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TECHNICAL ARTICLE

ENHANCING OIL RECOVERY

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ENHANCING OIL RECOVERY

Terry Tomlinson,
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Costain Natural Resources, UK, give an overview of the use of carbon dioxide in enhanced oil recovery.

Enhanced oil recovery (EOR) using carbon dioxide requires processing of the gas associated with recovered oil. The carbon dioxide content can be very high. Processing of hydrocarbon gas that contains less than 10 mol.% carbon dioxide is well-established but for higher carbon dioxide content, as in EOR, conventional process technologies, including physical solvent and semi-permeable membranes, are not ideal; they can incur high capital and operating costs, cannot effectively meet sales gas product specifications and can suffer from low hydrocarbon recovery and reduced sales gas revenues.

EOR requires dry (to avoid corrosion), pure, liquid carbon dioxide. Liquid carbon dioxide product significantly reduces power consumption and cost in boosting to a pressure for injection into the oil reservoir. Only one process technology can effectively and economically achieve all these important objectives – cryogenic fractionation (distillation).

Low temperature processing is known to be effective for removing carbon dioxide from hydrocarbon gas containing over 20 mol.% carbon dioxide.[1] Costain has developed cryogenic technology to remove carbon dioxide from both hydrogen-rich synthesis gas (from gasification) and from oxyfuel fired flue gas. This article discusses cryogenic technology for hydrocarbon gas processing, including carbon dioxide rich natural gas, but particularly for lower cost processing of carbon dioxide rich gas from enhanced oil recovery (EOR).

Justification

Cryogenic process technology has been used for many years for carbon dioxide separation from associated gas on EOR projects, in which carbon dioxide levels can be very high. Many EOR plants were built and still operate in the Permian Basin of West Texas, using naturally occurring carbon dioxide for injection. The EOR technology is well-established. High pressure carbon dioxide is miscible with the reservoir oil and oil recovery can be increased to over 70% of oil in place. The life of depleted oilfields can be extended for many years. Today, several hundred thousand bpd are produced by EOR in North America using carbon dioxide sourced from power generation as well as natural sources.

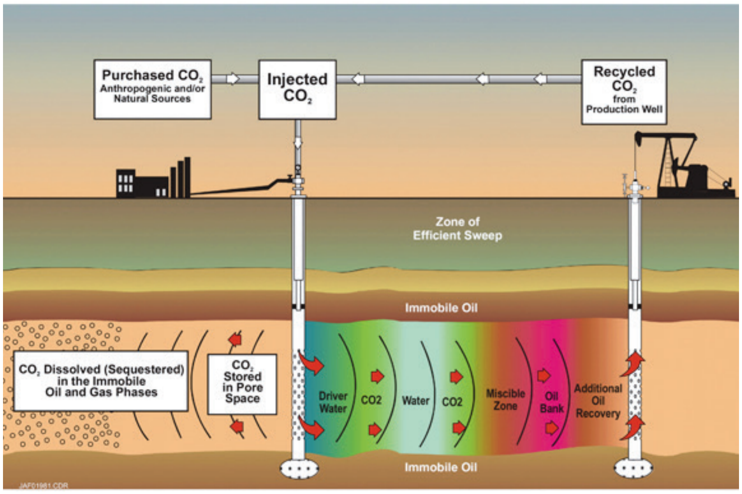

Figure 1. *Carbon-dioxide EOR.*[6]

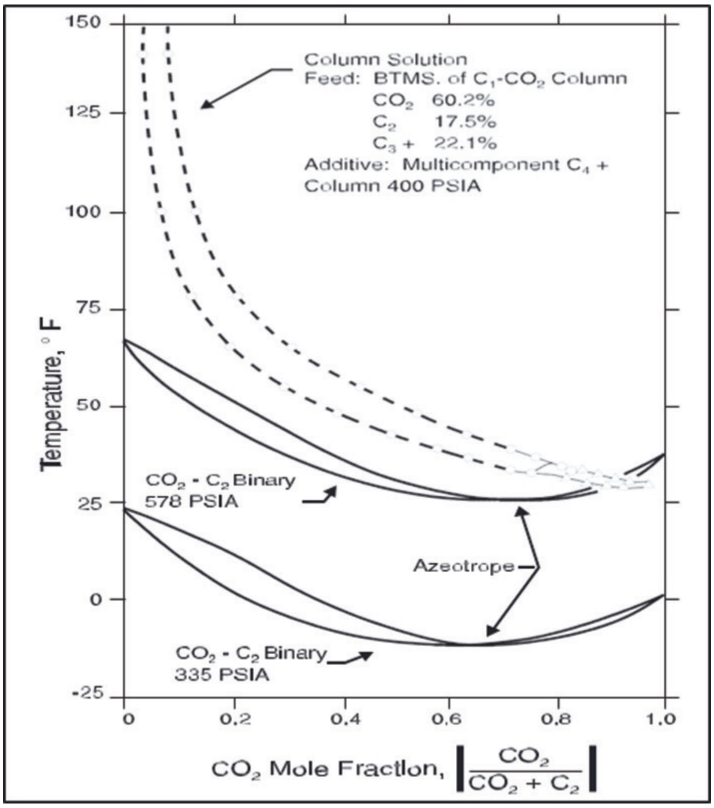

Figure 2. *Vapour-liquid equilibrium for carbon dioxide – ethane.*[9]

Over 70 million t per year of carbon dioxide is effectively sequestered. Up to 11.5 billion t of carbon dioxide could be sequestrated in this way, to produce 128 billion bbls in the US alone.

EOR via carbon dioxide injection is particularly valuable in oilfields with relatively low recovery rates, and which are located close to a carbon dioxide producer (to minimise carbon transportation costs).[2] Work by ADNOC and Masdar on large scale carbon capture and storage (CCS) in the UAE is targeting 70% oil recovery.[3] Studies in Kuwait are promising.[4] It is expected that carbon dioxide injection will dominate EOR in the Middle East, possibly as soon as 2020.

Processing requirements

On an EOR project (Figure 1) the carbon dioxide content of the gas associated with the recovered oil increases to 80 - 90% before abandonment after 20 to 30 years. The amount of natural gas liquids (NGL) in the gas also increases substantially over time, as the lighter hydrocarbons are stripped from the oil, before falling as carbon dioxide levels increase. Three products are required from gas processing – methane, usually to sales gas quality with a carbon dioxide content not exceeding 4 mol.%, pure carbon dioxide for recycle to the oil reservoir and NGL. Recycled carbon dioxide purity is dictated by the need to exceed the oil 'minimum miscibility pressure' (MMP) and to also be within agreed transportation limits. A typical specification is 3 mol.% maximum of nitrogen and methane, as these components are essentially immiscible.[5] The NGL can be fractionated into commercial grade products in a conventional fractionation plant. Any hydrogen sulfide present needs to be removed.

The product slate has an important bearing on plant design and on process technology choice, but for any processing configuration the separation of carbon dioxide from methane is very important. Therefore, process technology for removing carbon dioxide from high carbon dioxide content gas is very relevant for EOR facilities.

Cryogenic technology

The large difference in the boiling points of methane and carbon dioxide makes separation by distillation relatively easy. Carbon dioxide can be produced to high purity with minimal methane losses. Fractionation can also produce liquid carbon dioxide (at a pressure of up to about 35 bar), which can be pumped to high pressure for injection and oil recovery.

Benefits of cryogenic fractionation

- High methane/carbon dioxide relative volatility.
- High product recoveries.
- High purity and high pressure carbon dioxide.

The key drawback with low temperature fractionation of carbon dioxide-rich gas is that a typical sales gas specification, of about 4 mol.% carbon dioxide, cannot be achieved. To ensure demethaniser operating temperatures are high enough to avoid carbon dioxide freezing (higher than -60˚C) the carbon dioxide content of the overhead methane rich stream cannot be less than 15 mol.%, with 20 mol.% a pragmatic value for design.

'Ryan Holmes' cryogenic fractionation

Carbon dioxide solidification in the cryogenic demethaniser and the inability to meet sales gas quality can be resolved, by adding ethane and heavier hydrocarbons to the column. This increases the carbon dioxide solubility, increases operating temperatures and raises the critical pressure locus to make separation easier. As a result, a sufficiently pure methane product is obtained and no further sales gas processing is needed.[7] With this Ryan Holmes technology the carbon dioxide-rich demethaniser bottoms contains hydrocarbon solvent so further fractionation is needed.

As well as avoiding solidification, 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 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 by distillation requires addition of butane or heavier hydrocarbon, which changes the volatility so that carbon dioxide is more volatile than ethane for all compositions.[8] This enables carbon dioxide to be separated from ethane prior to the key methane–carbon dioxide separation, but this recovery of ethane in the NGL product adds to hydrocarbon recycle and thus leads to larger refrigeration and solvent regeneration duties.

Figure 3 shows a typical four column Ryan Holmes plant with ethane plus removal followed by bulk carbon dioxide removal and then the cryogenic demethaniser. The final column produces the hydrocarbon additive for the ethane removal column and the demethaniser.

Ryan Holmes technology was used on about 12 gas processing plants in the US over 20 years ago, before depressed gas prices restricted installation of new facilities.[10]

The technology is robust and produces carbon dioxide as a liquid with low methane content. However, the large recycle flows of hydrocarbons and carbon dioxide, high utility consumption for refrigeration and solvent regeneration, and large process equipment all contribute to processing cost.

As discussed, the separation of ethane from carbon dioxide (for ethane recovery) is relatively difficult. Ethane recovery may be valuable in an EOR venture but this is very case specific. Ethane required for cracking to ethylene needs very low carbon dioxide content – 100 ppmw being typical – and intensive processing. As ethane being present in the product carbon dioxide is acceptable, in terms of miscibility, then discrete ethane recovery would need to be justified by its value as a discrete product. Ethane recovery is unlikely to be a key project 'driver' on an EOR project when compared to the revenue from increased oil production. Therefore there is normally little reason to recover ethane and this affords an opportunity to avoid the separation of ethane from carbon dioxide and to reduce processing cost, as considered later.

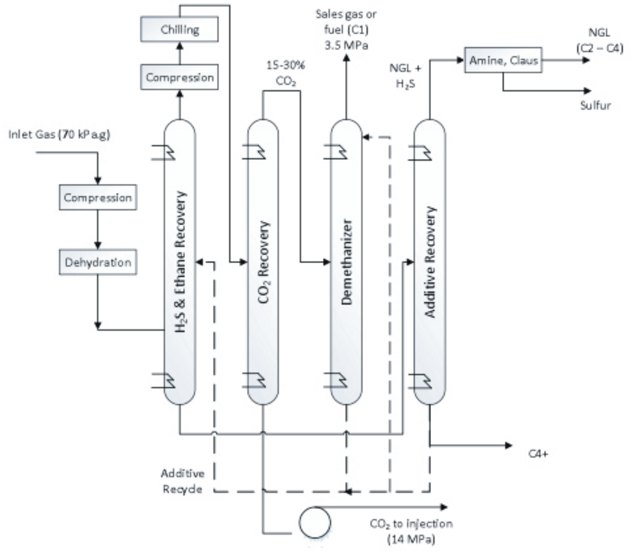

Figure 3. *Four column Ryan Holmes plant.*

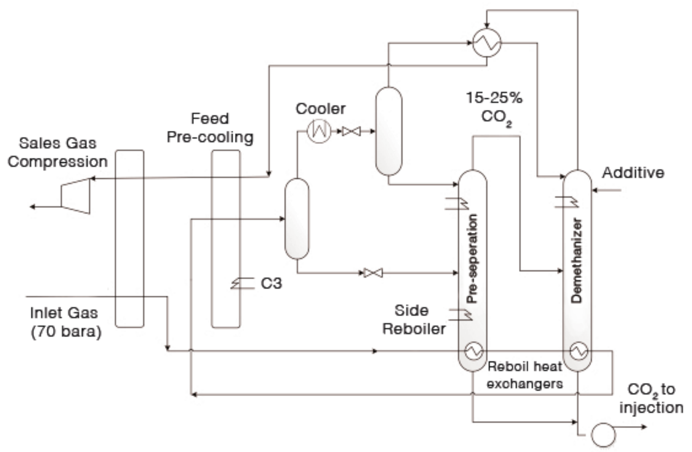

Figure 4. *Costain process technology.* [13]

Alternative fractionation processes

Carbon dioxide EOR plants have been built using a combination of cryogenic fractionation and downstream removal of carbon dioxide by another process technology[11] but these plants do not produce all carbon dioxide as liquid product, and may produce carbon dioxide contaminated with solvent and incur significant compression costs to boost the carbon dioxide to the pressure required for sequestration and EOR.

Process technology has been demonstrated at semi-commercial scale by ExxonMobil for carbon dioxide removal from low NGL content gas by freezing and sublimation of the carbon dioxide. This gives relatively pure products – methane as overheads and carbon dioxide as bottoms. Carbon dioxide is produced as a liquid with very low methane content. This Controlled Freeze Zone™ process minimises the number of equipment items but, as with Ryan Holmes, the high refrigeration duty and utilities cost is a key part of overall processing cost.

New process technology

New fractionation technologies need to reduce both capital and operating cost to improve the commercial viability of carbon dioxide EOR. By focussing on the thermodynamic efficiency of the carbon dioxide from methane separation and systematically analysing process improvements, a new process has been developed. It uses well proven distillation system design methods and energy integration to minimise column flows, refrigeration duties, recycle flows, equipment sizes and overall utility consumption.

The consequent reduction in plant size and complexity can provide a significant cost saving.

This new process technology, shown in Figure 4, minimises the feed gas chilling duty that is normally a significant refrigeration load, and minimises the need for solvent to avoid carbon dioxide solidification in the carbon dioxide – methane separation.

Ethane leaves in the carbon dioxide product thus avoiding the significant processing costs to separate carbon dioxide and ethane, as discussed above.

In the first fractionation column, carbon dioxide and ethane distribute between the top and bottom products with methane being stripped to produce a low methane content bottoms stream. This minimises energy consumption. The overhead vapour carbon dioxide level is such that carbon dioxide cannot freeze. A second fractionation column operates as a demethaniser in that carbon dioxide is separated from methane to give a sales gas quality overhead stream (of not more than 4 mol.% carbon dioxide) and a low methane content bottoms stream. Ethane in the feed to the second column helps reduce the solvent flow needed to avoid carbon dioxide freezing.

The two column bottoms streams of carbon dioxide, ethane and propane plus both flow to a downstream de-ethaniser with an operating temperature well above -40˚C and using propane refrigeration. The stream from the demethaniser enters the de-ethaniser above the stream from the first column to minimise energy consumption.

In the design of integrated distillation systems, minimising the thermodynamic work of separation normally results in the best integrated distillation sequences.[12] Due to varying feed gas compositions and flowrates in EOR applications it is important to not integrate too much to ensure an optimal balance of performance, operability and low energy consumption.

By setting the pressure of the first column above that of the demethaniser the feed gas is chilled by reboiling both columns. This is an excellent way of reducing both refrigeration duties and cost. Use of feed gas for reboiling essentially eradicates the need for a source of heat on most applications. In comparisons with other cryogenic distillation technologies, for a range of feed gas carbon dioxide levels, refrigeration duties were reduced by up to 50% by the new process.

The process solution provides

- Conventional low temperature gas processing technology similar to technology for high recovery of NGL and cryogenic nitrogen removal.
- Reduced power consumption and simple refrigeration system configuration.
- Minimal heat requirements.
- Plant design by using process evaluation, conventional process modelling and simulation to identify optimal equipment sizes and plant performance.
- Design for variation in feed gas over time, to ensure plant flexibility, operability and good performance.
- High plant reliability and availability by refrigeration system optimisation and machinery selection.
- Minimal environmental emissions.

The technology can be shown to achieve a high 'technology readiness level'. There is no need for a demonstration plant and trials before progressing to commercial scale plant as with some carbon dioxide removal technologies. All processing scenarios can be evaluated and designed for by conventional process simulation so as to give high confidence in the plant design.

Recent feasibility studies have investigated process technology solutions to optimise plant design and the sales gas carbon dioxide level. Work has included chilling train design, refrigeration system optimisation, selection of well-proven and reliable machinery and equipment, power supply optimisation, waste heat recovery, feed gas dehydration technology optimisation, environmental assessments and safety studies. Capital costs were benchmarked against alternative process technologies with very favourable results.

The process technology discussed in this articles is now suitable for application in both carbon dioxide based EOR projects and in the processing of carbon dioxide rich natural gas.

Acknowledgement

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