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Utilization of Associated Petroleum Gas via Small-Scale Power Generation

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Abstract—The utilization of associated petroleum gas via power generation in modern gas piston engines or gas turbines involves some difficulties due to a significant content of heavy C_{5+} hydrocarbons which are prone to detonation and soot and tar formation. Two pretreatment technologies were described for associated petroleum gas utilization via power generation. Selective oxycracking of heavy hydrocarbons in associated petroleum gas allows their conversion to lighter and high octane molecules. The conversion of associated petroleum gas into syngas with the use of volumetric radiant matrix not only enables utilization of associated petroleum via power generation but also opens prospects for its complete utilization with production of synthetic liquid hydrocarbons via Fischer–Tropsch synthesis route.

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Gas flares is a sight that leaves everyone perplexed as to why they do not find a better use, e.g., for power generation. However, there exist two serious obstacles to implementation of this option for utilization of associated petroleum gas (APG). The first obstacle is trivial: Most of oil and, thereby, APG is extracted in remote areas lacking in large power consumers, except for the extractive companies themselves. The amount of associated gas (100 m^3 per oil ton, on the average) is mostly too small for justifying the construction of large APG-fired power plants on the site. On the other hand, the costs of laying hundreds of kilometers of pipelines or cables to the sites of potential consumption of gas or electricity often makes such transportation economically impractical.

At the same time, APG is typically produced in amounts too large for this gas to be entirely spent for satisfying the internal needs of the oil field and its surrounding areas, for which purpose typically <20% of the APG extracted is sufficient, and this sends the extractive companies in the search for alternative applications for the remaining gas. However, those 20% alone constitutes a significant contribution to the reduction of losses. Moreover, this option provides a real alternative to liquid gas fuel which is typically used for satisfying the internal power engineering needs and whose price, considering the transportation costs associated with the delivery to oil field areas, may exceed several times the fuel prices in Central Russia.

Table 1. Octane number of normal alkanes

Hydrocarbon	Octane number determined by indicated method	
	motor method	research method
Methane	110	107.5
Ethane	108	107.1
Propane	100	105.7
n-Butane	91.0	93.6
n-Pentane	61.7	61.7
n-Hexane	26.0	24.8
n-Heptane	0	0
n-Octane	–17[a]	–19[a]
Straight-run gasoline	41—56	43—58

[a] For calculation, see [1].

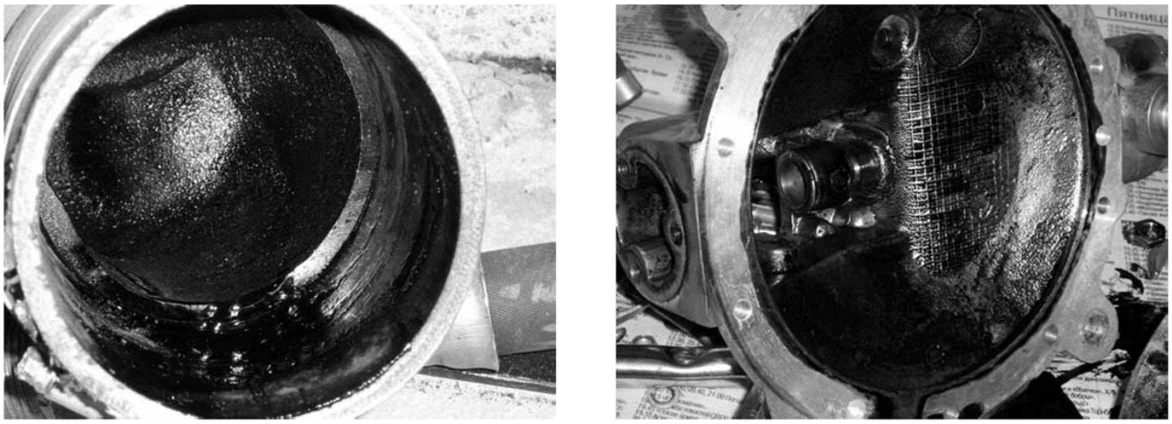

Fig. 1. Soot and tar formation in the fuel system of an associated gas-fueled gas-piston engine.

The second obstacle lies in the nontrivial nature of APG utilization via power generation. Crude natural, and especially associated, gases cannot be directly used in many of the modern power generation units, particularly those based on gas-piston engines because they contain heavy fractions of C_{5+} hydrocarbons with low octane numbers (Table 1). Associated gas typically contains C_1–C_8 hydrocarbons in various proportions. Even minor (1–2 vol %) impurity levels of heavy hydrocarbons lead to detonation in engines, thereby preventing them from achievement of nominal capacities. Also, the intensified coke formation and wear of engine parts (Fig. 1) drastically decrease the service life of engines.

Depending on the composition of natural gas, its octane number (ON) ranges from 105 to 110 [motor octane number, MON) and from 110 to 115 [research octane number (RON)], which allows the use of natural gas in internal combustion engines (ICEs) with the compression degree of 12–14. Methane has the best antiknock characteristic among hydrocarbons, being superior in this parameter to isooctane whose antiknock value was taken as the reference (ON = 100).

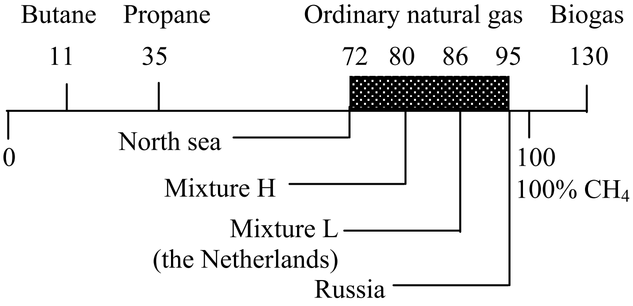

Fig. 2. Detonation characteristic of natural gas and individual alkanes on the "methane" scale.

For ICE modifications operating purely on gas, characterized by a high compression ratio of 12–14, it is difficult to fairly precisely determine the antiknock index on the octane scale. The currently accepted methods for determination of this important characteristic of liquid fuel are unhandy for gas fuel applications, in which situation a "methane" scale was proposed which takes the antiknock index of methane as 100, and that of hydrogen, as 0 [2, 3]. The antiknock value is actually estimated from the H/C ratio for a gas fuel. It is not absolutely clear why specifically hydrogen (whose RON ranges from 88 to 130 [4]) was chosen as the zero reference point, but the methane scale is actually suitable for estimation of the detonation characteristics of various gaseous fuels.

Alkanes heavier than methane, even when as minor impurities, cause the antiknock index of gaseous fuel to drastically decrease (Table 2, and Fig. 2).

The determination of the actual methane numbers (antiknock indices) of gaseous fuels requires special engines with variable compression ratio, inaccessible for most of research laboratories, and also entails large costs and takes much time. In view of the above-said, foreign counties estimate the methane numbers of gaseous fuels with the use of various programs, diagrams, and empirical equations for calculations based on the H/C ratio for a gas mixture. Given below is one of such equations [CARB (California Air Resources Board) method] [3, 5]:

$$MN = 1.624[-406.14 + 508.04(H/C) - 173.55(H/C)^2 + 20.17(H/C)^3] - 119.1.$$

For methane-rich mixtures this formula gives MN values that exceed the actual values by 8.6%, on the average, with this error rapidly increasing with increasing content of heavy components in the mixture.

Another empirical formula allows the MN to be tentatively estimated from the known motor octane number of the fuel [2]:

$$MN = 1.445\times MON - 103.42.$$

Today, Russian and foreign companies (Caterpillar, Cum-mins, Doitz, Willson, Jenbacher, Waukesha, etc.) offer at the Russian market a broad range of gas-piston power plants (GPPPs) whose design and operation modes were optimized for operation with network natural gas characterized by the lowest calorific value of up to 34–36 MJ m^{-3}. Along with intensive resin and soot formation, the main obstacle to application of associated petroleum gas at these GPPPs is its low methane index (typically much lower than 50) and high calorific value of up to 47 MJ m^{-3} and above. The real operation of GPPPs fired by APG with the methane content under 70% may necessitate reduction in the capacity to ≤50% of the nominal level to avoid detonation and overheat of engine, associated with a high calorific value of fuel.

According to various producers' data, there are typically no detonation problems with fuels characterized by antiknock indices above 70, which makes this value suitable as the standard criterion to be satisfied by a candidate fuel for GPPP applications. The minimal methane number acceptable for reference power plants is typically ~52 (Cummins' criteria), but methane numbers of 55–56 are desirable for safeguarding the operability of GPPPs.

Some producers, in the strive to be able to declare the operability of their facilities with associated gas, use gas-piston engine modifications with decreased compression ratios, i.e., go into decreasing the committed level by 25–30% and above relative to the actual capacity. For example, in the case of a VHP9500GSI Waukesha engine with the nominal capacity of 1250 kW a decrease in the compression degree from 10.5 to 8.0 for reference fuel enables decreasing the methane index requirements to 36, but this is paralleled by a decrease in the engine capacity to 1050 kW.

The methane number of a gas fuel is conventionally increased by removal of heavy components. Fractionation techniques for gaseous hydrocarbon mixtures are fairly sufficiently developed but they all involve intricate procedures which require expensive equipment for their implementation and entail high energy consumption associated with gas compression or cooling. The use of low-capacity complex gas-fractionation plants, whose operation is underlain by low-temperature separation of gas mixtures, is an unprofitable option for processing of small gas amounts (0.2–20 mln m^3 $year^{-1}$) to be consumed by power plants with the capacity ranging from several tens of kilowatts to several megawatts; it can be economically justified in rare cases solely.

Table 2. Methane number of normal alkanes

Hydrocarbon	Methane number
Methane	100
Propane	35
n-Butane	11
Hydrogen	0

The major drawbacks suffered by compression-based and low-temperature methods of gas mixture separation aimed to increase their methane number include the loss of a large part of fuel (isolated heavy fractions) and the need in expensive cryogenic, heat-exchange, and compression facilities and in constant high-quality maintenance. All this makes the above-described methods economically unjustified for small-scale power engineering applications with respect to small amounts of associated gas to be processed.

Since recently, adsorption and membrane-based methods of removal of C_{5+} heavy hydrocarbons have been actively developed. Along with the already mentioned loss of a significant part of the fuel, further shortcomings of these methods consist in the need for replacement or regeneration of adsorbents, large quantities of equipment, and increased pressures. In the case of multiphase systems like APG this is a complicated technological task whose accomplishment, moreover, consumes much energy.

Below, two alternative approaches to APG utilizetion as fuel for power plants will be considered. One approach is based on selective oxidative conversion of heavy hydrocarbon components of the mixture to lighter and high-octane compounds suitable as engine fuel. The other approach implies preliminary conversion of APG to syngas which is an efficient fuel for virtually all types of energy drives. This is a

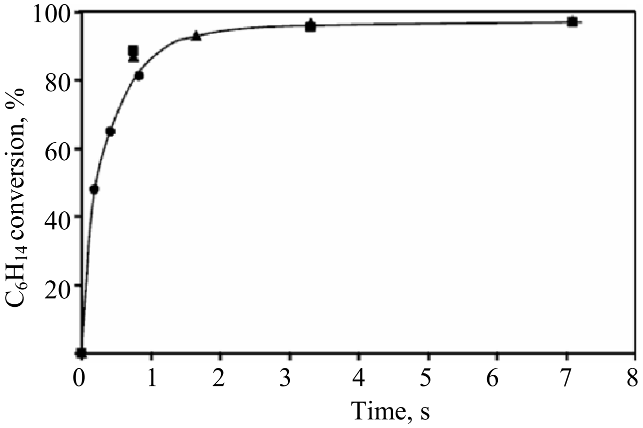

Fig. 3. Kinetics of conversion at 730°C in an empty reactor for hexane mixed with nitrogen at $[O_2]$ = 3.4% at the reactor diameter of (●) 3 and (▲) 6 mm and (■) with methane at $[O_2]$ = 1.6% and the reactor diameter 6 mm [16].

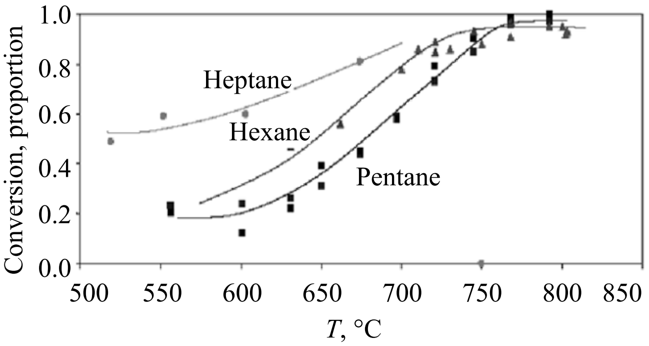

Fig. 4. Temperature dependence of the conversion of impurity C_5–C_7 alkanes in nitrogen. $[C_n]_0$ = 4.4%, $[O_2]_0$ = 3.4%, time of residence in the reactor ~2 s.

universal route by which APG can be completely utilized, because a syngas excess which is not involved in power engineering can be fairly easily converted to synthetic liquid hydrocarbons (via Fischer-Tropsch process) or to other chemical products.

Oxycracking for Selective Conversion of Heavy Hydrocarbons in Associated Petroleum Gas

One way to carry into practice the utilization of APG as engine fuel for power plants is via soft selective oxycracking (selective oxidative conversion) of heavy hydrocarbons to lighter and higher-octane compounds. A similar procedure was suggested for thermal oxidative cracking of liquid hydrocarbons as early as 1930s [6] as a means to increase the octane number of engine fuels. Today, such processes generate increased interest, above all, in an effort to more efficiently use hydrocarbon feedstock in petroleum refining and petrochemistry. For example, the possibility of oxidative activation of thermal cracking of heavy hydrocarbons (tar) was demonstrated [7]: Just 1% oxygen causes the yield of light fractions to double.

Oxidative conversion (oxypyrolysis, oxycracking) of C_{3+} alkanes has since recently attracted much attention as a candidate procedure for preparation of lower olefins [8–13]. It was shown that efficient oxidative conversion may be achieved in the presence of catalysts analogous to those used in oxidative methane conversion (OMC) involving formation and successive transformation of free radicals (see, e.g., [14] and reference therein). This allows the oxycracking processes to be described in terms of the approaches and kinetic schemes that were earlier developed for the OMC process [15]. However, under certain conditions, uncatalyzed conversion of hydrocarbons during oxycracking can be fairly efficient [10] and in some cases can exhibit better characteristics compared to the process run in a catalytic reactor [9].

The known catalysts used in such processes accelerate the conversion of hexane, a typical representative of heavy APG components, but do not afford its exhaustive conversion [16]. At the same time, hexane impurity (~6%) in nitrogen or methane may be virtually exhaustively converted within ~2 s as a result of a gas-phase process run at temperatures above 700°C in an empty reactor (Fig. 3). Minor oxygen additions (1–1.5%) not only accelerate the conversion but also preclude soot formation observed in the absence of oxygen.

Hexane conversion yields lower olefins C_2–C_3 (mostly ethylene), lower alkanes C_1–C_2 (mostly methane), hydrogen, and CO. In the absence of a catalyst, CO_2 is formed in negligible amounts. All these compounds are highly resistant to detonation and, correspondingly have high octane numbers, which makes them suitable as combustible gases for any type of power plant. There are only limited amounts of olefins in engine fuel, e.g., 18 wt% in gasoline, as stipulated by the corresponding technical regulation-2008. However, this concentration, first, exceeds several times that in conversion of C_{6+} hydrocarbons.

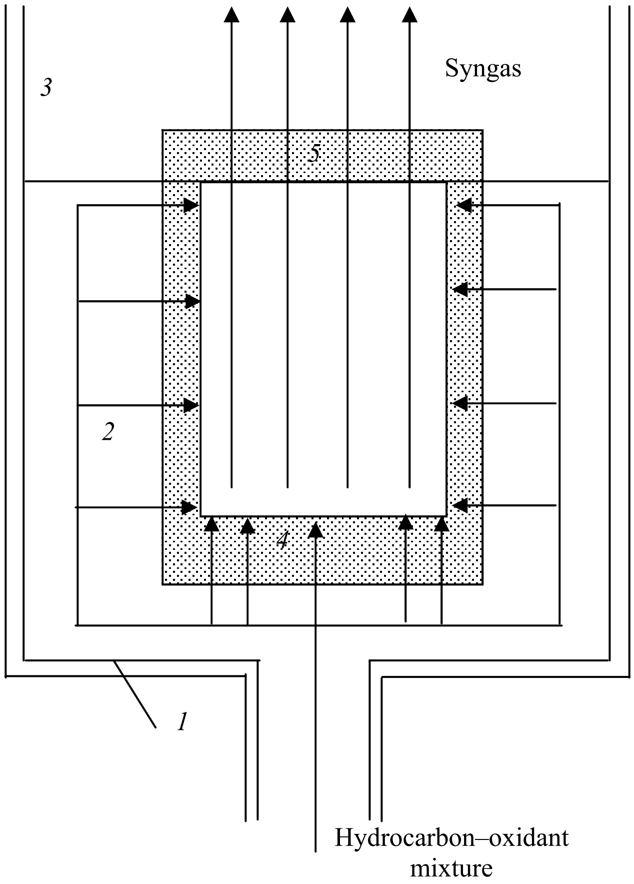

Fig. 5. Radiant burner with a deep volumetric matrix: (*1*) outer casing, (*2*) volume with a gas-air mixture, (*3*) gas outlet, (*4*) perforated ceramic burner side walls and bottom, and (*5*) perforated ceramic burner cavity top.

Second, the regulation refers to heavier liquid olefins. Third, this limitation is aimed primarily at ensuring the stability of gasoline during storage. Oxycracking of hexane yields exclusively light olefins C_2–C_3 whose content in gaseous engine fuel is not subject to regulations. Being much less prone to soot formation and more stable in thermal oxidation reactions than are alkanes C_{6+}, they are accumulated in the system. Therefore, it can be reasonably supposed that C_2–C_3 olefins in gaseous fuel will create no problems.

Similar results and the same products were obtained in conversion of all the C_5–C_7 hydrocarbons which are the basic components of the low-octane part of APG (Fig. 4).

Thus, selective noncatalytic oxycracking of heavy alkanes, contained in APG, at temperatures up to 750°C offers a good option for dealing with the adverse impact they exert on the operation of gas-piston power plants [17].

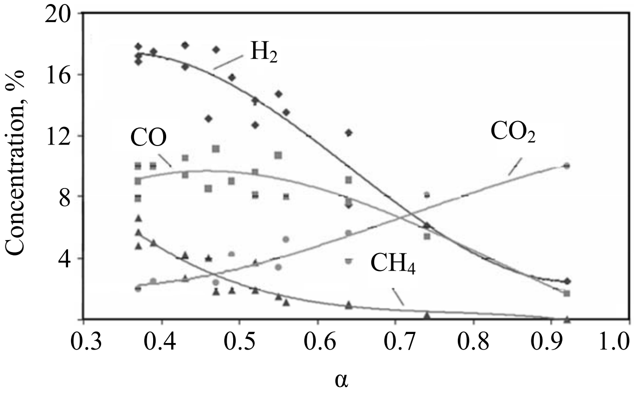

Fig. 6. Concentration of the methane–air mixture conversion products in the cavity of a permeable volumetric matrix vs. oxidant excess coefficient α [18, 19].

Use of Volumetric Radiant Burners for Low-Tonnage APG Conversion to Syngas

Another promising application for small-scale power generation may be found in APG conversion to syngas or hydrogen. However, the currently existing industrial methods of syngas preparation by steam or steam and oxygen conversion of hydrocarbon gases hardly plays a significant role in low-tonnage APG utilization because they are based on complex processes, entail high capital costs, and consume much energy. They account for over 60% of all the expenses in the price of the end product resulted from hydrogen- and syngas-based processes, and may exhibit an acceptable profitability in very large-scale production solely. Moreover, conversion of associated gas to syngas is a more complex task compared to that of

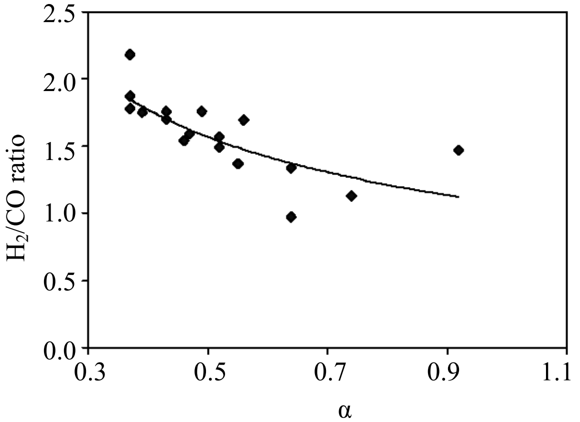

Fig. 7. The H_2/CO ratio vs. oxidant excess coefficient α [18, 19].

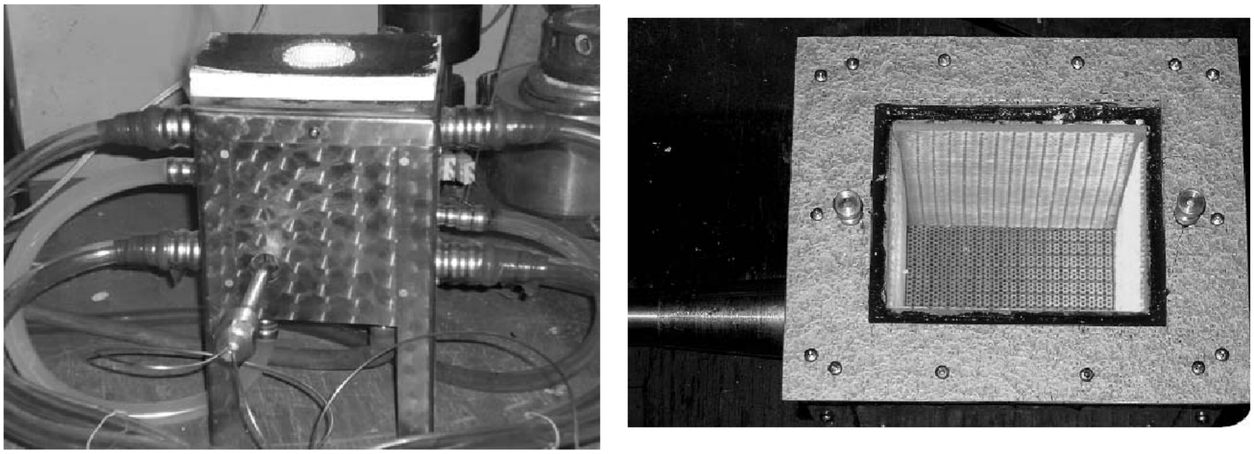

Fig. 8. Layout of the converter based on a 5-kW volumetric matrix burner.

natural gas because of a large difference in the reactivities and, correspondingly, in the conditions of conversion of the hydrocarbons they comprise.

A simpler and a more compact alternative to the existing methods is provided by stable conversion to syngas of very rich hydrocarbon-air mixtures in the surface combustion mode in a volumertic permeable matrix under locked IR radiation conditions [18, 19]. Because of intense convection and radiation heat exchange with the surface, flameless combustion in the vicinity of the inner surface of the permeable volumetric matrix proceeds at much lower temperatures (Fig. 5). In this process, partial locking in the matrix volume of the flame front which accounts for a significant proportion (up to 40% in the case of flameless combustion near the surface of flat-flame IR burners) of the chemical energy of hydrocarbon gas allows the combustion limits to be significantly extended to rich hydrocarbon-oxidant mixtures, up to the oxidant excess coefficient $\alpha = [O_2]_0/2[CH_4]_0 = 0.36$. Under these conditions, it is possible to carry out oxidative conversion of mixtures whose combustion under normal conditions is virtually impossible. As a result, a noncatalytic process gives syngas in a yield close to that achieved under thermodynamic equilibrium conditions (Fig. 6).

Under optimal conversion conditions and small oxidant excess coefficients the H_2/CO ratio is very close to the value of 2 that ideally suits the subsequent engineering application of syngas (Fig. 7).

On this basis, a compact device was developed for syngas preparation from hydrocarbon gases virtually irrespective of their composition [20]. Figure 8 shows the layout of a breadboard model of such generator of syngas, as well as the internal cavity of the perforated ceramics volumetric matrix in service (with a permeable top of the matrix cavity removed).

This burner is much simpler than are the known reactors used for syngas preparation, in particular, catalytic reforming reactors, and is suitable for consistently providing the methane conversion characteristics and hydrogen and carbon monoxide yields close to those achieved in the known processes. Its efficiency can vary extensively depending on the amount of the combustible mixture spent. Considering the fact that the capacity and modular design of the burners can be broadly varied, this type of hydrogen and syngas generators can cover the entire range of capacities that are of practical interest for APG conversion purposes.

Along with the autothermal nature of the process, the syngas generator based on a radiant burner with a volumetric matrix offers advantages in terms of broad capacity range, compactness (specific thermal power of up 30 W cm^2), simple design, and easy maintenance, as well as no need in catalyst and lack of soot formation in the reactor cavity; also, the structural materials need not satisfy special criteria. Importantly, this generator is suitable for conversion of hydrocarbon gases virtually irrespective of their composition, in particular, of APG (and, possibly, heavier hydrocarbons), and its operation does not lead to contamination of the working surface of the matrix with combustion products. It should be noted that conversion in a radiant burner with a volumetric matrix can be implemented at enhanced pressures as well.

This makes the process attractive for preparation of syngas to be used in industrial processes that require high pressure of syngas. Depending on the specific requirements posed on syngas, the generator may use air, enriched air, or oxygen as oxidants.

The syngas generator can be supplemented with a catalytic converter which effects conversion of carbon monoxide to hydrogen via reaction with steam, so that which the hydrogen yield can be increased by half. This type of hydrogen generator could supply power to low-capacity autonomous plants, e.g., in distributed energy resource systems based on electrochemical generators (fuel cells). Specifically the lack of compact autonomous sources is one of the main obstacles to development of hydrogen power engineering.

A major advantage offered by the approach based on the APG conversion to syngas is its versatility and flexibility, which enables not only conversion of hydrocarbon gases of any composition but also their complete utilization: A syngas excess can be converted without significant efforts to easily transportable synthetic liquid hydrocarbons and other compounds (methanol, dimethyl ether). As to power consumption differences, they could be compensated by changing the volume of syngas intended for further chemical conversion.

REFERENCES

1. Emel'yanov, V.E. and Skvortsov, V.N., *Motornye topliva: Antidetonatsionnnye svoistva i vosplamenyaemost'* (Engine Fuels: Detonation Properties and Inflammability), Tekhnika: Moscow, 2006.
2. *Rossiiskaya gazovaya entsiklopediya* (Russian Gas Encyclopedia), Vyakhirev, R.I., Ed., Moscow: Bol'shaya Rossiiskaya Entsiklopediya, 2004, pp. 102–104.
3. Lapidus, A.L., Krylov, I.F., Zhagfarov, F.G., and Emel'yanov, V.E., *Al'ternativnye motornye topliva: Uchebnoe posobie* (Alternative Motor Fuels: Textbook), Moscow: TsentrLitNefteGaz, 2008.
4. Verhelst, S. and Wallner, T., *Prog. Eng. Comb. Sci.*, 2009, vol. 35, pp. 490–27.
5. *Paper Study on the Effect of Varying Fuel Composition on Cummins Gas Engines, Los Angeles (CA): Southern California Gas Company,* May 4, 2005, *http// www.socalgas.com.*
6. Dubovai, K.K. and Sheinman, A.B., *Okislitel'nyi kreking* (Oxidative Cracking), Moscow: Glav. Red. Gorno-Topl. Liter., 1936.
7. Galiev, R.G., Luganskii, A.I., Moroz, I.V., and Ermakov, A.N., *Mir Nefteprodukt*., 2008, no. 7, p. 16.
8. Leveles, L., *Ph.D. Thesis, Enschede*, The Netherlands: Univ. Twente, 2002.
9. Leveles, L., Seshan, K., Lercher, J.A., and Lefferts, L., *J. Catal*., 2003, vol. 218, p. 296.
10. Huynh, L.K., al Shoaibi, A., Carstensen, H.-H., and Dean, A.M., *Prepr. Pap.-Amer. Chem. Soc., Div. Fuel Chem*., 2009, vol. 54(1), p. 56.
11. Liu, X., Li, W., Zhu, H., Ge, Q., Chen, Y., and Xu, H., *Catal. Lett.,* 2004, vol. 94, p. 31.
12. Liu, X., Li, W., Xu, H., and Chen, Y., *React. Kinet. Catal. Lett*., 2004, vol. 81, p. 203.
13. Boyadjian, C., Lefferts, L., and Seshan, K., *Appl. Catal. A: Gener*., 2010, vol. 372, p. 167.
14. Arutyunov, V.S. and Krylov, O.V., *Okislitel'nye prevrashcheniya metana* (Oxidative Transformations of Methane), Moscow: Nauka, 1998.
15. Kondratenko, E.V. and Sinev, M.Yu., *Appl. Catal. A: Gener*., 2007, vol. 325, p. 353.
16. Arutyunov, V.S., Bykhovskii, M.Ya., Sinev, M.Yu., and Korchak, V.N., *Izv. Ross. Akad. Nauk, Ser. Khim*., 2010, no. 8, pp. 1493–1496.
17. Arutyunov, V.S., Bykhovskii, M.Ya., Sinev, M.Yu., and Korchak, V.N., RF Patent no. 2385897, 2010.
18. Arutyunov, V.S., Shmelev, V.M., Lobanov, I.N., and Politenkova, G.G., *Teor. Osnovy Khim. Tekhnol*., 2010, vol. 44, no. 1, pp. 21–30.
19. Arutyunov, V.S., Sinev, M.Yu., Shmelev, V.M., and Kiryushin, A.A., *Gazokhimiya*, 2010, no. 1(11), pp. 16–20.
20. Arutyunov, V.S. and Shmelev, V.M., RF Patent no. 2374173, 2009.