

New Potentialities for Utilization of Associated Petroleum Gases in Power Generation and Chemicals Production

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Abstract

New possibilities for the utilization of associated petroleum gases (APG) and monetization of small-scale and remote Natural Gas resources by power generation and chemicals production are considered and tested. One possibility is the oxy-cracking of APG. This technology allows selective transformation of heavier hydrocarbons that have low octane (methane) numbers and inclined to soot and tar formation, into lighter compounds with higher octane numbers, thus producing gas suitable to feed different types of power engines. Another possibility is the small-scale conversion of APG to syngas to produce more easily transportable and more valuable chemicals or liquid fuels via well-known Fischer–Tropsch process or catalytic synthesis of methanol. For this purpose we have suggested principally new technology for natural gases conversion into syngas, based on the use of 3D (volumetric) matrixes. It allows the relative simple and very compact non-catalytic reformers to be designed for small-scale gas-to liquid (GTL) technologies. Their main advantages are autothermal character of the process without any need in additional heating or power supply, absence of catalyst that allows processing hydrocarbon gases of practically any composition, including APG, without additional pretreatment, very high specific volume capacity, at any rate 10 times higher than that of steam reforming, and simplicity in construction and operation.

1. Introduction

The utilization of associated petroleum gases (APG) is one of the most sensitive issues for oil industry. Every year, about 140 billion m³ of associated gas is wastefully burned at thousands of oil fields. This amount accounts for more than 300 million tons of carbon dioxide emitted to the atmosphere, equivalent to emissions from about 77 million cars. For example, only about 72% of APG production is captured now in North Dakota, the second-largest oil-producing state in the US. The remaining 28% is flared [1]. The same situation is for Bakken Formation, where is flared about a third of the total gas produced [2]. The share of APG utilization by Russian oil companies also doesn't exceed 75% [3].

Reducing gas flaring can make a contribution towards mitigating climate change. World Bank has launched the “Zero Routine Flaring by 2030” initiative that has been endorsed by 10 oil companies, nine countries, and six development institutions [4]. However, the utilization of APG is not a trivial task. It is very difficult and economically inefficient to transport low volumes of APG from remote producing wells by specially built pipelines or converting them into more valuable and easily transportable products using state-of-the-art industrial gas chemistry [5]. It is also difficult to use APG as a fuel to feed gas piston or gas turbine engines due to the high content of heavy hydrocarbons. Strong decrease of methane number of such fuels makes APG very inclined to detonation, soot and tar formation. As it turned

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out, all existing small-scale methods for removing heavy hydrocarbons from APG are too costly and unprofitable. World oil industry urgently needs more effective and profitable technologies for utilization of APG. In this work we discuss several new possibilities for utilization of associated petroleum gases in power generation and chemicals production.

2. New possibilities for using APG in power generation

At present, the most evident and profitable way to use APG from small-scale remote fields is electricity and heat generation for local use. But the use of APG with unstable content of $C_1 - C_7+$ hydrocarbons with very high difference in reactivity as a fuel for power generation is not a trivial task. Even very low, about 1% admixture in fuel of heavier C_5+ hydrocarbons with low Methane Number (MN) in APG significantly decreases its self-ignition delay (Fig. 1), thus making them inclined to detonation, and doesn't let to reach nominal capacity of engine [6].

Apart from making knocks in the engine, the higher content of C_3+ hydrocarbons in gas mixture is accompanied by an increase in the formation of sludge that leads to the wear of engine parts. Both factors reduce its service life. Therefore, to ensure the normal operation mode and the stated performance characteristics, manufacturers of gas power engines (GPE) impose certain requirements on the quality of the fuel gas. The most important parameters of the fuel gas are the Methane Number (MN), which characterizes its antiknock properties, and Lower Heating Value (LHV). The high LHV leads

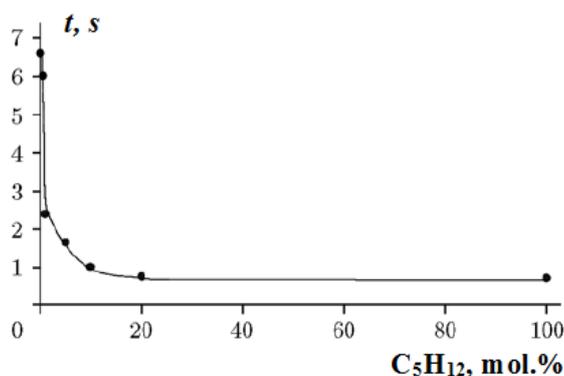


Fig. 1. Dependence of self-ignition delay of stoichiometric methane-pentane-air mixture on concentration of pentane in fuel. $P_0 = 1$ atm, $T_0 = 890$ K [6].

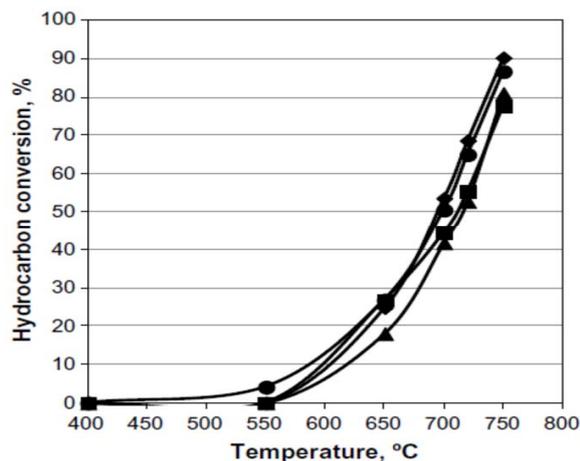


Fig. 2. Results of pilot testing at the conversion of the typical oil associated gas (C_3H_8 (■), $n-C_4H_{10}$ (▲), $n-C_5H_{12}$ (●), $n-C_6H_{14}$ (◆)). The composition of gas (mol.%): 75.0% CH_4 , 2.8% C_2H_6 , 12.6% C_3H_8 , 3.0% C_4H_{10} , 2.8% C_5H_{12} , 3.8% C_6H_{14} . The amount of added air – 15%. $\tau \sim 1$ s [8].

to overheating of engine thereby it must be in the range of 30–36 MJ/m³. According to [7], the methane number for GPE gas fuel must be higher than 52, while APG typically have the MN lower than 52, and LHV higher than 40 MJ/m³.

The most common method of preparing such gases for use in power plants is the extraction of heavy C_3+ hydrocarbons using expensive and energy-intensive deep-cooling installations. However, existing technologies of separation of heavier hydrocarbons from APG at its annual flows less than 20 million m³ that are typical for its small-scale sources, are unprofitable. Therefore, we have developed new technology, based on the selective oxy-cracking of heavier components of APG at its oxidative conversion with small admission of air [8]. Pilot plant testing has shown that the selective oxy-cracking let to convert up to 90% of C_5+ hydrocarbons (Fig. 2) into lighter and more octane components, predominantly methane, C_2 hydrocarbons, H_2 and CO practically without involving methane itself in oxidation. Moreover, the content of methane in gas even increases due to its additional production from the converted heavier hydrocarbons.

Selective oxy-cracking, as well as the partial oxidation, let to significantly increase the MN and to decrease the LHV of gas fuel (Fig. 3) thus making APG acceptable for fueling gas-piston engines. As it was revealed by laboratory-scale experiments, the most favorable conditions for the selective oxy-cracking of C_3+ hydrocarbons can be attained at slightly increased pressures, up to 4–5 atm.

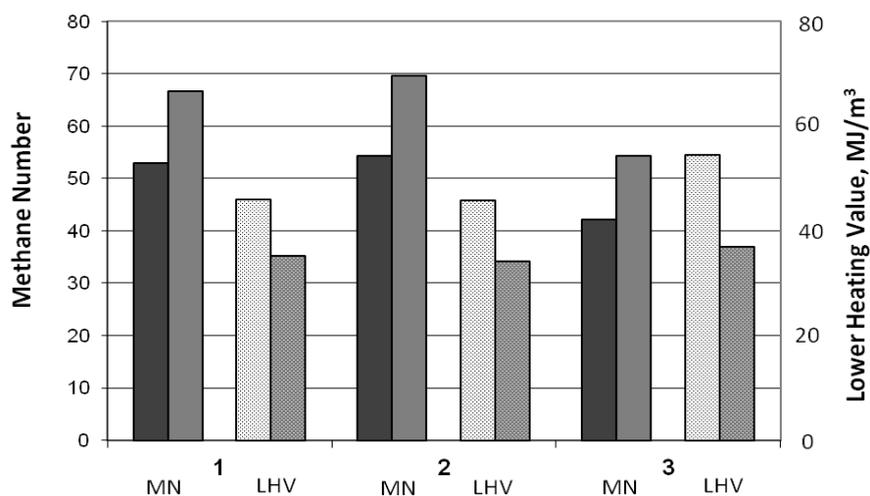


Fig. 3. The change in fuel parameters of different gas compositions after oxy-cracking at 750 °C: 1 – gas composition: 88% CH₄, 6% C₃H₈, 6% C₅H₁₂, oxidizer – 60% O₂ + 40% N₂, 160 l/h per 1000 l/h of gas; 2 – gas composition: 82% CH₄, 6% C₂H₆, 8% C₃H₈, 4% C₄H₁₀, oxidizer – technical grade O₂, 170 l/h per 1000 l/h of gas; 3 – gas composition: 75.0% CH₄, 2.8% C₂H₆, 12.6% C₃H₈, 3.0% C₄H₁₀, 2.8% C₅H₁₂, 3.8% C₆H₁₄, oxidizer – air, 200 l/h per 1000 of gas. The first column – value before oxy-cracking, the second column – the same value after oxy-cracking.

Enhanced pressures make it possible to accelerate the process and to decrease its temperature by more than 100 °C. The same results were obtained at high pressure (20–30 atm) during partial oxidation of different gas mixtures simulating the APG [9].

3. Small-scale production of syngas from APG

Although nowadays the use of APG for power generation is simpler and possibly most profitable for its utilization, there is no need in high power in remote oil and gas producing sites to consume the all APG volumes. Of course, more universal and in many cases more preferable way of its utilization is its conversion into more valuable and easy transportable liquid chemicals or fuels. At the same time the modern gas-chemical technologies for conversion of gas-phase hydrocarbons in liquid products, so call GTL (Gas-to-Liquid) technologies, are very complex and costly and can be profitable only at huge capacities, no less than 1 million ton of annual product output [10, 11]. It makes them absolutely unacceptable for the small-scale processing of low APG flows that rarely exceed several dozens of million m³ annually. The most capital and energy consuming stage of these technologies, which takes up to 2/3 of all process expenditures is the conversion of gas-phase hydrocarbons into syngas. And they become especially complicated when it is necessary processing not methane, but such complex gas mixtures as APG. Thus, small-scale technologies for processing small-scale APG flows

directly at producing wells must rely on fundamentally new technologies for conversion of APG into syngas.

Recently, we have suggested principally new possibility for natural gases conversion into syngas, based on the use of 3D (volumetric) matrixes [12, 13]. Intensive internal convective and radiation recuperation of conversion products heat and locking of IR radiation of flame front during the flameless combustion near the inner surface of penetrable volumetric matrix let to significantly widen the combustion limits, thus providing efficient non-catalytic conversion of hydrocarbon gases into syngas. This possibility allows the relative simple and very compact converters to be designed which serve as a base for small-scale GTL technologies. Their evident advantages especially important at small-scale operation are:

- autothermal character of the process without any need in additional heating or power supply;
- absence of catalyst that allows processing hydrocarbon gases of practically any composition, including APG, without additional pretreatment;
- compactness (specific volume capacity at any rate is 10 times higher than that of during steam reforming);
- high range of possible capacities including very small gas flows;
- simplicity in construction and operation which is very important at operation in remote producing sites without the developed industrial infrastructure.

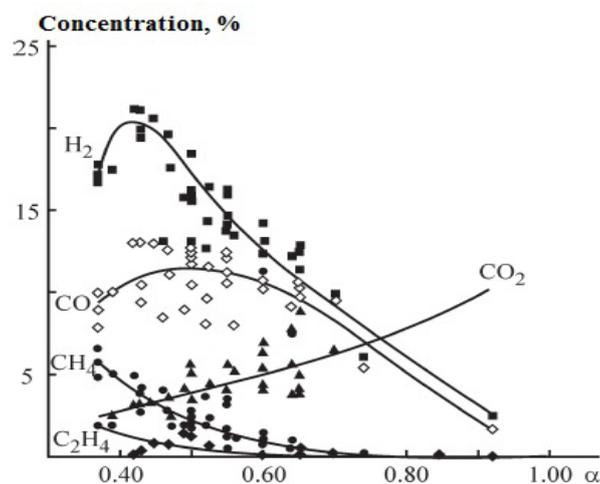


Fig. 4. Laboratory obtained experimental dependence of concentration of products on oxygen excess coefficient α .

Our preliminary experiments (Fig. 4) have shown the promising possibility for methane conversion to syngas even in small-size laboratory devices with gas flows of about 10 l/h that is not very favorable due to relatively large heat losses. In such simple non-catalytic converters with using air as an oxidant it was possible to reach such low values of oxygen excess coefficient α (for methane $\alpha = [\text{O}_2]/2[\text{CH}_4]$) as $\alpha = 0.37\text{--}0.4$. At that, the yield of syngas was very close to thermodynamically equilibrium with H_2 concentration up to 22%, and that of CO up to 13%. The ratio H_2/CO was $\sim 1.6\text{--}1.8$.

When the oxygen excess coefficient α is below 0.37–0.38, the matrix temperature decreases, leading to the decrease in methane conversion and, therefore to the lowering H_2 and CO concentrations. Because of the strong dependence of matrix conversion on the heat balance on its surface, it is difficult to obtain better results in small-dimension laboratory devices with high losses of specific heat. Nevertheless, several addition possibilities including additional external recuperation of heat and catalytic activation of gases by matrix surface were examined [12, 13].

More interesting results were obtained during pilot testing of converters with significantly higher, up to 10 m³/h gas flows (Fig. 5).

During the atmospheric air operation in such converters it was possible to reach the lowest values of α in the range 0.32–0.34 and the yield of syngas close to thermodynamically equilibrium with concentrations $[\text{H}_2] \approx 24\%$, $[\text{CO}] \approx 14\%$ and the ratio $[\text{H}_2]/[\text{CO}] \approx 1.6\text{--}1.7$ (Fig. 6, Table 1). As it can be seen from Fig. 6, at lower values of α the yield of syngas decreases due to the decrease of

conversion of methane. Therefore, the optimal α values during the operation with atmospheric air are approximately equal to 0.34–0.36.



Fig. 5. Different types of pilot matrix converters with gas flows up to 10 m³/h.

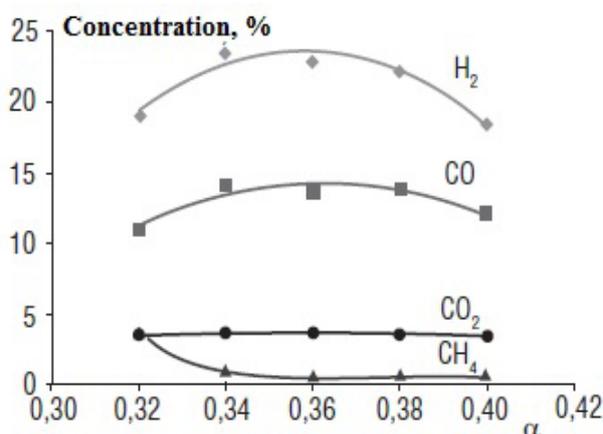


Fig. 6. Concentrations of the main products vs oxygen excess coefficient α during the pilot converter operation with atmospheric air. Total flow of gas-air mixture is constant and equal to 19.3 m³/h.

The use of slightly enriched air with oxygen content $[\text{O}_2] = 26\%$ let significantly decrease the values of oxygen excess coefficient up to $\alpha = 0.28$ (Table) and even lower. It also allows improving practically all key parameters of conversion including the concentrations of $[\text{H}_2]$ and $[\text{CO}]$ and the ratio $[\text{H}_2]/[\text{CO}]$.

Table
Characteristics of syngas during methane oxidation
by air and enriched air

Parameters of syngas at methane oxidation by air and enriched air	Air [O ₂] = 21%		Enriched air [O ₂] = 26%	
	Run 1	Run 2	Run 1	Run 2
Oxygen excess coefficient	0.34	0.36	0.28	0.32
Conversion of methane, %	94.3	96.6	98.7	93.7
Conversion of oxygen, %	95.0	95.3	95.3	95.8
Concentration of H ₂ , %	23.7	23.0	29.0	27.3
Concentration of CO, %	14.2	14.4	15.7	16.2
Concentration of CO ₂ , %	3.7	3.6	3.6	3.6
Concentration of CH ₄ , %	<1	0.6	0.3	1.4
Ratio H ₂ /CO	1.67	1.60	1.85	1.69
Selectivity of H ₂ , %	71.3	67.2	64.2	65.8
Selectivity of CO, %	85.4	84.1	69.5	78.0

4. Small-scale conversion of APG into nitrogen-rich syngas as an effective route for its utilization

Although we have shown the principal possibility of matrix converters to operate with highly enriched air and even technical oxygen with oxygen concentration up to 99%, we believe that the use of cheap and accident-free air can be more promising for small-scale operation in remote gas and oil deposits to process low flows of APG. Very important principal advantages of using air instead of oxygen to convert APG into syngas in remote producing sites are low capital costs, simplicity of equipment and safety of operation. The last point is especially important for operation in producing sites with high probability of leakages of liquid and gas phase hydrocarbons.

There are several studies [14–18] that have demonstrated not only the possibility but also the evident advantages in using nitrogen-rich syngas in Fischer-Tropsch- synthesis [14, 15], in production of dimethyl ether and even methanol [18]. Authors of [14, 15] believe that the use of nitrogen-rich syngas (50 vol.%) could be an alternative process to the classical ones using nitrogen-free syngas because the investment costs are probably lower: syngas is produced by partial oxidation with air, which eliminates the need for an air separation

plant, and the process with nitrogen-rich syngas does not utilize a recycle loop and a recycle compressor. It was shown that nitrogen only dilutes syngas and has no influence on the kinetics, if the partial pressures of carbon monoxide and hydrogen are kept constant [14, 19].

The concept of the low-cost F–T-process based on nitrogen-rich syngas was investigated on a semi-technical scale at the Engler-Bunte-Institute of the University of Karlsruhe [14, 15]. The semi-technical F–T-plant has used the F–T-unit with three single-tube fixed bed reactors in series with iron catalyst. The diameter of the semi-technical F–T-reactors corresponds to a single tube of a typical industrial multitubular reactor, thus the experimental results are, therefore, directly transferable to a technical scale. Syngas diluted by 50% of N₂ passes through the single tube reactors and is converted at a total pressure of about 24 bar and temperatures of 220 °C up to 260 °C.

This plant was successfully run for a period of altogether about 1400 h (8 weeks). The CO-conversion in the F–T-unit was 55%. A typical product-distribution is shown in Fig. 7, indicating that, under the given reaction conditions, diesel oil and wax were the main organic products of F–T-synthesis. The selectivity to the (unwanted) product carbon dioxide was about 25 C%, which is typical for iron-catalysts.

These investigations have also indicated that in the operation of multitubular reactors nitrogen is helping to remove the heat generated by the F–T-reaction. This leads to an optimum diameter of the tubes of 70 mm for nitrogen-rich syngas with respect to a stable and safe operation of the reactor, whereas for nitrogen-free syngas, the diameter is limited to about 45 mm. The production rate of diesel oil and wax per tube is, in case of nitrogen-rich syngas, about three times higher, which will decrease the number of tubes and the investment costs of industrial multitubular reactors.

The possibility to use nitrogen-rich syngas in F-T process with supported cobalt catalysts was shown in [16, 17]. With gas mixture CO:H₂:N₂ = 1:2:5 modeling typical air-produced syngas the all catalysts investigated have shown high selectivity to C₅+ hydrocarbons and low selectivity to methane.

Methanol synthesis from nitrogen-rich syngas with N₂ concentration 40–60% was investigated in [18] and used in experimental installations “Syn-top” where nitrogen-containing syngas was produced by partial oxidation of natural gas in cylinders of diesel engine [19].

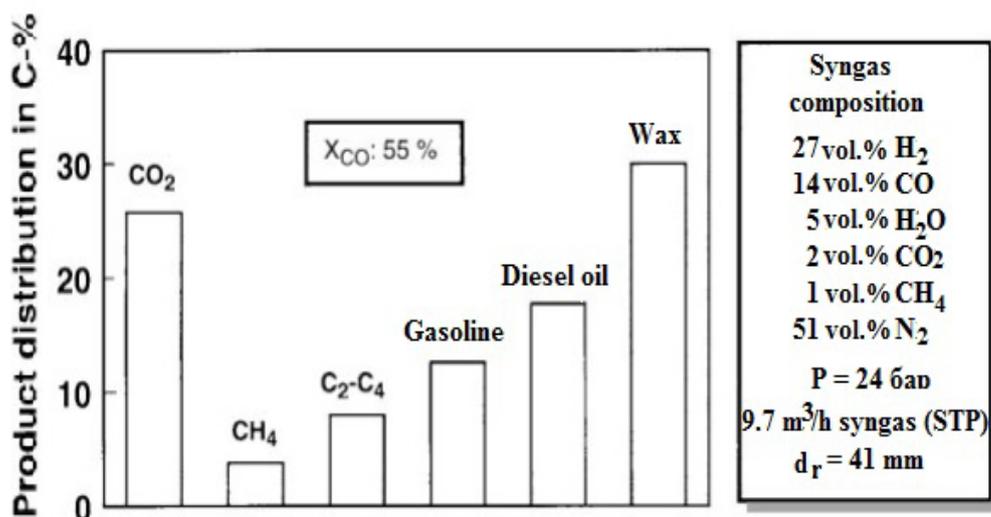


Fig. 7. Typical product-distribution of F–T-synthesis obtained with nitrogen-rich syngas (about 50% of N₂) at the semi-technical F–T-unit [14].

However, the usage of nitrogen-containing syngas is more evident and effective in small-scale synthesis of dimethyl ether. The important advantage of dimethyl ether synthesis based on nitrogen-rich syngas is that CO conversion per pass through reactor to dimethyl ether is significantly higher than to methanol and theoretically can reach 90% [21]. It let to refuse from recirculation of gas. Another advantage of dimethyl ether production is that the syngas with low ratio H₂/CO may be used. Dimethyl ether produced in this way can be exploited for the small-scale conversion into gasoline [22].

Completing this section, we would like to specify the next main advantages of using of nitrogen-containing syngas for small-scale processing of APG at remote producing sites:

- significant decrease in capital costs;
- no need in recycling;
- low partial pressure of steam is favorable to process kinetics and increases extends the life cycle of catalyst;
- lower specific heat release makes it possible to exploit the reactor tubes of higher diameter;
- decrease of local overheating increases the selectivity to higher hydrocarbons;
- operating safety in field conditions.

5. Conclusions

There is a number of promising possibilities for the utilization of APG and monetization of small-scale and remote Natural Gas resources including chemicals production and power generation, based on gas phase partial oxidation of hydrocarbons.

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