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Orientations for efficient treatment and processing of high CO_2 content natural gas resources in Vietnam

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Summary

CO_2-rich natural gas sources are popular in Vietnam, with their CO_2 contents in the range of 10 - 60 mol%. Based on various CO_2 contents of natural gas sources, a certain number of technologies are recommended for their wise uses. If the gas contains less than 10 mol% of CO_2, it can be used where urea production. In the case where its CO_2 content is up to 25 mol%, methanol and dimethyl ether (DME) production could be considered. Gas with CO_2 content of up to 50 mol% could be a good feedstock for carbon nanotube (CNT) production. On the other hand, if gas contains more than 50 mol% of CO_2, CO_2 removal should be an option, and separated CO_2 could be used as feedstock for production of various products, including methanol, DME, and CNTs.

Key words: CNTs, CO_2-rich natural gas, DME, methanol, urea.

1. Introduction to CO_2-rich natural gas sources in Vietnam

Vietnam is in the region of CO_2-rich gas fields. It currently holds 700 billion cubic metres of proved natural gas reserves [1]. A number of gas fields have been discovered with high reserves but their gas composition contains a significant amount of CO_2, ranging from 10 - 60 mol%. In 2011, the biggest gas field, Ca Voi Xanh, was discovered with the reserves of more than 150 billion cubic metres of natural gas [2]. However, Ca Voi Xanh gas has a high contents of impurities, especially CO_2. Table 1 shows its hydrocarbon and non-hydrocarbon composition.

Besides Ca Voi Xanh, other gas fields and wells have also been found with high contents of CO_2, including Block B, Ca Ngu Vi Dai, Ca Map Trang, and some wells in the Southern Song Hong basin. The presence of CO_2 in gas composition decreases its quality due to its low heat value and related issues during its storage, transportation and processing. In Vietnam, more than 80% of natural gas is currently used for power production. It can be seen that these CO_2-rich gas sources are not ideal for this usage because CO_2 is a zero-heat-value component. However, CO_2 consists of carbon and oxygen elements that are present in the composition of chemicals used in industries and civil life. In fact, CO_2 should be considered a resource rather than a waste. Therefore, it is interesting and important to determine suitable ways for efficient use of these gases via technologies that can process both hydrocarbons and CO_2 into high-value products. In this paper, suitable technologies for natural gas processing in relation to its CO_2 content are recommended. Their maturity is also pointed out.

Table 1. *Composition of Ca Voi Xanh gas [2]*

Component	Composition (mol%)
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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2. Natural gas with its CO_2 content up to 10 mol% - A feedstock for urea production

Urea (NH_2CONH_2) is of great nutrition to soil as a nitrogen-rich fertiliser. Natural gas is one of the important feedstocks to produce hydrogen that is used for ammonia synthesis in urea production. The transformation of natural gas with methane as a representative component into urea is described by Equations 1 - 6.

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \quad (1)$$

$$CH_4 + 2H_2O \rightleftharpoons CO_2 + 4H_2 \quad (2)$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \quad (3)$$

$$3H_2 + N_2 \rightleftharpoons 2NH_3 \quad (4)$$

$$2NH_3 + CO_2 \rightleftharpoons NH_2COONH_4 \quad (5)$$

$$NH_2COONH_4 \rightleftharpoons NH_2CONH_2 + H_2O \quad (6)$$

In fact, natural gas accounts for more than 95% of ammonia production worldwide [3]. Ammonia and urea have been produced in large quantities from natural gas since 1950s. Therefore, it is a mature and widely implemented technology with minimal technology risk [3]. For urea synthesis, CO_2 is needed (in addition to ammonia) and commercial processes are available for processing high-CO_2-content gas feedstock, such as Haldor Topsoe, Uhde, KBR. Based on a carbon balance for the whole urea production, a natural gas containing 8 mol% of CO_2 is a good feedstock for urea production such as in the case of the Ca Mau Fertilizer Plant, Vietnam.

3. Natural gas with its CO_2 content of 10 - 25 mol% - A feedstock for methanol and dimethyl ether (DME) production

If the natural gas contains 10 - 25 mol% of CO_2, it is a preferable feedstock for methanol and dimethyl ether (DME) production. CO_2 is needed for methanol synthesis as described by the following equation:

$$3CH_4 + CO_2 + 2H_2O \rightleftharpoons 4CH_3OH \quad (7)$$

Stoichiometrically, it can be seen that a mixture of CH_4 and CO_2 with its molar ratio of 3 (i.e. gas contains 25 mol% of CO_2) is the right feedstock for methanol production. Methane reforming for methanol production is a well developed and implemented technology. It is worthy to notify that the presence of CO_2 in the natural gas brings two impacts: (1) enhancement of coke formation during the reforming; and (2) contribution to methanol synthesis. In order to overcome reforming catalyst deactivation due to fast coke formation, two solutions could be considered: (1) increase in the ratio of steam/C used; or (2) development of new generation catalyst based on noble metal. Haldor Topsoe has established a chart showing the relationship between the ratios of steam/C and CH_4/CO_2 with coke formation during methane reforming (Figure 1). In 2014, Haldor Topsoe demonstrated a pilot plant to perform a bi-reforming of CH_4 - CO_2 mixture using a noble metal-based catalyst with a reduced ratio of steam/C without significant coke formation in Brazil [4].

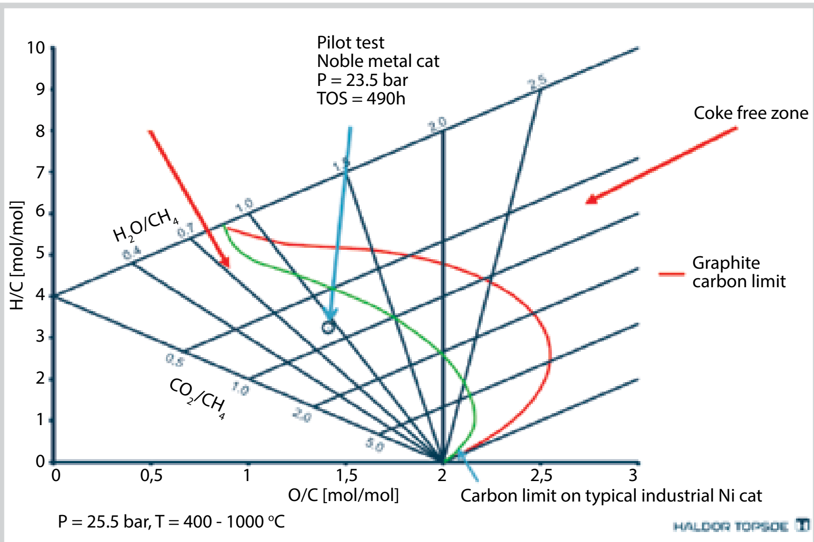

Figure 1. *Relationship between the ratios of steam/C and CH_4/CO_2 with coke formation (used with Haldor Topsoe's permission) [4].*

Recently, DME has been promoted as an alternative fuel for LPG and diesel. In industry, DME can be produced via one of the two routes: (1) one-step process using a direct conversion of syngas into DME in a single reactor; or (2) two-step process using methanol synthesis and DME synthesis in separate reactors [5]. DME production processes are relatively well established with a number of technology licensors, including Haldor Topsoe, JFE Ho., Korea Gas Co., Air Products, and NKK for the one-step process, and Toyo, MGC, Lurgi, Uhde for the two-step process.

It is interesting to develop a new process that can transform CO_2-rich natural gas into methanol and DME in the one-step process as described by the following equations:

$$CH_4 + CO_2 \rightleftharpoons CH_3OH + CO \quad (8)$$

$$2CH_4 + 2CO_2 \rightleftharpoons CH_3OCH_3 + CO + H_2O \quad (9)$$

Until now, this route has only been performed in lab scale due to very low methanol yield (<5%) [6]. Accordingly, an equimolar mixture of CH_4 and CO_2 is converted into methanol under non-thermal plasma condition (600 - 1000°C and atmospheric pressure) without catalyst. It is expected that the integration of an acidic catalyst into the system will promote this conversion for DME formation.

4. Natural gas with its CO_2 content of 25 - 50 mol% - A feedstock for dry reforming and carbon nanotube (CNT) production

For natural gas sources containing up to 50 mol% of CO_2 in their gas composition, carbon nanotube (CNT) production could be an option. In fact, a natural gas with its molar ratio of CH_4 and CO_2 of approximately 2 is a good feedstock for CNT production via methane decomposition pathway. CNT is applied in various areas, including plastics, electronics, fuels, and batteries. CNT's current sale price varies in a wide range and can be well above USD 1,000/gram depending upon its quality and application. This value is much higher than that of amorphous carbon. The market for CNTs is predicted to be 20,000 tons/year by 2022 [7].

Methane decomposition is described by the following equation:

$$CH_4 \rightleftharpoons C + 2H_2 \tag{10}$$

The presence of CO_2 in the feedstock has been shown to bring benefits to CNT formation. Accordingly, both CNT yield and its quality are enhanced [8 - 10]. CO_2 is assigned to participate in a series of reactions, including methane dry reforming, Boudouard, and reverse water-gas shift to produce steam that has been well known as a good agent to remove defects during CNT production [8]. As a result, a natural gas containing approximately 33 mol% of CO_2 can be a good feedstock for CNT production as described by the following reactions:

$$2CH_4 + CO_2 \rightleftharpoons 3C + 2H_2 + 2H_2O \tag{11}$$

$$2CH_4 + CO_2 \rightleftharpoons 2C + 3H_2 + CO + H_2O \tag{12}$$

For gas containing 50 mol% of CO_2, that will be the great to process it without CO_2 removal. In this case, a technology to convert both hydrocarbon and CO_2 is needed. A process to satisfy this requirement is dry reforming. Equation (13) shows how an equimolar mixture of methane and CO_2 can be transformed into a mixture of CO and H_2 known as syngas, which is an important feedstock for petrochemical synthesis and H_2 production.

$$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2 \tag{13}$$

Dry reforming is considered an environmentally friendly syngas production route. It was estimated that the production cost of methanol using dry reforming is lower than using the traditional steam reforming [13]. This process has been studied for a long time in the lab but cannot be implemented in the industry due to its strong coke formation, leading to fast catalyst deactivation. However, in 2015, it was reported that the Linde Group officially opened a dry reforming pilot facility in Germany [13]. The following reactions are responsible for coke formation during methane dry reforming.

$$CH_4 \rightleftharpoons C + 2H_2 \tag{14}$$

$$2CO \rightleftharpoons C + CO_2 \tag{15}$$

Recently, this process has drawn interests back again for CNT production. Braga et al. reported the appearance of CNTs in coke formed during methane dry reforming [11]. It has been found that a high CO_2 conversion and high carbon yield can be achieved with a mixture of CH_4 and CO_2 with its molar ratio of 2 as feedstock. In comparison with methane decomposition, dry reforming results in much lower CNT yield but its CNT owns higher quality and is formed at a lower temperature [12]. In order to bring this process into the industry, a number of issues need to be solved, including: (1) enhancement of CNT yield and catalyst life; and (2) development of a reactor type that is more effective for CNT collection and catalyst regeneration.

It is worth noting that CNT production via both pathways also produces hydrogen that can be sold for refineries, and hence, increases its economic efficiency. Nowadays, CNT is commercially manufactured from ethylene at not large capacities with high production cost due to difficulties of CNT purification and its quality control. CNT production from methane as feedstock has been reported at lab scale but only a few papers mentioned the impact of CO_2 during CNT formation. Therefore, in order to add more value to CO_2-rich natural gas sources of Vietnam, it is important to develop an efficient process to transform both CO_2 and hydrocarbons into CNTs.

5. CO_2 - A feedstock for CNT, methanol and DME production

Natural gas contains more than 50 mol% of CO_2 should be considered for CO_2 removal, then the treated gas can be processed by traditional technologies. CO_2 separated from CO_2-rich natural gas, along with other CO_2-rich sources such as flue gas from power and fertiliser plants, can be feedstocks to produce dry ice and liquid CO_2 for the food industry. Besides, it can also be used for production of a number of products, including methanol, methane, dimethyl ether (DME), and carbon nanotubes (CNTs). Figure 2 shows possible pathways for CO_2 use, including storage, direct use and conversion into chemicals.

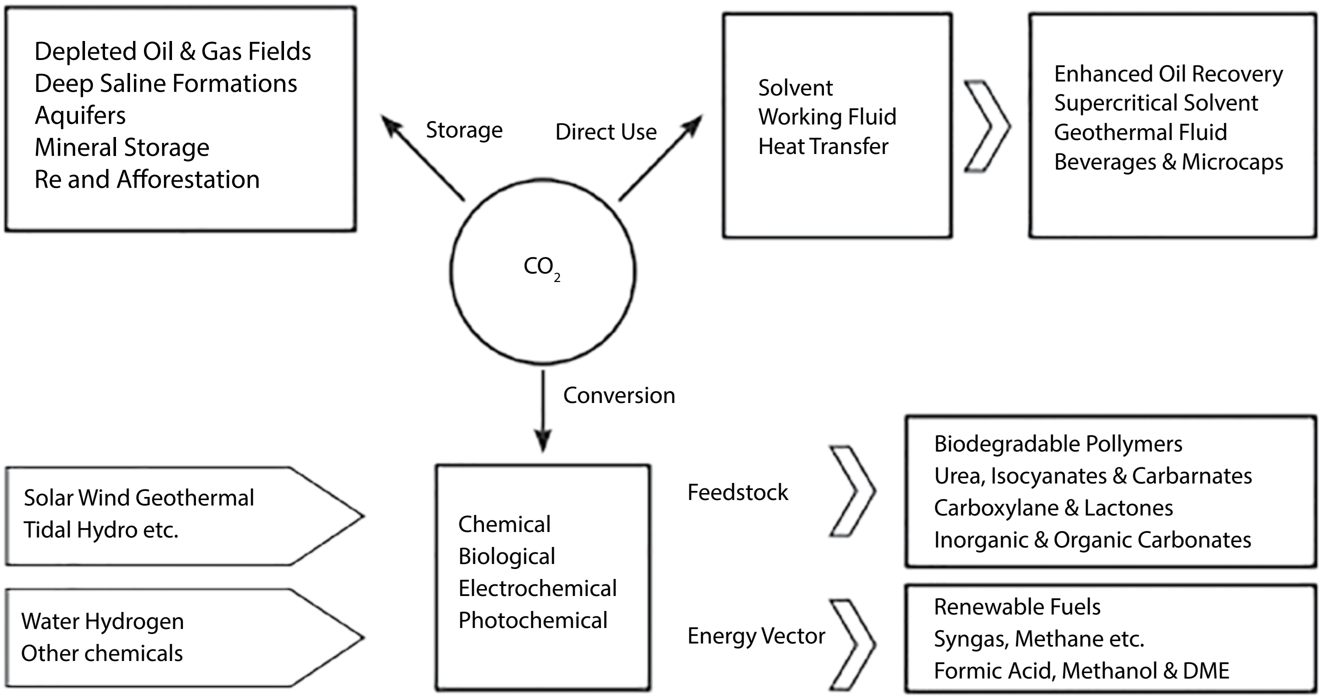

Figure 2. *Possible pathways for CO_2 use [13].*

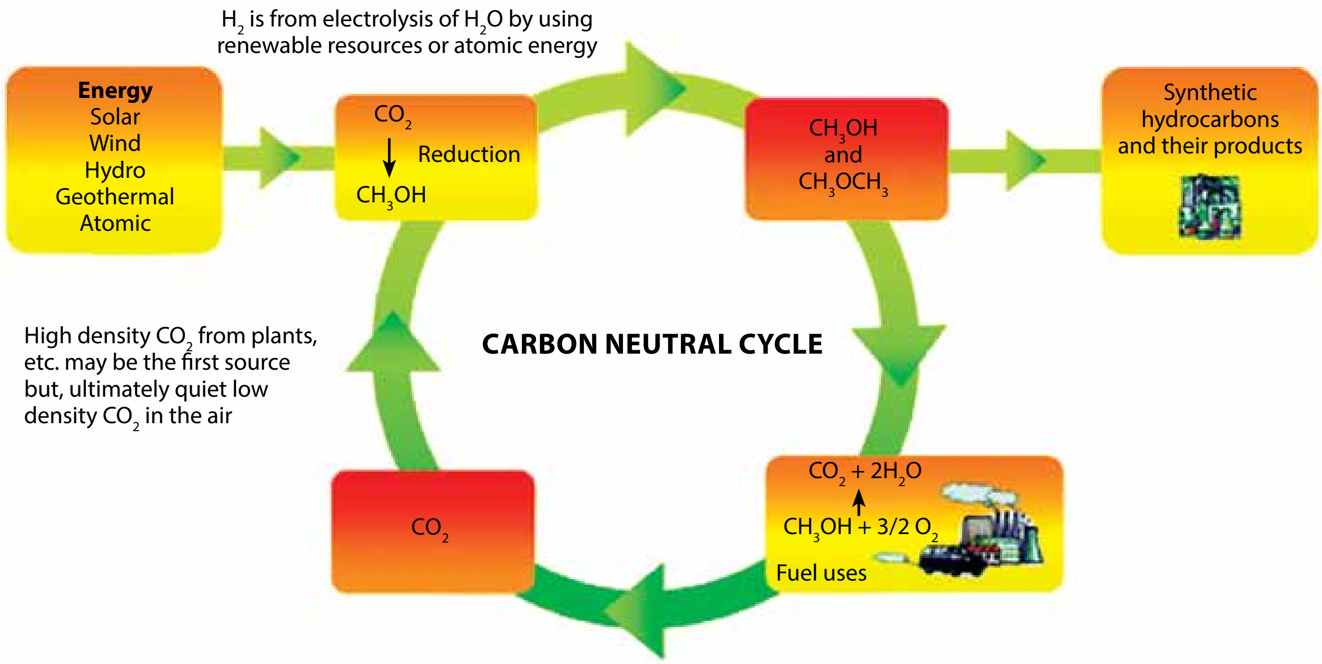

Figure 3. *A methanol economy was proposed by Olar et al. [14].*

Methanol is an important feedstock for petrochemical production or alternative fuel. Via a series of commercial technologies, namely MTO (methanol-to-olefins), MTP (methanol-to-propylene), MTA (methanol-to-aromatics), and MTG (methanol-to-gasoline), methanol serves well for both petrochemical and fuel industries. On the other hand, methanol is also used directly as an alternative fuel in some countries. In fact, a methanol economy was proposed by Olar et al. [14]. Directions of this economy are illustrated in Figure 3, thus, there is an interest in transforming CO_2 into methanol. A large number of research groups are participating in this subject [15 - 18]. In 2013, the Vietnam Petroleum Institute (VPI) carried out a study to hydrogenate CO_2 into methanol using a membrane reactor and a multifunctional catalyst. It has been shown that both membrane reactor and multifunctional catalyst bring positive impacts on the CO_2 conversion and methanol yield [19 - 20]. However, this

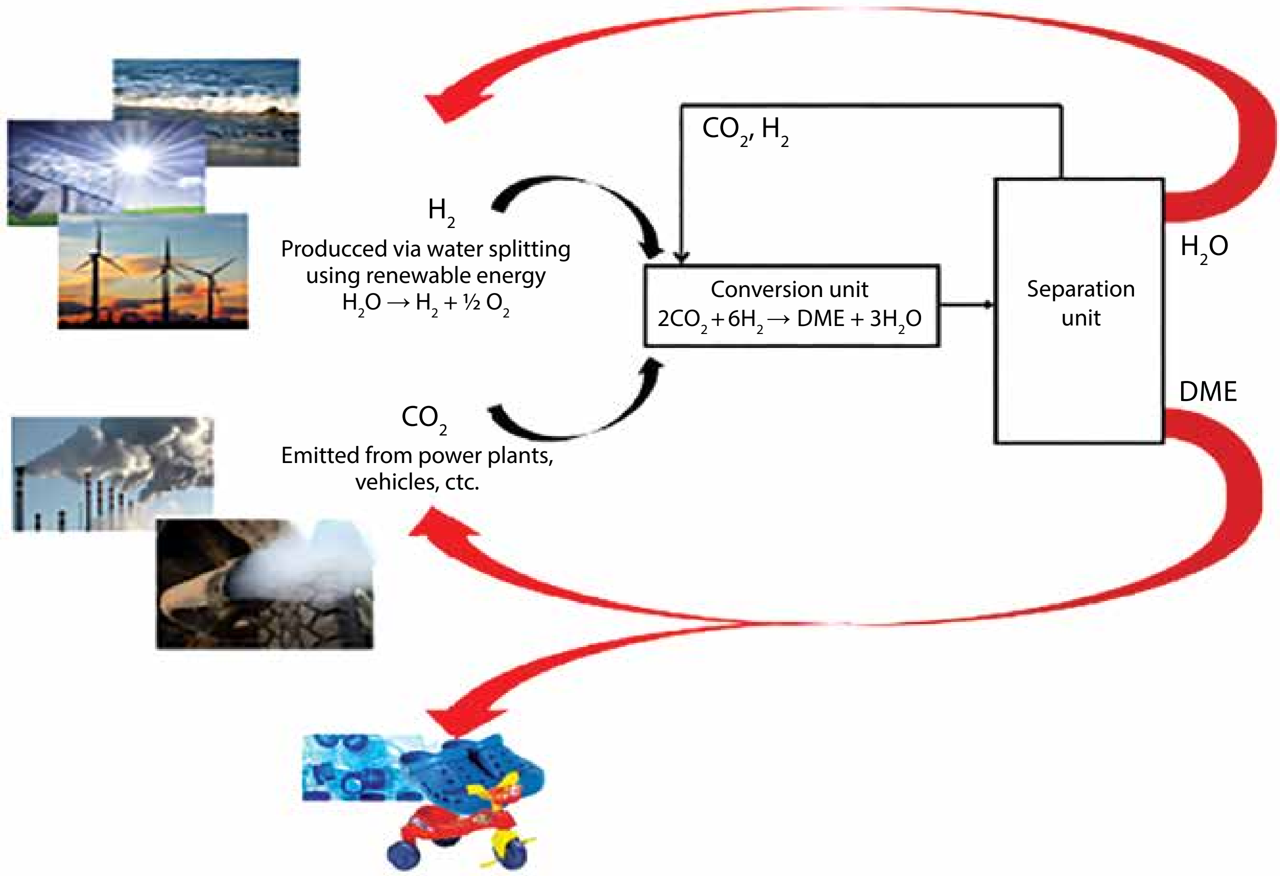

Figure 4. *A "zero-CO_2 emission" concept from DME [22].*

process is not economic due to the high cost of hydrogen consumption. In 2011, a semi-commercial methanol plant with the capacity of 4,500 tons/year was commissioned in Iceland, using CO_2 and H_2 as feedstock [21]. Cheap H_2 is supplied by water splitting using available geothermal energy in Iceland. It has been reported that the CO_2-to-methanol process will become more realistic when methanol price roughly doubles or hydrogen price decreases almost 2.5 times [13].

Methanol can be dehydrated into dimethyl ether (DME) using a number of commercial processes by licensors such as Haldor Topsoe, Air Products, Lurgi, and Uhde. On the one hand, it is interesting to combine methanol synthesis and methanol dehydration into one step to reduce DME production cost. An integration of acid sites into methanol synthesis could be a solution. Accordingly, along with the usage of renewable energy, this will be a green process and an effective way to store renewable energy as DME [22]. Figure 4 shows a "zero-CO_2 emission" concept from DME. In order to bring this concept into the industry, the following issues need to be solved, including the supply of cheap hydrogen, water-resistant catalyst, and efficient water separation.

On the other hand, CO_2 can also be used to synthesise high-value products, such as carbon nanotubes (CNTs). This is a highly potential direction to add more value to CO_2. There is no evidence that CNTs can be synthesised from CO_2 until the report by Motiei et al. in 2001 [23]. CO_2 can be transformed into CNTs using the following methods: (1) supercritical CO_2; (2) reduction of CO_2 over oxygen-deficient ferrite catalysts (ODF); (3) reduction of CO_2 over supported and unsupported transition metal catalysts; and (4) CO_2 electrolysis using molten salts [24 - 25]. The electrolysis method seems to be the most efficient route for CNT production from CO_2. In 2017, the team of George Washington University, US, developed a process named C2CNT that can electrolyse CO_2 into CNTs and O_2 [25]. C2CNT technology directly removes, transforms and stores CO_2 in various concentrations: 5% CO_2 (removed from the air without preconcentration), 12.5% CO_2 (removal of coal power plant CO_2 emissions), 33% CO_2 (complete removal of CO_2 from cement production plants), or 100% [26]. It is planned to construct a demonstration unit of C2CNT with a capacity of 5 tons/day of CO_2 at a power plant in Alberta, Canada [26].

6. Conclusion

A number of CO_2-rich natural gas sources have been discovered in Vietnam, with their CO_2 contents in the range of 10 - 60 mol%. Therefore, processes to efficiently convert both hydrocarbons and CO_2 are required. Based on various CO_2 contents of natural gas sources, a number of technologies are recommended for their wise uses. If the gas contains less than 10 mol% of CO_2, it can be used for urea production. In the case where its CO_2 content is up to 25 mol%, methanol and DME production could be considered. Gas with its CO_2 content of up to 50 mol% could be a good feedstock for CNT production. On the other hand, if gas contains more than 50 mol% of CO_2, CO_2 removal should be an option, and separated CO_2 could be used as feedstock for production of various products, including methanol, DME, and CNTs. While the maturity of technologies has been investigated, further techno-economic and environmental assessments should be performed for each case.

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