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Approaches to enhance the value of Ca Voi Xanh gas via its transformation into nanocarbon materials

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Summary

Ca Voi Xanh gas has high contents of impurities, namely H_2S, CO_2 and N_2. The transformation of this gas into high-value products is a potential approach to enhance its value without pre-treatment. In fact, it is a promising feedstock for nanocarbon production, including carbon nanotubes (CNT) and carbon nanofibres (CNF). Their applications can be found in various areas of which markets are promising. Two methods for nanocarbon production can be considered, namely methane decomposition and dry reforming of methane. Methane decomposition brings higher nanocarbon yields while dry reforming of methane can produce better quality nanocarbon products. A number of issues need to be solved before these processes can be commercialised, such as improvements of nanocarbon yields and their recovery methods.

Key words: Ca Voi Xanh gas, carbon nanotubes, carbon nanofibres, methane decomposition, dry reforming.

1. Introduction

In 2011, Ca Voi Xanh gas field was discovered about 100km off the coast of the central region of Vietnam. Its reserve was found more than 150 billion m^3 of natural gas. However, its gas composition consists of 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 this gas contains significant contents of undesired components, including 0.21% of H_2S, 9.88% of N_2 and 30.26% of CO_2. As fuel for power generation, the gas will be treated for H_2S removal so that its remaining H_2S content is less than 30ppm. On the other hand, CO_2 and/or N_2 removal should be considered upon its uses and available technologies for its treatment and deep processing. It is, therefore, interesting and significant to develop new technologies that can transform Ca Voi Xanh gas into high-value products without pre-treatment for CO_2 and/or N_2 removal.

Table 1. Composition of Ca Voi Xanh gas

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

A potential approach to enhance the value of Ca Voi Xanh gas is to transform it into high-value products such as carbon nanotubes (CNT) and carbon nanofibres (CNF). Nanocarbon materials can be produced from hydrocarbons, oxygens, and even CO_2. One of the popular feedstocks for CNT production is methane. In terms of economy, a preliminary estimation shows that dry reforming of methane and methane decomposition are possible approaches to compete with the current method of hydrogen production using steam reforming of methane if the values of CNT and CNF as by-products are included [2]. In fact, by this approach, Ca Voi Xanh gas can be processed without any pre-treatment for CO_2 and N_2 removal. However, a number of issues need to be resolved before it can be commercialised, including the improvement of feed conversion and nanocarbon selectivity, as well as recovery methods. Therefore, it is important to investigate the potential of transformation of this gas into nanocarbon materials.

2. Markets for nanocarbon materials

The world demand for CNT was 5,000 tons/year in 2014 and predicted to be 20,000 tons/year by 2022. CNT's

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Table 2. Market analysis for various carbon products [3]

Type of carbon	Types of applications	Expected price for carbon	Size of the market (current/ projected)	Corresponding hydrogen production(a)
Carbon black	Tires, printing inks, high-performance coatings and plastics	USD 0.4 - 2+/kg depending on product requirements	U.S. market • ~2M MT (2017) Global market • 12M MT (2014) • 16.4M MT(2022)	U.S. market • 0.67M MT Global market • 4M MT (2014) • 5.4M MT (2022)
Graphite	Lithium-ion batteries	USD10+/kg	Global market • 80K MT (2015) • 250K MT (2020)	Global market • 27K MT (2015) • 83K MT (2020)
Carbon fibre	Aerospace, automobiles, sports and leisure, construction, wind turbines, carbon-reinforced, composite materials and textiles	USD 25 - 113/kg depending on product requirements	Global market • 70K MT (2016) • 100K MT (2020)	Global market • 23.3K MT (2016) • 33.3K MT (2020)
Carbon nanotubes	Polymers, plastics, electronics, lithium-ion batteries	USD 0.10 - 600/gram depending on application requirements	Global market • 5K MT (2014) • 20K MT (2022)	Global market • 1.7K MT (2014) • 6.7K MT (2022)
Needle coke	Graphite electrodes for electric arc steel furnaces	~USD 1.5/kg	Global market • ~1.5M MT(2014)	Global market • ~0.50M MT (2014)

(a) Based on stoichiometric ratio of carbon to hydrogen present in methane. Does not take into account process efficiency or use of hydrogen to provide process heat or loss of hydrogen during hydrogen recovery.

sale price is in the wide range of USD 0.1 - 600/gram depending upon its quality and application [3]. For high quality SWCNT (single-walled CNT), the market price can be well above USD 1,000/gram. Applications of CNT can be found in various areas, including plastics, electronics, and batteries, etc. The global demand for CNF is even higher than for CNT, with 70,000 tons/year in 2016 and is forecasted to be 100,000 tons/year by 2022. The sale price of CNF is in the range of USD 25 - 113/kg [3]. CNF can be used in various industries such as energy, materials, aerospace, textiles, and construction, etc. Table 2 shows market analysis for various carbon products.

The CNT market is predicted to grow from USD 3.95 billion in 2017 to USD 8.7 billion by 2022 [4]. A certain of current CNT producers can be listed as Arkema S.A. (France), Arry International Group Ltd. (China), Carbon Solutions Inc. (US), Cheap Tubes Inc. (US), CNano Technology Ltd. (US), CNT Company Ltd. (South Korea), Hanwha Chemical Co. Ltd. (South Korea), Hyperion Catalysis International Inc. (US), Kumho Petrochemical Company Ltd. (South Korea), Nano-C Inc.(US), Nanocyl S.A. (Belgium), NanoIntegris Inc. (US), NanoLab, Inc. (US), Nanoshell LLC (US), Nanothinx S.A. (Greece), Showa Denko K.K. (Japan), SouthWest NanoTechnologies Inc. (US), Thomas Swan & Co. Ltd. (UK), and Toray Industries, Inc. (Japan). Currently, the United States, China, and Turkey are the top countries in CNT production with productivity of 34%, 32%, and 12%, respectively [3].

3. Methods to transform natural gas into nanocarbon materials

Being a valuable material, it is evident that much focus in academia and industry is on the synthesis of this material, especially from abundant sources such as natural gas. Based on methane or natural gas as feedstock, CNT and CNF can be produced in two ways: (1) methane decomposition; (2) dry reforming [4 - 10]. These processes also generate hydrogen or syngas that can be used as feedstock for refineries and petrochemical plants.

3.1. Methane decomposition

To date, CNT is often produced via arc discharge, laser ablation or catalytic chemical vapour deposition (CCVD). Of these approaches, CCVD is the most promising for medium scale production due to its high yield of CNT from the precursor, low energy cost and good controllability [10]. Currently, CNT and CNF production is mainly based on methane decomposition (Equation 1). It has been found that selectivity to CNT and CNF is 50 - 70% and depends on feed purity, reaction temperature, and catalyst nature. From Table 1, it can be seen that Ca Voi Xanh gas owns very low concentration of C_{2+} hydrocarbons, therefore, it seems to be an ideal feedstock for high quality CNT and CNF production.

$$CH_4 \rightarrow C + 2H_2 \qquad (1)$$

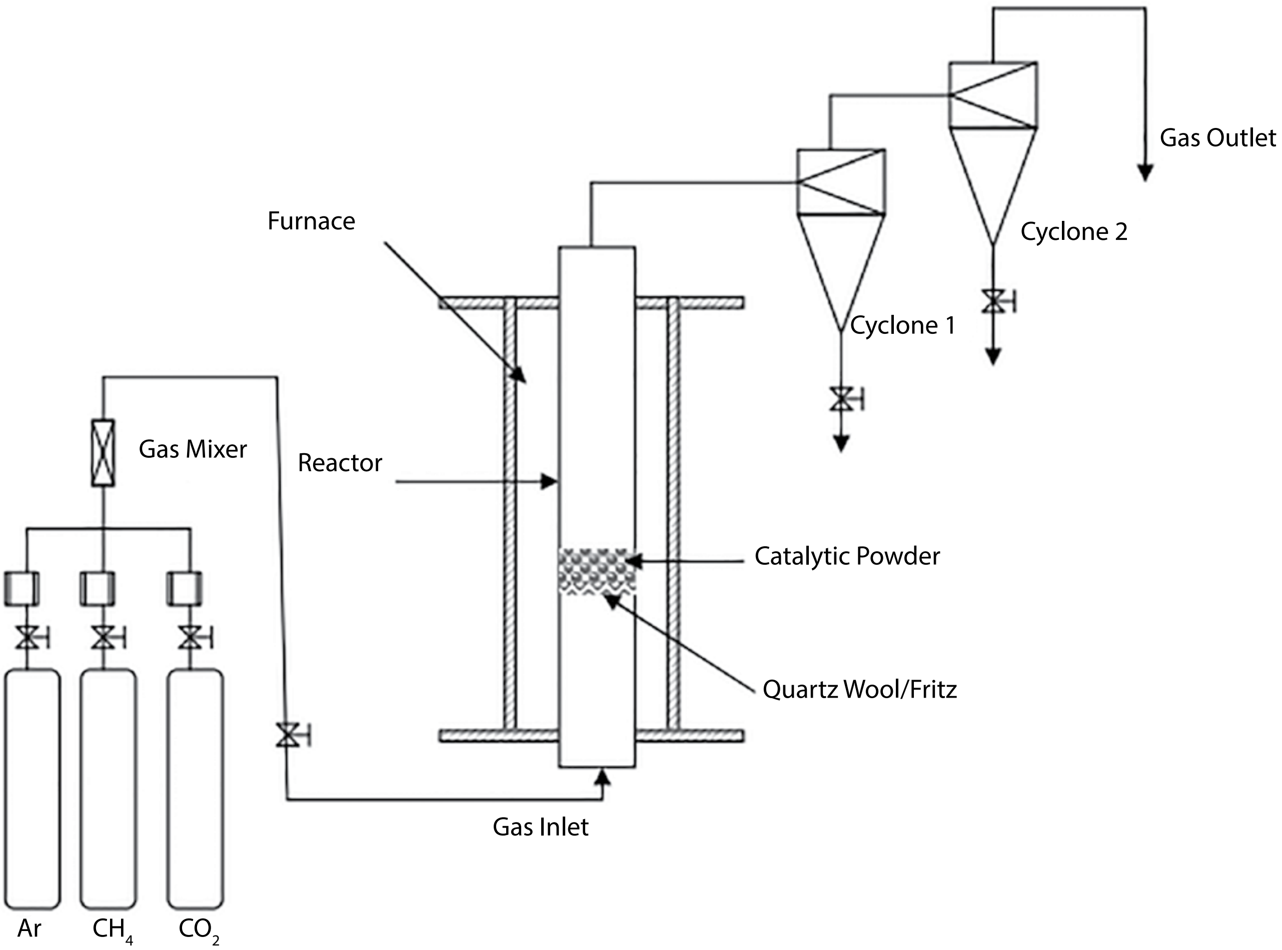

Figure 1. *Diagrammatic representation of the CCVD for CNT production [11].*

The CCVD process of natural gas principally involves the decomposition of methane molecules to form deposited carbon and hydrogen gas, which is a valuable by-product. Due to strong C-H bonds, this decomposition process is typically conducted inside the range of 750 - 1,000°C [11, 12]. It is well known that CNT is formed at elevated temperature, whilst carbon nanofibres (CNF) is formed at lower temperature. This fact is explained by the competition between carbon nucleation step on the catalytic surface and diffusion of carbon atoms along the formed CNT. A diagrammatic representation of the CCVD is illustrated in Figure 1.

Main catalysts used in the synthesis of CNT are Ni, Fe and Co because these materials are economical, catalytically active and having good carbon solubility [9, 12]. Particularly for Ni, the formation of amorphous carbon at high temperature is an issue which requires special design of carrier phase [13]. Depending on the strong or weak interaction between catalytic particles and carrier phase, base-growth (e.g. most Fe-based catalysts) or tip-growth are the two widely accepted mechanisms for the formation of CNT. The use of substrate with well-defined distribution of catalytic particle sizes successfully permits the alignment and diameter control of SWCNT growth from ethylene [14] and highly pure methane [15]. Synthesis of SWCNT from methane was also reported at "soft" conditions (i.e. 680°C) using Fe and promoter Mo on alumina as catalyst, though the product yield (by catalyst weight) is only about 20% [16]. Production of CNT from usual catalyst powder is possible, but potential drawbacks are the lack of directional control and additional purification step, which can be time-consuming. Growth of CNT from metal-free substrate such as SiO_x or SiC is attractive since metal impurities in end products are low but the underlying mechanism is less well understood [17, 18].

Although the presence of CO_2 in the feedstock reduces carbon yield during CCVD process, the following benefits are also included: (1) CNF selectivity is increased because amorphous carbon is removed; (2) required temperature for CNF formation is lowered, from higher than 700°C down to 600°C; and (3) smaller tube diameter and improved oxidative properties of the CNF/CNT products [8]. It has been found that feed with an equal molar ratio of CH_4/CO_2 brings the best result. In addition, if the reaction is carried out at 700°C, CNT is found to be the main nanocarbon product. However, several challenges still need to be addressed before CNT production technology reaches maturity, for example the selective growing of metallic or semi-conducting CNT, control of wall number, chirality and defects in the final products [18]. Ca Voi Xanh gas contains approximately 30% of CO_2, it is therefore worthy to investigate its transformation into CNF and CNT products.

3.2. Dry reforming of methane

Dry reforming of methane has been studied for syngas production (Equation 2) but could not be commercialised due to strong coke formation, leading to fast catalyst deactivation.

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \qquad (2)$$

Recently, this process has been interested in the aspect of CNT and CNF production. This process generates high-quality nanocarbon products but its conversion is much lower than methane decomposition [8]. Therefore, it is necessary to develop more effective catalysts and nanocarbon recovery methods. Compared with the way of methane decomposition, dry reforming can be carried out at lower temperature and produce syngas as feedstock for petrochemical industry. Table 3 shows results for CNT production by various methods.

It has been reported that factors, namely ratio of CH_4/CO_2, reaction temperature, and catalyst composition, have significant influences on CNT yield and quality during dry reforming of methane. The optimum condition for the best result was obtained at the CH_4/CO_2 ratio of 2.125, temperature of 700°C, and Ni-based catalyst [5]. Thus, Ca Voi Xanh gas is a good candidate as feedstock for this process. Similar to CCVD, there are still a number of issues to be resolved so that this process can be commercialised, including: (1) development of new catalysts that lower the reaction temperature to below 700°C and improve conversions of CH_4 và CO_2 for CNT formation, as well as catalyst life; (2) development of effective methods of nanocarbon recovery; and (3) controllability of product physical and chemical properties.

4. Applications of nanocarbon materials

CNT has promising applications in development of materials science, electronic products and medical engineering. Because CNT is a good conductor, the material has been commercially used as a conducting additive for lithium-ion battery anode and cathode. Furthermore, loading of iron oxide into multi-walled CNT

Table 3. *A summary of various methods of CNT production [19]*

Synthesis method		Reaction catalyst	Conditions	Products
Dry reforming reactions	CH_4 dry reforming	NiAl, NiAlMg, NiAlCe, NiAuAl, NiPtAl, NiAuPtAl, NiAuPtAlMg, NiAuPtAlCe	750°C, 1atm pressure, 24 hours long run test	9.48wt% bamboo-like CNTs on NiAuPtAl
	Glycerol dry reforming	Ni/Al_2O_3, 3wt% $La\text{-}Ni/Al_2O_3$, 5wt% $La\text{-}Ni/Al_2O_3$	750°C, 1atm pressure	55wt% and 30wt% bamboo-like CNTs on Ni/Al_2O_3 and 5wt% $La\text{-}Ni/A1_2O_3$
Hydrocarbon thermal decomposition	Methane thermal decomposition	Ni nanoparticles	930°C, 1atm pressure	86wt% - 87.5wt% bamboo-like CNTs on Ni nanopartides
		$Ni\text{-}Cu/Al_2O_3$	720 - 770°C, 1atm pressure	0.7 - 33mg C/mg Ni bamboo-like CNTs on $Ni\text{-}Cu/Al_2O_3$
		Ni and Ni-Cu alloys	750°C, 1atm pressure	407g C/g Ni bamboo-like CNTs on $Ni_{47}Cu_{53}/CNT$
Special chemical vapor deposition	Catalytic chemical vapor deposition	$LaNiO_3$ perovskite	800°C and 900°C, 1atm pressure	68.8wt% and 49.3wt% bamboo-like CNTs on $LaNiO_3$
	Detonation-assited chemical vapor deposition	Ni nanopartides with the doping of sulfur	900°C, 40MPa pressure	High quality bamboo-like CNTs on Ni without S
	Microwave plasma enhanced chemical vapor deposition	Thermally oxidised silicon substrates with a platinum thin film catalyst	1,000°C, 2,780Pa pressure	Vertically aligned bamboo-like CNTs on Pt film
Pyrolysis and gasification of plastic	Pyrolysis of low density polyethylene feedstock	Nickel, iron, cobalt and copper catalysts	800°C, 1atm pressure	45.7mg C/g plastic and ~180mg C/g plastic bamboo-like CNTs on Ni/Al_2O_3 and Fe/Al_2O_3

(MWCNT) has shown stable and high specific capacity after many cycles [19]. Protocol for development of field-effect transistor based on SWCNT has even been proposed, but widespread applications are yet to be seen due to inconsistent electrical performance [20, 21]. CNT can also be used as cathode in high-performance Field-Emission Lamp (FEL) thanks to the material's excellent conductivity and mechanical/chemical stability. In addition, the CNT-based cathode has low energy consumption, good efficiency and is able to generate different colours [21].

Thanks to exceptional stiffness and strength, CNT holds great promise for fabrication of nanoelectromechanical systems (NEMS), including mass/force sensors and actuators. Another area for potential application of CNT is biomedical engineering such as drug delivery system and tissue engineering scaffolds [22]. Especially regarding the latter, the inclusion of CNT into the natural tissues helps improve material resilience. However, issues of cytotoxicity need to be resolved to ensure safe applications of CNT-based components in human body. Combination of engineered polymers and MWCNT is another area which currently attracts attention [2]. Finally, CNT can also be used in paint coating, drilling muds and water purification systems [23].

5. Conclusions

Ca Voi Xanh gas is a promising feedstock for nanocarbon production, including carbon nanotubes (CNT) and carbon nanofibers (CNF). Two methods for nanocarbon production can be considered, namely methane decomposition and dry reforming of methane. Methane decomposition brings higher nanocarbon yield while dry reforming of methane can produce better quality nanocarbon products. However, several challenges still need to be addressed before CNT and CNF production technology reaches maturity, including: (1) development of new catalysts that lower the reaction temperature to below 700°C and improve conversions of CH_4 và CO_2 for CNT and CNF formation, as well as catalyst life; (2) development of effective methods of nanocarbon recovery; and (3) controllability of product physical and chemical properties.

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