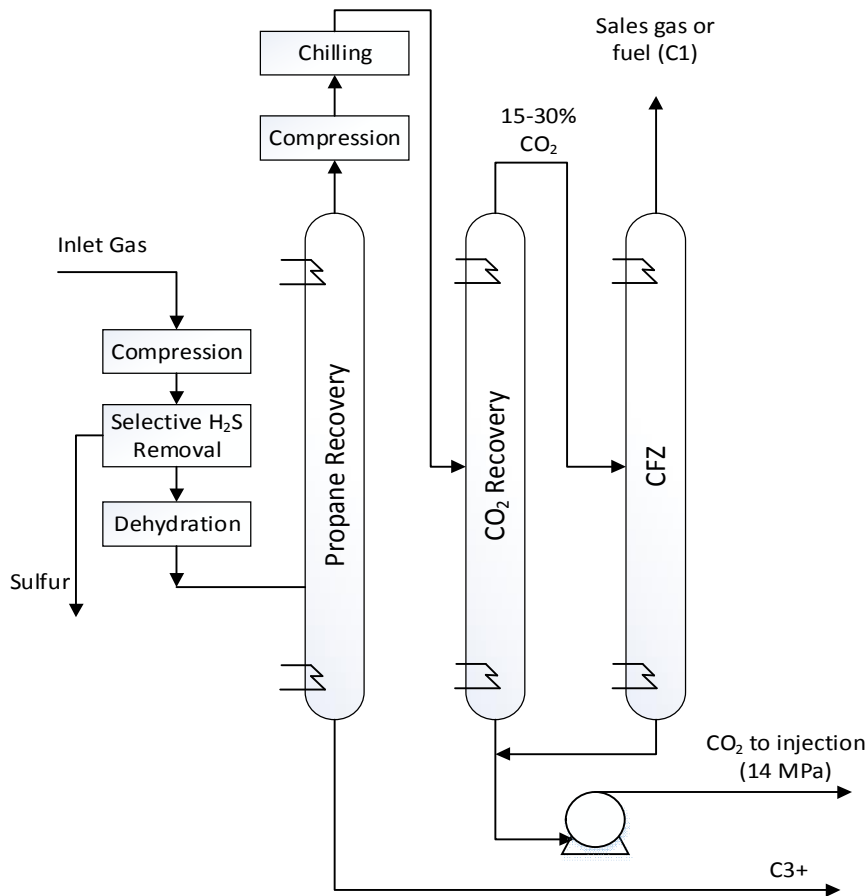


Figure 7 Two Column Process Integrated with CFZi

## Gas for Power Generation

In some scenarios the CFZi demethaniser could be eliminated as shown in Figure 8. The methane rich product stream contains 15 . 30 mol. % carbon dioxide. This can be used as fuel in gas turbine drives with the pressure of the bulk carbon dioxide removal column being set to match that required by the gas turbines. Clearly this configuration would save on capital compared to producing pure methane. It is clearly less effective in terms of carbon dioxide sequestration and EOR but for marginal fields and especially those containing nitrogen it provides a gas stream suitable for power generation, along with the carbon dioxide for EOR.

## Processing of Carbon Dioxide Rich Gas

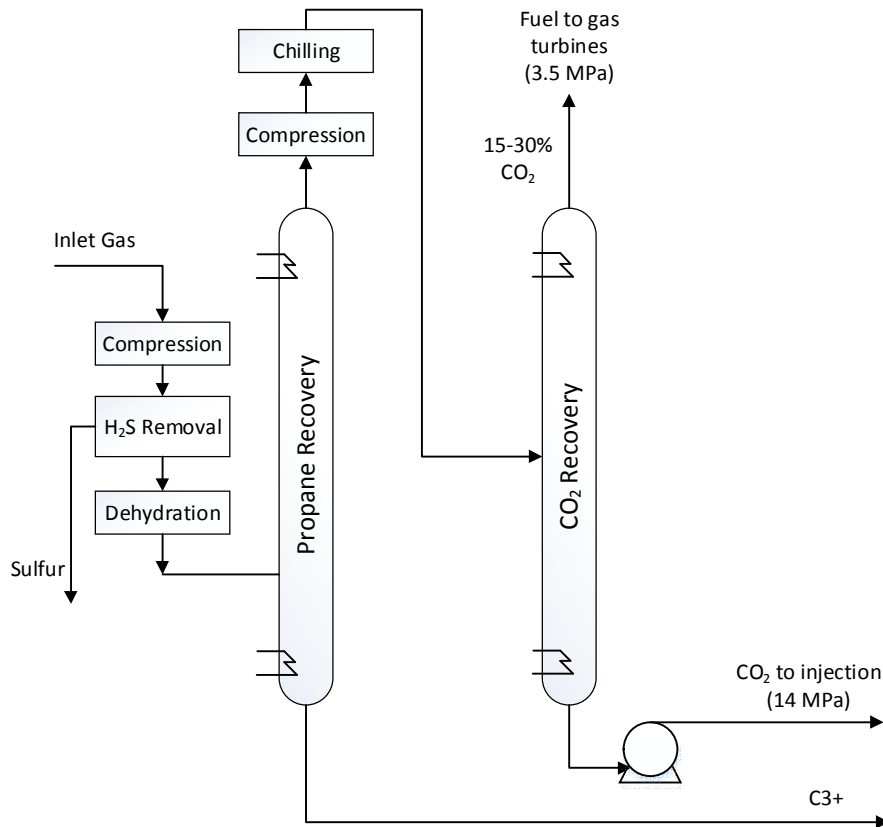


Figure 8 Two Column Process

## Conclusion

Processing of high carbon dioxide content natural gas will increasingly need to consider storage of carbon dioxide. Cryogenic fractionation provides important benefits for removal of carbon dioxide against other technologies as it produces pure carbon dioxide as a high pressure liquid so significantly reducing overall investment cost and operating cost. Established Ryan Holmes technology and emerging CFZi stand out in this regard, though the latter is still under development.

Enhanced oil recovery (EOR) is increasingly being considered as a way of obtaining revenue from sequestering carbon dioxide and cryogenic fractionation is especially appropriate for processing the arising carbon dioxide rich associated gas to recover high pressure carbon dioxide for recycle to the oilfield. The need to extract NGL prior to carbon dioxide removal favours the use of Ryan Holmes technology but this can incur high capital cost due to the recycle of hydrocarbon for both ethane removal and avoidance of carbon dioxide solidification in the demethaniser.

Using Ryan Holmes NGL removal technology upstream of a CFZi column (in place of a Ryan Holmes demethaniser) could provide savings in refrigeration, power consumption, machinery cost and equipment cost. This approach (and a related one without ethane recovery) could be of major importance in reducing carbon dioxide EOR costs and in simplifying processing in terms of design, engineering, installation and operation. Gas processing costs are an obstacle to carbon dioxide EOR and the proposed processes go some way to reducing these costs.

## **Footnote**

Ryan Holmes is a Chart Industries licensed process.

## **Acknowledgments**

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