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Utilization of Waste Hydrocarbon Gases

V. Arutyunov^{1,2}*, I. Sedov², V. Savchenko², A. Nikitin^{1,2}, A. Arutyunov^{1,3}

 ¹N.N. Semenov Federal Research Center for Chemical Physics, Russian Academy of Sciences, Kosygina 4, Moscow, 119991, Russia
 ²Federal Research Center of Problems of Chemical Physics and Medicinal Chemistry, Russian Academy of Sciences, Semenova 1, Chernogolovka, Moscow oblast, 142432, Russia
 ³Faculty of Computational Mathematics and Cybernetics, Shenzhen MSU-BIT University, Shenzhen 518172, China

Article info	Abstract
Received: 23 March 2023	A variety of natural and anthropogenic sources of hydrocarbon gases make a significant contribution to the global emission of greenhouse gases. Reducing
Received in revised form: 2 May 2023	the anthropogenic emission of industrial hydrocarbon gases is impossible without new technologies that would allow their cost-effective utilization.
Accepted: 16 June 2023	The paper describes a number of new promising technologies based on autothermal gas-phase processes of partial oxidation and oxidative cracking of various hydrocarbons, such as associated petroleum gases, coalbed methane,
Keywords: Natural gas; Petrochemicals; Associated petroleum gas; Coalbed methane; Biogas; Syngas; Methanol; Refinery gases.	refinery gases, and biogas, which open up prospects for a significant reduction in their flaring or emission into the atmosphere. Among the technologies under consideration are those involving their processing for subsequent use in the energy sector and low-tonnage production of various demanded chemicals.

1. Introduction

Natural gas is the most affordable, mobile, and environmentally friendly energy resource on our planet, with which neither renewable energy sources [1] nor hydrogen [2] can compete on the global scale. Its widespread use in petrochemistry and for the production of energy raises the issue of its reliable sources, including those in remote regions, as well as the rational use of its diverse unconventional resources, such as associated petroleum gas (APG), coalbed methane, refinery gases, biogas and others. In addition, the high greenhouse impact of hydrocarbon gases, primarily methane, which is 28 times higher than that of CO₂ [3], and the possibility of their serious climate feedback [4] require maximum utilization of all potential sources of their emission into the atmosphere. This is not an easy task, given that hydrocarbon gases of various compositions

*Corresponding author.

E-mail address: v_arutyunov@mail.ru

are formed in many natural geological and biological processes, as well as in various industrial and agricultural processes.

In contrast to CO₂ emissions, the anthropogenic contribution of which is still two orders of magnitude lower than the natural, for methane emission the picture is the opposite. In the 2008-2017 decade, the global CH₄ emissions constituted 576 Tg/ yr, with \sim 60% of it being of anthropogenic origin [3]. For this decade, the global mean emissions from fossil-fuel-related activities, including transport, were estimated as 128 Tg/yr, which accounts for 35% of the total anthropogenic emissions [3]. Although its proportion is lower than global emissions from agriculture and waste over this period, which adds up to 206 Tg/yr constituting 56% of total anthropogenic emissions [3], it is very significant. Thus, the development of methods for the utilization of hydrocarbon gases to prevent their emission into the atmosphere is an important part of the global problem of reducing greenhouse gas emissions.

Note, however, that the problem is complicated by the fact that the vast majority of natural and anthropogenic sources of hydrocarbon gases have a low flow rate, a factor that makes their accumulation, transportation or processing by existing largescale industrial methods unprofitable. This is the main reason for the ongoing flaring of APG [5, 6], the global volume of which, despite all the efforts made, has not been reduced in the last decade, remaining at the level of ~140 billion m³/yr (Fig. 1).

Until now, a significant part of valuable petrochemical raw materials, such as refinery gases, containing, in addition to alkanes, a significant concentration of unsaturated hydrocarbons and hydrogen has not been used. Only a few countries in the world (USA, China, Canada, Australia, and India) practice a large-scale industrial production of coalbed methane, the resources of which are practically not inferior to those of traditional natural gas [9]. Thousands of small natural gas fields with reserves of less than several billion cubic meters, located far from consumers, remain unused due to the low profitability of the existing gas transportation methods and technologies for their conversion into chemicals. The biogas production and productivity of individual plants are still too low to talk about any industrial use of it, in addition to energy production for local consumption.

The main problem on the way to a more complete utilization of limited sources of hydrocarbon gases of both anthropogenic and natural origin is the lack of cost-effective low-scale technologies for their processing. A number of our previous works were devoted to the prospects of developing such technologies [10, 11]. Nevertheless, the problem still remains acute and requires constant attention.

2. Energy generation from APG

At present, the most important and large-scale problem in reducing the anthropogenic emission of hydrocarbon gases is the cessation of APG flaring at numerous small producing fields both on land and offshore platforms. In this regard, various possibilities of APG use and processing are analyzed [5, 6]. Among possible methods for gas transformation are gas to hydrate (GTH), gas to liquid (GTL), gas to wire (electricity) through combined heat and power (CHP) systems, compressed natural gas (CNG), liquefied petroleum gas (LPG) recovery, and liquefied natural gas (LNG) [5]. Other possibilities, such as compression and reinjection of gas into oil wells to enhance oil production, NGL refinery, fuel production, production of chemicals, for example, methanol and dimethyl ether (DME), and power generation are also considered [6].

None of these technologies is universal and suitable for all gas sources, almost all of them being unprofitable for sources with a flow rate of less than several million cubic meters per year. According to [5], the CNG with LPG recovery alternative provides the highest net profit. The LNG technology is the least economically beneficial option. GTH and GTL technologies, due to their high estimated costs, do not compete economically with the CNG + LPG or CHP alternatives.

The most economically reasonable use of APG could be associated with energy generation to cover the needs of the oil field. Estimates show that up to 30% of the flared APG can be used for this, which would significantly increase the share of its utilization. However, the possibility of using APG, a mixture of methane with heavier hydrocarbons, for the



Fig. 1. Oil production and global gas flaring in 2011–2021 (according to data from BP Statistical Review of World Energy 2022 [7] and The World Bank [8]).



Fig. 2. (a) Conversion of alkanes during their selective oxycracking on the number of carbon atoms *N*c in the molecule (according to [14]). (b) Results of pilot testing for the conversion of the typical APG (C_3H_8 (\blacksquare), $n-C_4H_{10}$ (\blacktriangle), $n-C_5H_{12}$ (\bullet), $n-C_6H_{14}$ (\bullet)). The composition of gas (mol %): CH₄ – 81.0; C₂H₆ – 1.22; C₃H₈ – 17.0; ΣC_4H_{10} – 2.81; ΣC_5H_{12} – 1.50; $n-C_6H_{14}$ – 1.83. The amount of added air was 15%, $t_r \sim 1$ s (according to [13]).

generation of electricity based on modern gas-piston or gas turbine power plants, remains a serious technical problem. Even a small admixture of heavier methane homologues in gas fuel dramatically increases the formation of soot and tars in the power generation equipment, which increases its wear and leads to rapid failure. In addition, even a small admixture of C₂+ alkanes in methane, at a level of just above 1%, reduces the time of autoignition delay of gas fuel several times, that is, reduces its resistance to detonation [12], and does not allow operating the power plant at its rated power. Note that the detonation characteristics of the gas fuel do not strongly depend on the actual composition of C_2-C_5 alkane admixtures in APG, being largely determined by their total concentration [12].

The usual methods for extracting heavy components from hydrocarbon gases require sophisticated equipment and high energy. Therefore, they are not suitable for small (up to 10 MW) power plants. A relatively simple and economical method for reducing the content of heavy methane homologues in APG can be their selective oxidative conversion (selective oxycracking) into lighter high-octane compounds [13–15]. The possibility of deep conversion of methane homologues by selective oxycracking with the production of conditioned gas fuel was demonstrated on the laboratory scale [14, 15] and during pilot tests with an incoming gas flow of up to 20 m³/h [15] (Fig. 2).

Selective oxycracking provides an increase in the methane number MN of gas and a decrease in its



Fig. 3. Dependences of the methane number MN and lower calorific value Q_L for the oxidation of a gas mixture containing (vol.%) 71.9 CH₄, 2.5 C₂H₆, 22.5 C₃H₈, and 3.1 C₄H₁₀ with air and oxygen on the oxygen content at the reactor inlet. The pressure is 30 bar, with the maximum oxidation temperature ranging from 450 °C (at 4 vol.% O₂) to 640 °C (at 16 vol.% O₂) (according to [14]).

lower calorific value (LHV) QL [14], which is necessary to meet the requirements for fuel gas of gas-piston engines manufacturers (Fig. 3).

Therefore, a relatively simple process of selective oxycracking of APG allows converting 90–95% of C_2 + alkanes and, thus, meets the requirements of manufacturers of gas-piston power plants. This opens up an opportunity for using small sources of APG or natural gas to generate electricity for the needs of oil and gas producers.

3. Production of chemicals from APG in oil fields

Note, however, that, because most of the oil producing fields are located in remote regions with low energy consumption, the use of APG for electricity generation does not completely solve the problem of stopping its flaring. Since the pipeline transportation of small volumes of APG, even over short distances, can be economically justified in some rare cases, technologies are needed to cost-effectively process small volumes of APG, from 10 to 50 mln m³ per year, into more demanded or easily transported products. Ideally, these should be products required immediately in the areas of oil and gas production, such as methanol, used in gas production as an inhibitor of hydrate formation, formaldehyde, or liquid motor fuels.

Although large-scale industrial processes of conversion of gas phase hydrocarbons into these products have become mature long ago [16, 17], their complexity and high specific capital costs practically exclude their economically justified use for lowscale APG processing. An alternative method of small-scale conversion of APG to methanol can be a relatively simple autothermal process of direct oxidation of methane to methanol (DMTM) [18], which does not require a complex and energy-intensive stage of preliminary conversion of APG to syngas. The process occurs under relatively mild conditions (T < 550 °C, P < 80 atm) at an absolutely safe concentration of oxygen $[O_2] < 5\%$, which can be supplied in the form of atmospheric or oxygen-enriched air. Using oxygen-enriched air in a flow sectioned reactor with gas recycling makes it possible to obtain a sufficiently high methanol yield (Fig. 4). The DMTM process is very well combined with the production of electricity, by using for the power generation a nitrogen-diluted purged gas, which significantly reduces NOx emissions.

An important advantage of DMTM from the point of view of APG processing is that, unlike the known catalytic processes of natural gas conversion, which require preliminary conversion of methane homologues under milder conditions (pre-reforming) [19], their presence favorably influences the DMTM, making its conditions milder and thereby increasing the yield of methanol [18]. The main disadvantage of this process is a relatively low methanol yield, but its simplicity, low capital and operating costs, as well as compatibility with power generation make it possible to consider it as a real way to process APG in remote oil fields, especially if there is demand for methanol, as an inhibitor of hydrate formation.

However, a more universal method of processing APG and other low-yield sources of hydrocarbon gases is their conversion into synthetic liquid hydrocarbons and motor fuels based on the Fischer-Tropsch process. The main obstacles to this remain high complexity, high energy consumption, and significant capital costs of modern processes of conversion of hydrocarbon gases into syngas, which



Fig. 4. Methanol yield (\blacksquare) and N₂ concentration in recycling and purged gas (\blacktriangle) as a function of the blowing in the DMTM process with enriched air ([O₂] = 50%) [18].



Fig. 5. (a) General view and (b) the scheme of the matrix reformer for hydrocarbon gases conversion into syngas by their oxidation with enriched air and oxygen: (1) – core vessel; (2) – flange; (3) – discharge nozzle; (4) – mixing chamber; (5) – combustion chamber; (6) – matrix; (7) – radiation screen; (8) – inlet aperture. Gas flow rate was up to 10 m³/h [21].

account for up to 2/3 of the cost of the final products obtained [20]. Since the existing technologies for the conversion of hydrocarbon gases into syngas are mature industrial processes, it is difficult to expect substantial progress in their improvement. Therefore, serious attempts are continuing to develop simpler technologies economically efficient even at a low-scale capacity. It is worthwhile to mention some popular trends in recent years, such as the use of ceramic oxygen-transmitting membranes, microchannel reactors, short time catalysis, and syngas production based on energy technologies. Unfortunately, despite strenuous efforts, none of these technologies have found their way into industry.

One of the most promising technologies for lowscale conversion of APG and other hydrocarbon gases into syngas may be their matrix conversion [21]. The underlying idea of matrix conversion is the recuperation of the heat of produced syngas for preheating the incoming hydrocarbon-oxidant mixture by convective and radiative heat transfer from the combustion products to the porous matrix, which transfers this heat to the incoming mixture. The stabilization of the flame zone in the near vicinity (~1.5–2 mm) of the matrix surface facilitates the heat transfer from the flame zone to the surface (Fig. 5). This internal preheating of very rich gas mixture ensures their stable conversion, providing a high syngas yield.

The non-catalytic autothermal process of matrix conversion makes it possible to convert hydrocarbon gases of practically any composition at a very high volume rate, at least tenfold exceeding that for steam reforming, and provides a very high productivity and low operation cost. Any type of oxidizer can be used, for example, air, enriched air or oxygen. Combining matrix conversion with subsequent catalytic water gas shift reaction (WGSR) allows obtaining syngas with any desired H_2 /CO ratio, including the production of hydrogen.

The possibility of oxidation by air ensures a safe and profitable small-scale field operation, for example, the processing of small flows of APG or any other local gas resources directly on the site [22]. The partial oxidation of natural gas with air, followed by the conversion of the nitrogen-containing syngas into liquid synthetic hydrocarbons, methanol, DME, or other products can be a good solution for the utilization of any small resources of hydrocarbon gases. The use of nitrogen-containing syngas at the stage of its conversion into liquid products requires a high conversion per pass to eliminate the recycling of the diluted residual gas. At present, about 90% degree of conversion is achieved in the synthesis of dimethyl ether over combined Cu-Zn-Al zeolite catalysts. For various reasons, the conversion to methanol or hydrocarbons (Fischer-Tropsch synthesis) proceeds with a lower degree of conversion and requires a cascade of two or three successive reactors. However, the dilution of syngas with nitrogen reduces the specific heat release in the catalyst bed, thereby allowing the use of shell-and-tube Fischer-Tropsch synthesis reactors with an increased diameter. Therefore, the capital costs for the construction of two reactors optimized for nitrogen-containing syngas may not be higher than for a single reactor operating on the syngas without nitrogen [22].



Fig. 6. Schematic diagram of the conversion of coalbed methane and coal wastes into methanol-coal fuel: (1) – separator for enriching methane-air mixture; (2) – stages of compressor for enriched methane-air mixture; (3) – recuperative heat exchanger for heating methane-air mixture; (4) – two-step reactor for methane-air mixture oxidation with an inter-sectional heat exchanger; (5) – steam generator, (6) and (8) – heat exchangers; (7) – air cooler; (9) – separator; (10) – turbo expander; (11) – adsorber for residual oxidation products from the exhaust gas; (12) – cavitation mixer of liquid and solid products; (13) – gas turbine; (14) – electric generating unit [23].

4. Utilization of coalbed methane

Coal mining is one of the main sources of constant methane emissions into the atmosphere. According to estimates, methane reserves in coal deposits are not inferior to the resources of traditional natural gas [1]. In the USA, coalbed methane accounts for a significant share of natural gas production. In most countries, however, when coal is mined, methane is simply released into the atmosphere. During mining, methane is emitted from ventilation wells, when large volumes of air are pumped into the mine to keep the CH_4 concentration below 0.5% to avoid accidental ignition. Estimates of global CH_4 emissions from coal mining range widely, from 29 to 61 Tg/yr for 2008–2017 period [3].

The problem with using coalbed methane is the low flow rate of ventilation wells during the natural degassing of coal seams and very strong dilution with air in the case of forced ventilation of coal seams with air. The paper [23] considers the possibility of a combined utilization of coalbed methane and another type of environmentally problematic coal mining waste – a large amount of coal waste accumulated during mining and concentrating. Fine coal sludge accumulates in enormous amounts and creates a substantial ecological problem in coal mining regions.

The proposed process is schematically shown in Fig. 6. Coalbed methane containing an admixture of air enters the oxidation section, where it is compressed to a pressure of 6-7 MPa, heated in the heat recuperation unit, and admitted into the reactor. The liquid oxidation product (methanol product) containing up to 40% methanol and up to 5-8% other organic products is released after cooling the partially oxidized vapor mixture, and then it is transferred, together with crushed and concentrated coal waste, without any treatment or rectification, to the preparation of methanol-coal suspension fuel. The outlet gas containing methane with a concentration of not less than 25% can be supplied to the energy plant to produce power for coal mining facilities. One of the major advantages of this process is the



Fig. 7. Scheme of possible procedures for oil refinery gas processing [27].

possibility to use the produced liquid crude methanol directly without any preprocessing or rectification to prepare methanol-coal fuel.

The process of obtaining crude methanol through methane oxidation by atmospheric oxygen is almost identical to the conventional flowchart of methanol production by the direct methane oxidation to methanol [18], except for the absence of the necessity to supply compressed air, because, as a rule, coalbed methane already contains it in a sufficient amount. The flow process, which is the simplest technology, allows the production of methanol with a specific yield of up to 16 kg/1000·m³ of methane. In this case, the exhaust gas meets all the requirements to fuel gas for gas piston engines and to combustible gases for industrial and household purposes.

5. Processing of refinery gases

Methane emissions from the oil industry (e.g. refining) and charcoal production are estimated as a few teragrams of methane per year [3]. Increasing the efficiency and extent of utilization of the hydrocarbon feedstock remains a topical problem of the petrochemical industry. Along with target commercial products, hydrocarbon-cracking installations produce large amounts of saturated C_2 + gases, which are typically burnt for heat production [24–26]. Such utilization of these gases is not efficient because of the need to pretreat the cracking feedstock (drying, desulfurization) and of a relatively low calorific value of such mixtures.

Since the saturated hydrocarbons present in oil refinery gases strongly differ in reactivity, and oil refinery gases have varied compositions, the processing of such gases without separation is a complex problem. In [27], a demonstration unit with a capacity of 5 m³/h was used to examine the possibility of the processing of refinery gases based on their selective oxidative cracking according to the scheme shown in Fig. 7.

Experiments on this demonstration unit aimed at producing ethylene and CO by oxycracking of ethane, propane-butane mixture, and ethane–propane-butane mixture (all diluted with methane) were performed. The major products of the oxidative cracking of oil refinery gases were ethylene, CO, and hydrogen; their total yield can exceed 90%. The ranges of parameters within which further optimization of the processes should be performed were determined [27].

The ethylene yield increases with the temperature of the initial hydrocarbon mixture. However, at temperatures above 650 °C, the contribution of ethylene conversion processes with the formation of condensation products increases; thus, the optimum temperature for performing oxycracking of C_2-C_4 alkane mixture is 600–650 °C. The ethylene yield is determined by the total concentration of C_2 + alkanes in the mixture.



Fig. 8. Flow sheet for the low-cost conversion of biogas to liquid fuels based on carbon dioxide and nitrogen diluted syngas [28].

The addition of oxygen results in a significant increase in the total process rate relative to that of the thermal cracking but insignificantly affects the hydrogen yield. At the same time, the hydrogen concentration decreases considerably with an increase in the alkane chain length. The CO concentration monotonically increases with the addition of oxygen, while its yield is determined by the total content of C_2 + components in the mixture. The demo unit showed high efficiency in the production of ethylene, CO, and hydrogen by oxidative cracking of oil refinery gases.

6. Conversion of biogas

In their contribution to greenhouse gas emissions, the anthropogenic sources of biomethane are practically not inferior to the industrial sources, representing 56% of the total anthropogenic emissions. The total emissions from enteric fermentation and manure management for this period are estimated to be 111 Tg/yr, which is about one-third of the total global anthropogenic emissions [3]. In processing various biowaste, methane, as a rule, is released in the form of biogas, which is a mixture of methane with carbon dioxide and nitrogen. Biogas is produced by methane fermentation of biomass under the influence of several types of bacteria. Typical biogas contains from 50% to 87% of methane and 13–50% of CO₂ with minor impurities of N₂, H₂ and H₂S. At present, it is widely used as a low-cost renewable source for local power.

Low energy density in agricultural or biotechnological raw materials dictates the necessity for their local processing. Small-scale agricultural products or waste processing plants cannot profitably use technologies commonly met in large-scale petrochemistry, including the complex and expensive process of biogas steam reforming into syngas for its subsequent conversion to liquid fuel. It was suggested [28] to use small-scale sources of inexpensive and easily obtained biogas and other renewable hydrocarbon gases for the production of liquid biofuel through their air conversion on matrix reformers [21] into low-cost carbon dioxide and nitrogen diluted syngas, followed by Fischer-Tropsch synthesis in a cascade of sequential reactors. Autothermal matrix reformers are very compact, simple in design, with a specific volume capacity several times that of traditional technologies. They allow the processing biogas with a high concentration of CO₂ and N₂. The advantages of conversion of thus obtained low-cost syngas partly diluted with chemically inert gases into Fischer-Tropsch products, methanol or DME were discussed in [22] and in Section 3.

The high conversion of CO on the Co–Pt–ZrO₂/ Al₂O₃ catalyst [29] in combination with high selectivity for liquid hydrocarbons makes it possible to implement the process flowchart without syngas recycling, using instead two or three successive reactors (Fig. 8). The main advantage of the matrix conversion of biogas with air to CO₂ and N₂ containing lies in the significant reduction of capital and operating costs at this stage.

7. Conclusions

Natural and anthropogenic sources of hydrocarbon gases contribute significantly to the global emission of greenhouse gases. Among them, a significant share is made up of low-debit sources, such as APG, coalbed methane, refinery gases, and biogas, for the processing and disposal of which modern technologies based on complex catalytic processes are inapplicable. Reducing the emission of these gases requires fundamentally new technologies that would allow their cost-effective use in the local energy sector and the production of various petrochemicals for local use.

One of the most effective approaches to creating a new generation of such low-tonnage processes for the utilization of small sources of hydrocarbon gases can be relatively simple non-catalytic technologies based on autothermal processes of their partial oxidation or oxidative cracking. Several examples of such technologies were considered in this paper. All of them require no additional external energy sources because of the use of the energy of processed hydrocarbon gases, being characterized by a high volumetric capacity, low capital and operating costs, easy manageability, and a relatively straightforward production. An important advantage of all such non-catalytic technologies based on oxidative conversion is their low sensitivity to the composition and volume flow rate of processed gases, which is very important in view of significant fluctuations in the composition and productivity of most small sources such as APG or biogas.

It can be expected that the use of such relatively simple technologies not only opens up prospects for a significant reduction in the emission in the atmosphere or flaring of anthropogenic hydrocarbon gases but will also make it possible to more economically use local natural hydrocarbon resources in the energy sector and for low-tonnage production of demanded chemicals.

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