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PROCESS FOR THE ADJUSTMENT OF THE HHV IN THE LNG PLANTS

D. Chrétien

TOTAL

France

The world LNG market has recently been subject to some major changes which potentially impact the design of the liquefaction plants as well as that of the receiving terminals. The emergence of a more fluid market linked to the development of the spot market leads the operators to consider more flexible design, in particular for the receiving terminals. But the most important change lies in the growing demand from both the UK and the US which become large importers with significantly different specifications of LNG and will drive the expansion of the LNG market in the coming decades. This new situation forces the operators of the liquefaction plants to adapt their production and the design of the new plants for those two countries.

MARKET ASPECTS

The world LNG market was traditionally split in three main importing areas, which can be classified by the quality of the imported LNG characterised by the High Heating Value (HHV) and the Wobbe index. The first area, located in Asia with Japan and South Korea as main actors, is used to import rich LNG with high HHV over 1090 BTU/scf while UK and USA have similar LNG specifications with very low HHV requirement, below 1075 BTU/scf. Continental Europe specifications lie in between and most of the LNG terminals can accept LNG HHV in the range 990 to 1160 BTU/scf. The most important market is in Asia and the imported LNG in Japan and South Korea represents a significant fraction of the world LNG imported tonnage.

At the other end of the LNG chain, the existing liquefaction plants are designed for the supply of the main Asian importing countries with high HHV LNG and only half of them is equipped with LPG extraction facilities.

The rapidly growing demand from the UK and the US with significantly different LNG specifications is a major change in the world market and the liquefaction plants as well as the import terminals have to manage a gap between the currently produced rich LNG and the new and large demand for lean LNG.

There are different means to adjust the production to the demand. In the liquefaction plants, the best way to produce leaner LNG is the extraction of the heaviest components, namely the LPG's, propane and butane. However, the traditional design for this purpose consists in the scrub column which is mainly dedicated to the removal of the heavy end of the hydrocarbons (benzene and pentane +) which may freeze in the cryogenic section. Hence, the propane recovery is fairly low and may not be sufficient to comply with the UK and US specifications. Deeper propane extraction may be necessary requiring expansive revamp of the existing plants or additional extraction units (based for example on the use of turbo-expander) for the new projects. For example, the Qatar Gas II plant is designed with an upstream NGL recovery unit for deep propane extraction. But even if the propane is fully extracted, the remaining ethane content may lead to HHV above the accepted value. In that case, part of the ethane should be extracted from the gas. The valorisation of produced ethane may be a

concern since the only market for ethane is in the petrochemical plants for the production of ethylene and there is not always an ethylene complex in the vicinity of the liquefaction plant. The burning of ethane in the gas turbines of the liquefaction plants is also limited by the fuel gas specification of some gas turbine manufacturers.

In the LNG terminals, rich LNG can also be transformed in leaner export gas by different means. Nitrogen injection is sometimes used. If used on a spot basis, it can be supplied in the liquid form by truck and if continuously injected, a dedicated air separation unit is purchased and commissioned. In any case, nitrogen injection is expensive. Furthermore, the nitrogen content is limited to an upper value by the downstream gas network specifications (5 % in UK and usually 3 % in USA). For rich LNG, the reduction of the HHV may require higher nitrogen injection rates. The other solution consists, similarly to the liquefaction plants, in the extraction of the heaviest components. Propane and butane can easily be valorised but, if necessary, the production of ethane has to face the same difficulty of having a local market.

The description of the today LNG market and its challenges related to the new actors is extensively explained in the article “ Differing market quality specs challenge LNG producers” by Y. Bramoullé, P. Morin, J. Y. Capelle in Oil and Gas Journal/ Oct. 11, 2004.

From this situation, Total developed a new solution for the design of liquefaction plants producing lean LNG dedicated to the UK and US markets. Furthermore, this design allows the production of changing LNG qualities for the supply of two different markets from the same plant, provided of course that the necessary dedicated storage tanks are available. This solution can also be implemented in the LNG receiving terminals giving flexibility for the LNG importation and opportunities for spot supply.

PROCESS BASIS

This process is based on the partial extraction of ethane and its chemicals conversion to methane. This later is mixed with the product : the feed gas for the liquefaction plants or the export gas for the receiving terminals. Basically, the chemical conversion can be summarised in two steps : the ethane is first selectively reformed in synthesis gas ($H_2 + CO$) on catalyst and further transformed in methane in a methanator. This chemical conversion exists and is a referenced process commercialised with Johnson Matthey catalyst. This paper describes its most accurate location in the LNG chain.

The process is based on the selective conversion of the hydrocarbons heavier than methane in presence of methane and of the inert gases present in the gas. Methane is not involved in the chemical reactions.

In this process, the following three basic reactions take place :

- Steam reforming of the hydrocarbons : $\text{HC} + \text{H}_2\text{O} \text{ -----} \rightarrow \text{H}_2 + \text{CO}$. This reaction is endothermic.
- Catalytic methanation : $3 \text{H}_2 + \text{CO} \text{ -----} \rightarrow \text{CH}_4 + \text{H}_2\text{O}$. This reaction is exothermic.
- Shift reaction : $\text{H}_2\text{O} + \text{CO} \text{ -----} \rightarrow \text{CO}_2 + \text{H}_2$

When detailed to each hydrocarbon, these reactions lead to the overall chemical reactions :

- Ethane :
 $4 \text{C}_2\text{H}_6 + 9 \text{H}_2\text{O} \text{ -----} \rightarrow 21 \text{H}_2 + 7 \text{CO} + \text{CO}_2 \text{ -----} \rightarrow 7 \text{CH}_4 + 7 \text{H}_2\text{O} + \text{CO}_2$
- Propane
 $2 \text{C}_3\text{H}_8 + 7 \text{H}_2\text{O} \text{ -----} \rightarrow 15 \text{H}_2 + 5 \text{CO} + \text{CO}_2 \text{ -----} \rightarrow 5 \text{CH}_4 + 5 \text{H}_2\text{O} + \text{CO}_2$
- Butane
 $4 \text{C}_4\text{H}_{10} + 19 \text{H}_2\text{O} \text{ -----} \rightarrow 39 \text{H}_2 + 13 \text{CO} + 3 \text{CO}_2 \text{ -----} \rightarrow 13 \text{CH}_4 + 13 \text{H}_2\text{O} + 3 \text{CO}_2$
- Pentane
 $\text{C}_5\text{H}_{12} + 6 \text{H}_2\text{O} \text{ -----} \rightarrow 12 \text{H}_2 + 4 \text{CO} + \text{CO}_2 \text{ -----} \rightarrow 4 \text{CH}_4 + 4 \text{H}_2\text{O} + \text{CO}_2$

The first remarkable result is that the heavier the hydrocarbon molecule the lower the carbon efficiency. One carbon contained in the ethane molecule produces 7/8 of methane molecule while one carbon in the butane molecule only produces 13/16 of it. The lost in carbon efficiency is then about 15 % from ethane to butane. It is consequently advisable to preferably convert the light components in methane rather than the heavy ones. Ethane is the most efficient hydrocarbon for methane conversion.

This conversion process is known as “CRG Process Technology”, CRG for “Catalytic Rich Gas”. It was developed by British Gas. In 1998, Davy Process Technology acquired the right for the licence based on the use of a Johnson Matthey catalyst.

The figure 1 shows a simplified Process Flow Diagram (PFD). The heavy hydrocarbon feed is mixed with a portion of the CRG reactor exit gas and preheated against the hot gas from the plant before being further heated up to the temperature required for the desulphurisation system which provides protection of the catalyst against sulphur compounds. The desulphurisation system consist of a HDS reactor followed by two ZnO adsorption vessels (details are not shown). In the HDS reactor sulphur compounds react with hydrogen provided by the CRG exit gas recycle stream, to form H₂S which may then adsorbed on the ZnO catalyst. Two adsorption vessels are provided and arranged in such a manor that can take the lead position. This provides facility to change out the absorber catalyst while maintaining the plant online. In addition

to the zinc oxide absorbent a layer of fine ultrapurification catalyst is included to absorb sulphur to very low level to maximise the potential life time of the downstream CRG catalyst. Should the gas not contain sulphur components, the desulphurisation unit would be simplified.

Desulphurised gas is mixed with steam, reheated to around 375 °C and passed to the CRG reactor where reforming reactions take place to provide a gas containing methane, hydrogen, carbon oxides and unreacted steam together with the inert gases potentially contained in the feed. The hot gas leaving the reactor is cooled using the process heat to raise steam in the CRG Boiler. A portion of the gas is cooled against cooling water. Process condensates formed is separated in the recycle KO drum and passed to plant battery limits. Overhead gases from the KO drum are recycled to the recycle compressor.

The remaining gas leaving the CRG boiler is fed to the Methanator where reactions of the carbon oxides with hydrogen take place to further increase the methane content of the gas. Heat contained in the process gases leaving the Methanator is again recovered to the steam system via the Methanator boiler and the Boiler Feed Heater. Further heat recovery takes place in the Desulphur Preheater before the hot gas product is passed to battery limit for further heat recovery and cooling.

In a stream containing methane and heavier hydrocarbons, all these later are converted into methane. Since propane and butane are marketable products, it is advisable to use the CRG conversion on a stream containing only methane and ethane, this later being only converted. Hence, this process is optimally located in the LNG chain on streams where the ethane content is high and that of the heavier hydrocarbons is low. This location is rather similar for the liquefaction plants and the LNG terminals, i.e. on the overhead stream of the deethanizer.

LIQUEFACTION PLANTS

The figure 2 shows a schematic view of a liquefaction plant based on the APCI liquefaction process. The feed gas after compression is routed to the CO₂ removal unit and later to the dehydration and mercury removal. After precooling in the Propane Chillers (Cycle C3), the gas which is partly condensed enters the Scrubb Column (DC1) where most of the butane and heavier components are extracted as well as part of the propane and ethane with dissolved methane. This liquid mixture is withdrawn from the bottom of the Scrubb Column and routed to the fractionation unit. The top gas of the Scrubb Column is further cooled in the APCI liquefaction process and partly condensed at -65°C. The recovered liquid is used as reflux in the Scrubb Column. The gas is cooled and liquefied in the APCI liquefaction process and routed to the storage tanks for loading in the tankers.

The liquid from the bottom of the Scrubb Column is split into four products in the fractionation unit which classically comprises the deethaniser (DC2), the depropaniser (DC3) and the debutaniser (DC4). The produced propane, butane and condensates are routed to their respective storage tanks for further commercialisation. The ethane rich stream is usually mixed to the main gas stream and liquefied with it. Part of it can be used as fuel gas but the utilisation is limited by the maximum ethane content accepted in the fuel gas burnt in the gas turbines (15 % vol. for General Electric).

The figure 3 shows on the same flowsheet the best location for the conversion as identified by the Total : this is the head of the deethaniser. Besides ethane, this mainly contains methane and some nitrogen if present in the natural and is very lean in propane and butane. Hence, neither propane nor butane are converted into methane and their production and commercialisation are not penalised. Furthermore, only ethane is converted ; this hydrocarbon has the best efficiency in carbon conversion and the overall efficiency is improved. The flowrate of this stream is relatively small compared to the natural gas stream, leading to a reasonable size of the unit.

The head of the deethaniser is routed to the conversion unit which mostly produces methane, carbon dioxide, water and inert if any. This stream is recycled to the inlet of the plant and mixed with the feed gas. The carbon dioxide produced in the conversion unit is removed in the CO₂ removal unit at the same time as the CO₂ contained in the natural gas. The water produced in the conversion unit is a natural make-up for the CO₂ removal unit. Hence, the conversion is naturally integrated in the whole process of the plant and the changes in design are minimised.

The implementation of the conversion can be performed by revamping of an existing plant. The order of magnitude of the recycle gas to the CO₂ removal unit is from 5 to 7 % which can in general be accepted by the units from the CO₂ removal unit to the scrubb column.

In case of ethane extraction upstream of the liquefaction, the optimisation of the plant lead to the same location of the conversion unit on the overhead stream of the deethaniser.

The operation of the plant supplied with such a conversion unit is very flexible. The quality of the produced LNG may be adjusted by tuning the fraction of flowrate of deethaniser overhead stream routed to the conversion. The same plant is consequently able to produce two different qualities of LNG, provided that the plant has the necessary dedicated storage tanks and that operation precautions are taken for the prevention of roll-over in case of unintentional mixing.

The implementation of the CRG process has a marginal impact on the energy balance of the plant For example, the reduction of the ethane content in the gas from 6 to 5 % mole involves an increase of 0.25 % mole of CO₂ in the feed gas by recycling, which has not a major impact on the steam balance of the plant. The ethane conversion instead of its use as fuel gas has even a positive impact on the liquefaction

consumption. The fuel gas in a LNG plant is normally produced at the cold end of the cryogenics by flash of the LNG. If the ethane is used as fuel gas (if compatible with the burners of the gas turbines), the amount of flash gas is reduced accordingly. The cold end temperature is consequently lower, resulting in increased liquefaction power consumption.

The order of magnitude of the cost of such a conversion unit for the reduction of ethane content from 10 to 8 % in a 4 MMt/y LNG plant is in the range 15 to 25 MM\$ ex-works. The achievement of the same HHV by propane extraction would require the use of a deep propane extraction unit based on a turbo-expander on the whole gas flowrate and involve an higher investment cost.

LNG TERMINALS

An LNG terminal basically consists in unloading facilities, storage tanks and vaporisation facilities. It is schematically shown on figure 4. In this basic configuration, there is no change of composition of the LNG the HHV of which is not affected.

If a need of HHV adjustment arises, the composition of the LNG has to be changed. It was reminded in the introduction that the main means are the nitrogen injection with potential content limitation and the LPG's and / or the ethane extraction, with the drawback for this later to necessarily find a local market.

The ethane conversion can be implemented in a LNG terminal to adjust the HHV of the delivered gas. This integration is shown on the figure 5. For the LPG's extraction, this example is based on the process disclosed by Black and Veatch Pritchard in the patent n° US 6,564,579. It however can be implemented with any other process provided that the ethane is concentrated in the overhead stream of the deethaniser.

The LNG is pumped from the storage tank to the operating pressure of the demethaniser. The LNG is partly vaporised and enters the demethaniser where it is split in a vapour and a liquid containing the ethane + fraction. The overhead stream of the demethaniser is compressed and condensed against the vaporising feed. The resulting leaner LNG is pumped to the pipeline pressure and vaporised in SCV's in the present example. The liquid from the bottom of the demethaniser is fractionated into ethane which is routed to the conversion and propane, butane+. Since the conversion produces water, the converted gas needs to be dried. A TEG unit is sufficient to cope wit most of the pipeline specification. The converted gas is finally mixed with the main natural gas stream.

The extracted propane and butane can be separately valorised and sold.

The heat released by the conversion unit helps to the LNG vaporisation, resulting in energy saving. However, the heat released is not sufficient for the vaporisation of the LNG and can provide only one fourth to the half of the required duty, depending on the respective composition of the imported LNG and of the export gas.

In some cases, depending on the composition of the LNG and of the export gas, the conversion of ethane combined to the LPG extraction makes possible a so quick decrease of the HHV that only part of the LNG has to be treated.

The ethane conversion can be combined with other technologies for the HHV reduction giving the following combinations :

- Ethane extraction and conversion combined with nitrogen injection (option 1).
- Ethane extraction and conversion combined with LPG extraction and sale (option 2).

These processes can be compared to the more classical ones :

- Nitrogen injection (option 3)
- LPG extraction and nitrogen injection (option 4)

The OPEX and sale incomes of these four options have been compared in a theoretical terminal of 4 MMt/year. The investment costs have not been calculated. The comparison was made for 4 scenarios : North West Shelf LNG imported in the USA (scenario 1), Nigerian LNG to the USA (scenario 2), Nigerian LNG to the UK (scenario 3) and Qatar Gas II to the UK (scenario 4).

For the scenarios 1 and 2, the injection of nitrogen alone (option 3) is not able to achieve the required HHV within the allowed nitrogen content in the export gas.

For all four scenarios, options 2 and 4 give very similar results and provide net income between 30 and 50 MM \$ /year above the options 1 and 3, when feasible. Most of the income comes from the sale of the LPG's.

However, for the same LPG's extraction, the ethane conversion makes possible the production of a leaner export gas without the limitation of the nitrogen injection. It makes possible the supply of a wider range of LNG quality to the LNG terminal and offers the possibility of spot and cheaper supply.

CONCLUSION

The new fast growing demand of the UK and the USA in lean LNG forces the operators to reconsider the design of the LNG plants and the LNG terminals which are currently mostly dedicated to the supply of the Far East and continental Europe markets with richer LNG.

The LPG's extraction required to reach the HHV specification may exceed what is usually achieved by the existing plants and further extraction rate would involve additional investment cost. Furthermore, some LNG specifications are so lean with regards to the feed gas composition that the extraction of ethane may any way be necessary. There is not always a market for it in the vicinity of the LNG plant or of the LNG terminal.

The chemical conversion is of course an additional investment but it makes possible the reduction the HHV without a deep extraction of the propane which would be more expensive and energy consuming when using a turbo-expander process.

The best location of this unit is on the stream of the plant where the ethane concentration is the highest, i.e. at on the overhead stream of the deethaniser. The stream flowrate is relatively low and the integration of the conversion unit in the whole process for the removal of the by-products (CO₂ and water) is easy. Switching-off the unit or partially by-passing it makes possible to precisely fit the HHV of the produced LNG to the market.

The use of ethane extraction in LNG terminal is less attractive compared to the LPG's extraction alone or combined with nitrogen injection. OPEX and sales are in both cases comparable. It is however always cheaper than nitrogen injection, which, by the way, is limited by the acceptable nitrogen content in the export gas. It makes possible to go further than a simple LPG's extraction in the HHV decrease of the gas and offers a wider range of quality supply leading to possible spot market or supply from different LNG plants.

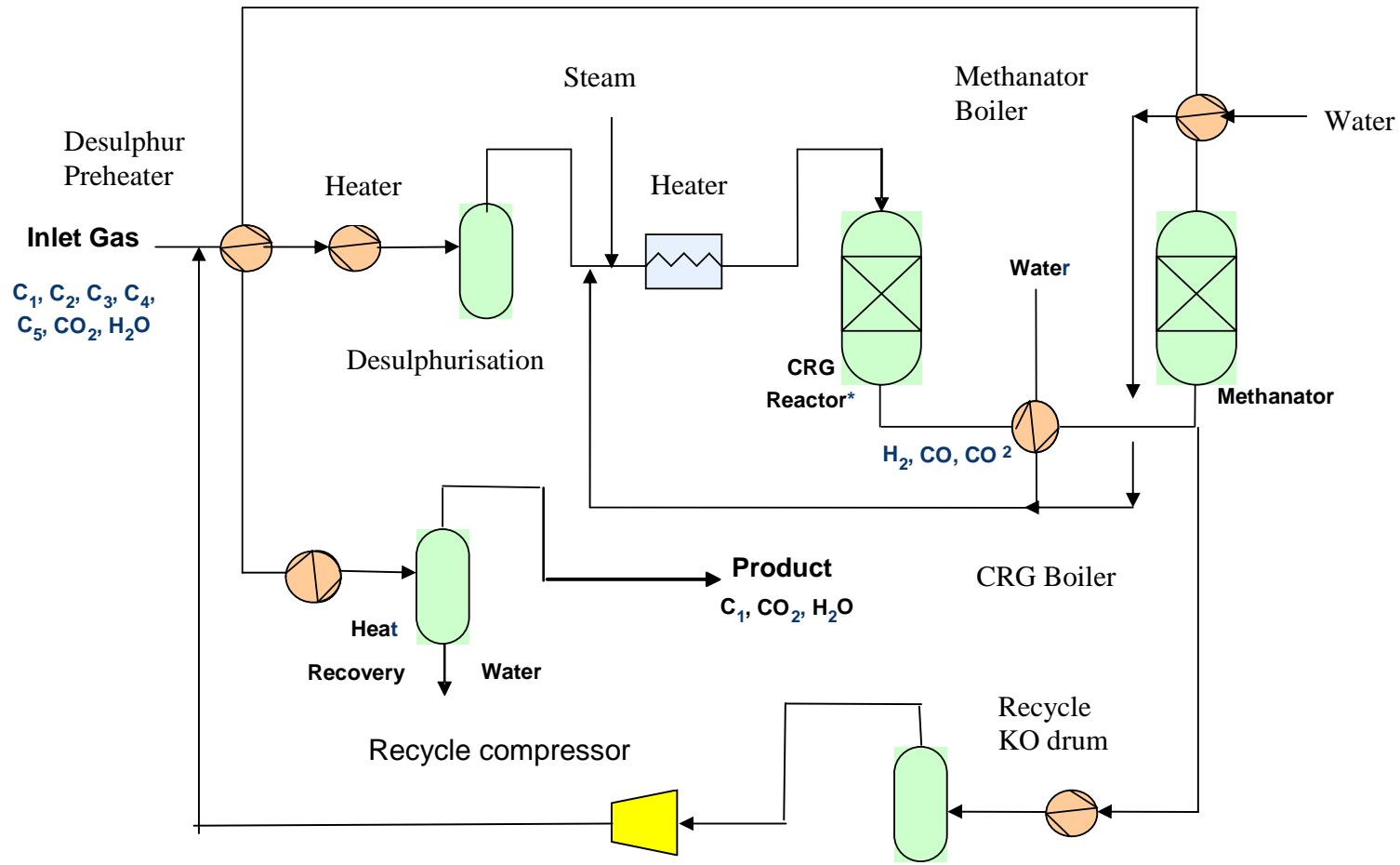


FIGURE 1

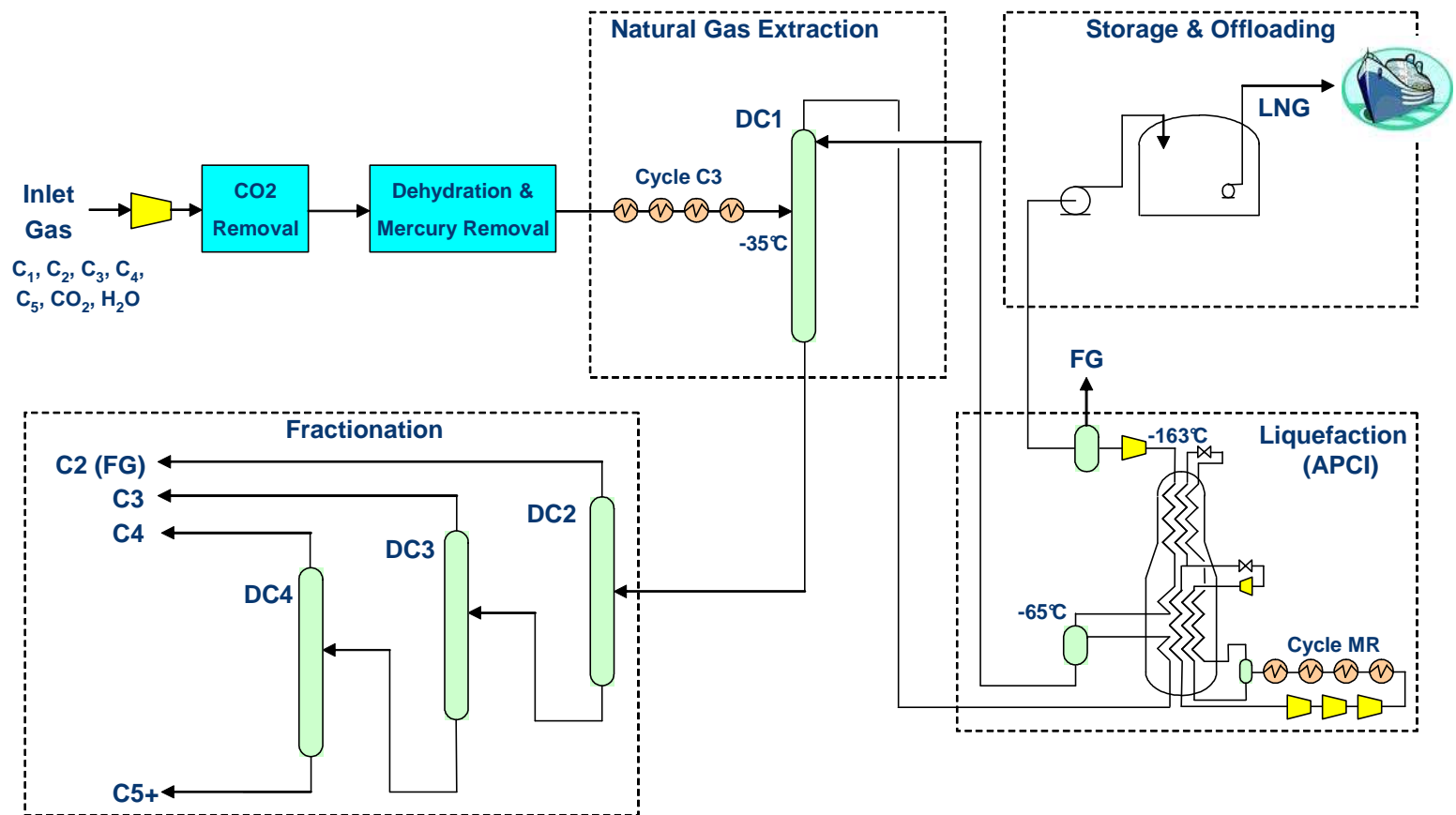


FIGURE 2

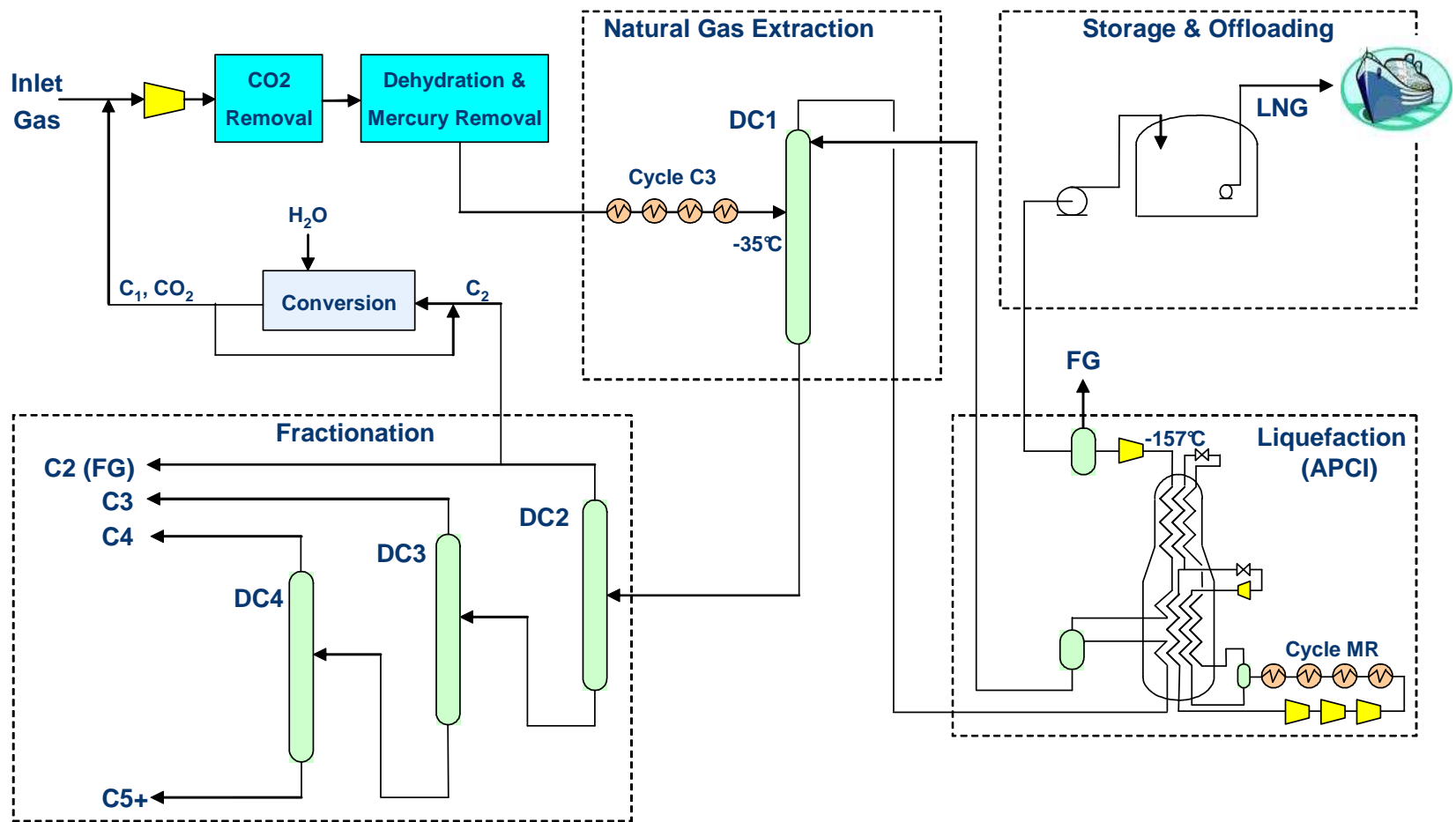


FIGURE 3

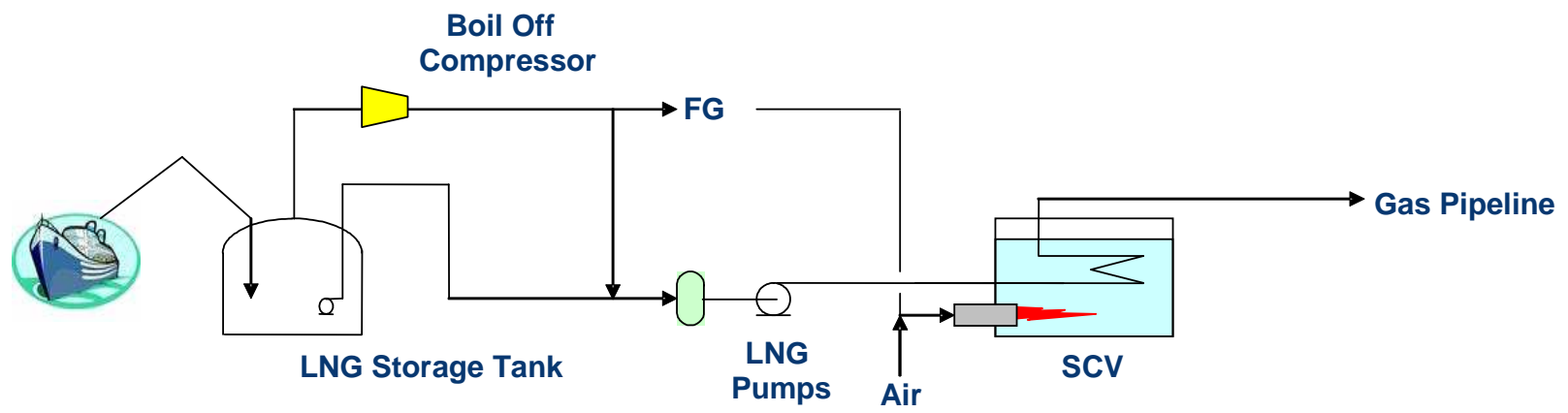


FIGURE 4

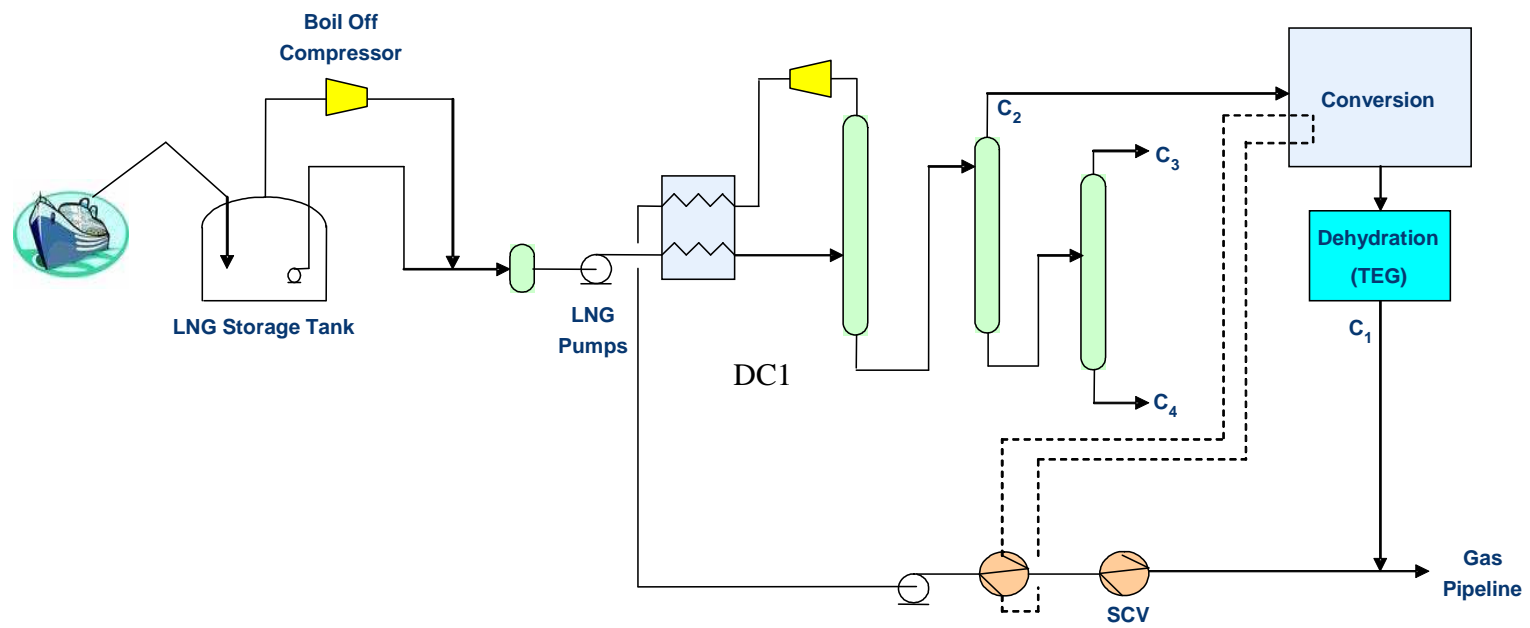


FIGURE 5