ORIENTATIONS FOR TREATMENT AND DEEP PROCESSING OF CA VOI XANH GAS

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Summary

Ca Voi Xanh gas field is located about 100km off the coast of the central region of Vietnam. This is the biggest gas field in Vietnam with its reserves of 150 billion m^3 of natural gas. However, gas from Ca Voi Xanh field has high contents of impurities, namely H_2S, CO_2 and N_2. Orientations for treatment and deep processing of Ca Voi Xanh gas are presented, including membrane separation of CO_2 and/or N_2; and processing of Ca Voi Xanh gas without CO_2 and/or N_2 removal to produce (i) syngas for methanol feed via combined reforming technology and/or (ii) ammonia for fertilizer via Haber process. Recovered CO_2 can be considered as a potential carbon supply to methanol and DME production if a sustainable and reasonable source of hydrogen is supplied. Development of advanced materials and catalysts for efficient processing of Ca Voi Xanh gas is discussed. It is highly expected that zeolite-based membrane would offer a techno-economically good approach of CO_2 and/or N_2 removal from a mixture of CH_4, CO_2, and/or N_2, and that nano-Ni-based catalyst brings a high conversion of methane (> 90%) towards lower temperature (550^{o}C) in comparison with current industrial conditions for methane reforming.

Key words: *Ca Voi Xanh, CO_2, DME, membrane, methanol, N_2, steam reforming.*

1. Introduction on Ca Voi Xanh gas field

Vietnam is in the region of high-CO_2-content gas fields. In 2011, the biggest gas field, named Ca Voi Xanh, was discovered about 100km off the coast of the central region of Vietnam with its reserves of 150 billion m^3 of natural gas. It is scheduled to have first gas in 2023 and its gas will be used for power and petrochemical production. However, Ca Voi Xanh gas has high contents of impurities, namely H_2S, CO_2 and N_2. Table 1 shows its hydrocarbon and non-hydrocarbon composition [1].

It can be seen that Ca Voi Xanh gas contains undesired components, including 0.21% of H_2S, 9.88% of N_2 and 30.26% of CO_2. At the gas processing plant (GPP), H_2S removal treatment is applied so that its remaining H_2S content is less than 30ppm. CO_2 and/or N_2 removal should be considered upon its uses and available technologies for its treatment and deep processing.

Table 1. *Composition of Ca Voi Xanh gas*

Component	Composition (mole %)
N_2	9.88
CO_2	30.26
H_2S	0.21
C_1	57.77
C_2	0.92
C_3	0.31
C_4	0.18

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Ca Voi Xanh gas is planned to be used for power production in priority. About 10 - 20% of produced gas could be considered for petrochemical production. In 2017, the Vietnam Petroleum Institute (VPI) conducted a study to evaluate the ability to use Ca Voi Xanh gas as feedstock for petrochemicals. It was shown that the best option to use Ca Voi Xanh gas for petrochemical production is to produce olefins via methanol production. Olefins can then be used to produce other products, including polypropylene (PP), methyl methacrylate (MMA), and styrene monomer (SM). Figure 1 shows two options for petrochemical production from Ca Voi Xanh gas.

2. Orientations for treatment and deep processing of Ca Voi Xanh gas

2.1. CO_2 and/or N_2 removal from Ca Voi Xanh gas using membrane technology

For CO_2 removal from Ca Voi Xanh gas, a membrane technology can be applied. Membrane separation offers the advantage of being highly impact, environmental friendly, scale-up flexible, and energy efficient relative to the more established gas separation processes such as adsorption and cryogenic distillation, and thus has been focused as subject of investigation for gas separation for years [3]. In the gas industry, some commercial

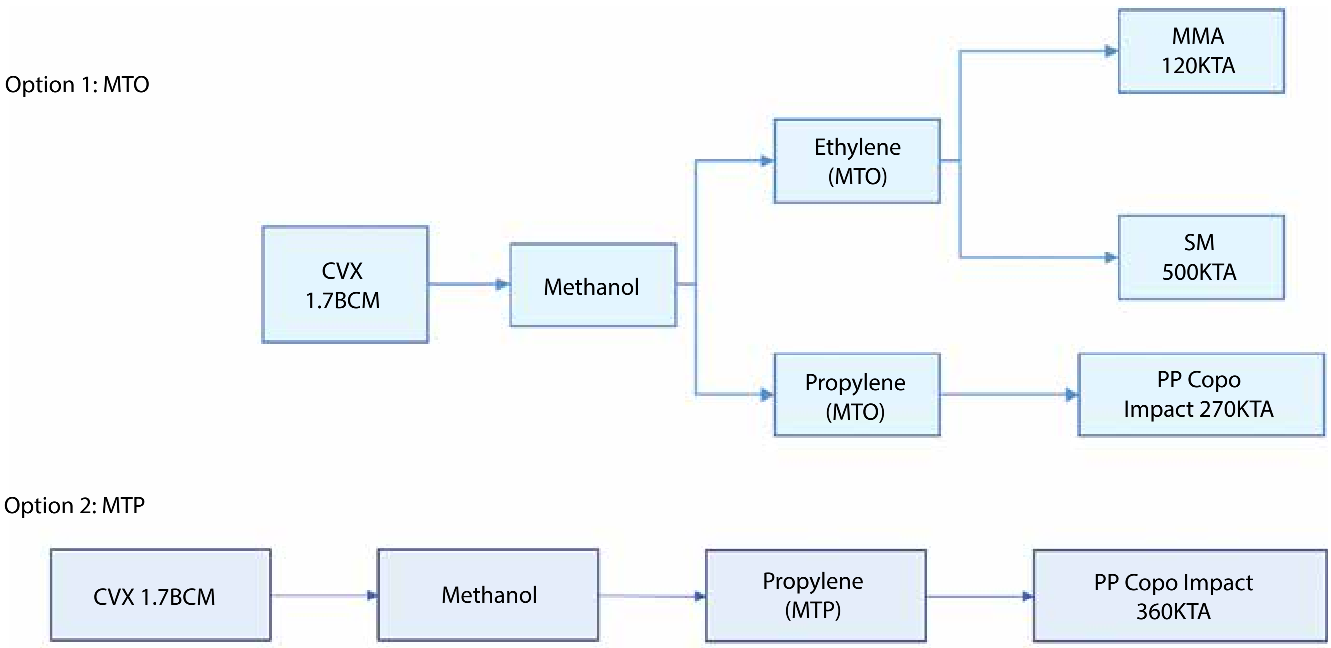

***Figure 1.** Two options for petrochemical production from Ca Voi Xanh gas [2]*

technologies are available for CO_2 removal using polymer-based membranes. Table 2 shows selected suppliers of membrane natural gas separation systems [3]. Currently, commercial polymeric materials can bring a selectivity of about 10 - 20% for separation of CO_2 from natural gas [3].

Although polymeric membranes have been commercialised for gas separation, they show a number of disadvantages, clean feed requirement, selectivity-permeability trade-off (upper bound), physical aging and plasticisation in exposure to harsh working conditions and acidic gas contaminants. On the other hand, for N_2 removal, current technology based on cryogenic separation is energy consuming. Membrane technology for N_2 removal is currently not available in the gas industry. The challenge is to develop membranes with the necessary performance related to permselectivity of N_2 over CH_4 with closely matched dynamic diameters of 0.36 and 0.38nm, respectively. A polymeric membrane has been tested for N_2 removal, but its selectivity is relatively low (0.3). Ceramic membranes are being developed for higher efficiency in gas separation. A zeolite-based membrane can bring a selectivity of more than 200 for CO_2 removal, and/or 10 - 20 for N_2 removal from natural gas. Table 3 shows the strength and weaknesses of polymer membranes and inorganic membranes (mainly zeolite membranes) for gas separation.

To date, some inorganic membranes have shown excellent performance in CO_2 separation as well as exhibited potentially good performance in N_2 separation.

***Table 2.** Selected suppliers of membrane natural gas separation systems for CO_2 removal*

Company/Technology	Membrane material
Medal (Air Liquide)	Polyimide
W.R.Grace	Cellulose acetate
Separex (UOP)	Cellulose acetate
Cynara (Natco)	Cellulose acetate
ABB/MTR	Perfluoro polymers silicone rubber

***Table 3.** Strengths and weaknesses of polymer membranes and inorganic membranes (mainly zeolite membranes)*

Criteria	Polymer membrane	Inorganic membrane
Gas permeation rate	Low	High
Selectivity	Low	High
Producibility of membrane modules	High	Low
Cost effectiveness	High	Low
Stability	Low	High

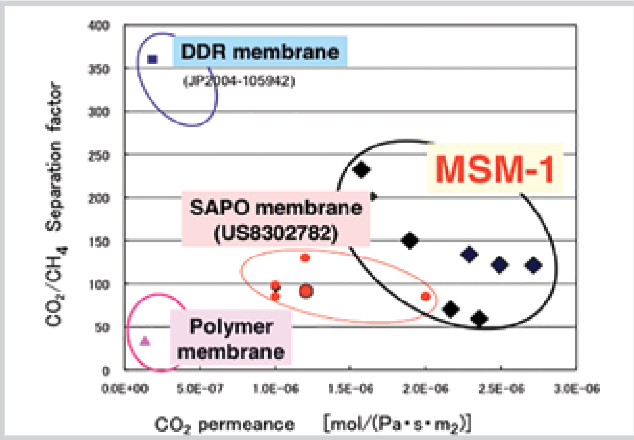

***Figure 2.** Comparison of CO_2/CH_4 separation effectiveness of various membranes [4]*

Chiyoda Corporation and Mitsubishi Chemical Corporation have collaborated to develop a zeolite-based membrane for CO_2 removal from natural gas and named it MSM-1. Figure 2 shows a comparison of CO_2/CH_4 separation effectiveness of various membranes. The outstanding performance of zeolite-based membranes compared to polymeric ones can be seen.

However, the current cost for zeolite-based membrane production is quite expensive, and hence, preventing their commercialisation. A more realistic approach is to develop a hybrid membrane based on a mixture of polymer and zeolite. Although a lot of works still need to be done to bring hybrid membranes to the market, this is a potential way to have highly efficient membranes for gas treatment.

2.2. Methanol and/or dimethylether (DME) production from high-CO_2-content natural gas

Ca Voi Xanh gas can be processed without CO_2 removal using a steam reforming process to produce syngas (a mixture of CO and H_2) that can be later converted into methanol and/or DME. Currently, DME is produced via dehydration of methanol as feedstock [5]. Several licensors are available for DME production, including Haldor Topsoe, Linde/Lurgi, and Toyo Engineering, etc. Another under development technology is one-stage DME production via catalytic conversion of syngas or CO_2. Accordingly, the catalyst should have both methanol synthesis and methanol dehydration activities. As a result, an amount of water is formed during DME synthesis, and hence, an efficient water removal technology should be applied.

The CO_2 content in Ca Voi Xanh gas brings two sides during processing. In fact, CO_2 is needed for methanol synthesis, but at the same time, it also results in more coke formation during the reforming reaction. In 2014, Haldor Topsoe introduced a noble metal based catalyst for steam reforming of high-CO_2-content natural gas. Application of this catalyst can reduce the steam amount needed to prevent a high coke formation during the reaction. Its pilot test was performed with time on stream of 490 hours.

Several studies have been being carried out to develop new catalysts that can be applied for steam reforming of natural gas at a considerably lower temperature, just about 550°C. Chihaia et al. showed that steam reforming of methane could be achieved with the methane conversion of 82% over Ni/CeO_2-Al_2O_3 catalyst at 550°C [6]. Currently, VPI is developing a nano-Ni-based catalyst that brings a high conversion of methane (> 90%) under lower temperature (550°C) in comparison with current industrial conditions for methane reforming.

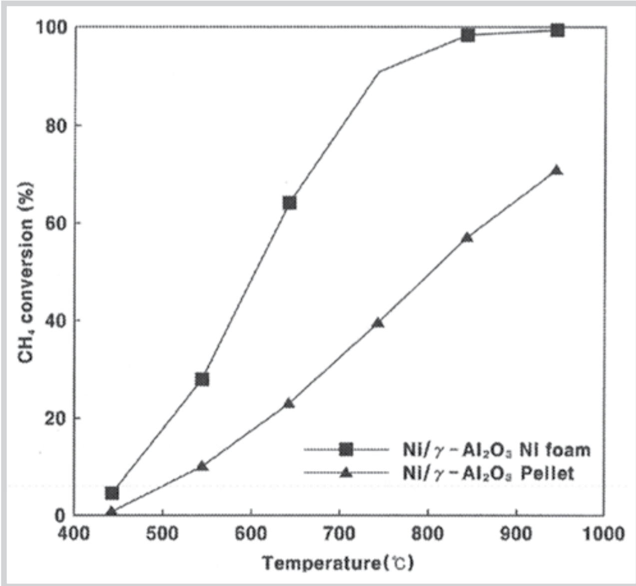

Figure 3. *Comparison of catalyst performance for foam and pellet shaped catalysts during steam reforming of a mixture of CH_4 and CO_2 (GHSV = 10,000^{h-1} and molar ratio for reactants of CH_4:$H_2$0:CO_2 = 1:2:1) [8].*

On the other hand, an integration of structured materials into catalysts for methane steam reforming has also been conducted to enhance the quality of mass and heat transfers inside the reactor, leading to a reduced reactor size or lower reaction temperature. Moon et al. showed that application of foam material into Ni-based catalyst for steam reforming of a mixture of CH_4 and CO_2 could bring a higher conversion of methane than that of conventional catalyst pellet under the same reaction conditions [7]. Figure 3 shows a comparison of catalyst performance for foam and pellet shaped catalysts during steam reforming of a mixture of CH_4 and CO_2. Therefore, application of advanced catalysts could bring high potential to improve energy efficiency during the steam reforming of high-CO_2-content natural gas.

2.3. Co-production of methanol and NH_3 from natural gas containing CO_2 and N_2

Another approach to use Ca Voi Xanh gas for petrochemical production is to produce methanol and NH_3. In this case, neither CO_2 nor N_2 removal is required. N_2 is reacted with part of H_2 in the syngas to produce NH_3, and a mixture of CO, CO_2 and remaining H_2 is a feedstock for methanol production. However, further study needs to be conducted to evaluate the facileness of NH_3 formation under this condition.

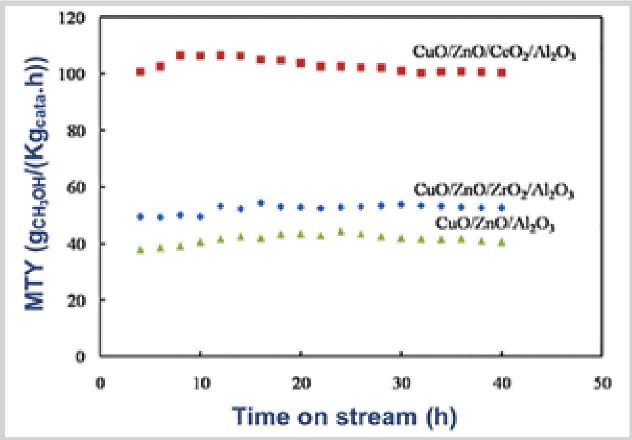

Figure 4. *Methanol yield from direct conversion of CO_2 to methanol over various catalysts (5 bar, 250°C, GHSV = 36,000h^{-1}) [9].*

2.4. Recovered CO_2 for methanol and/or dimethylether (DME) production

In the case that CO_2 is removed from Ca Voi Xanh gas, CO_2 could be considered as a potential carbon supply for methanol and DME production via CO_2 hydrogenation into methanol, and then, followed by methanol dehydration for DME. A one-stage technology is under development for direct DME production from CO_2.

In 2012, VPI conducted a study to develop new catalyst and apply membrane reactor for methanol production from CO_2 to improve its methanol yield. Figure 4 shows methanol yield from direct conversion of CO_2 over various catalysts. As a result, Cu-Zn-Ce-Al based catalyst and NaA based membrane reactor have been found to increase the methanol yield more than 1.5 - 1.7 times compared to the conventional catalyst and reactor for methanol synthesis [9]. A highlight was pointed out that this process only brings profits if a sustainable and reasonable source of hydrogen is supplied. Electrolysation of water using renewable energy could bring a good supply of hydrogen. This direction is highly potential for Vietnam because of its advantages in solar power production [10].

3. Conclusions

Ca Voi Xanh gas contains high contents of impurities, namely H_2S, CO_2 and N_2. Orientations for treatment and deep processing of Ca Voi Xanh gas include (1) CO_2 and/or N_2 removal using membrane technology; and (2) bi-reforming of Ca Voi Xanh gas to produce NH_3 and/or syngas that can then be used as feedstock for methanol production. Recovered CO_2 can be considered as a potential carbon supply for methanol and DME production if a sustainable and reasonable source of hydrogen is supplied. Development of new materials and catalysts brings opportunities for efficient processing of Ca Voi Xanh gas. It has been found that zeolite-based membrane creates a good separation of CO_2 and/or N_2 from a mixture of CH_4, CO_2, and/or N_2, and that nano-Ni-based catalyst brings a high conversion of methane (> 90%) under lower temperature (550°C) in comparison with current industrial conditions for methane reforming.

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