ISSN 1070-3632, Russian Journal of General Chemistry, 2011, Vol. 81, No. 12, pp. 2594–2603. © Pleiades Publishing, Ltd., 2011.

Original Russian Text © Yu.A. Kolbanovskii, I.V. Bilera, I.V. Rossikhin, A.A. Borisov, K.Ya. Troshin, 2010, published in Rossiiskii Khimicheskii Zhurnal, 2010, Vol. 54, No. 5, pp. 62–69.

Single-Stage Conversion of Associated Petroleum Gas and Natural Gas to Syngas in Combustion and Auto-Ignition Processes

Yu. A. Kolbanovskii[a], I. V. Bilera[a], I. V. Rossikhin[a], A. A. Borisov[b], and K. Ya. Troshin[b]

[a] *Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Leninskii pr. 29, Moscow, 119991 Russia*
phone: +7(495)9554897
fax: +7(495)6338520
e-mail: kolbanovsky@ips.ac.ru

[b] *Semenov Institute of Chemical Physics, Russian Academy of Sciences, ul. Kosygina 4, Moscow, 119991 Russia*
phone: +7(495)9397228
fax: +7(495)6512191
e-mail: troshin@chph.ras.ru

Received June 12, 2010

Abstract—Single-stage conversion of alkane mixtures simulating associated petroleum gas (APG) to syngas is studied in a static installation and in a flow reactor based on the rocket combustion chamber. Yields of the desired reaction products close to their thermodynamically equilibrium values are obtained. A range of experimental parameters, in which ignition delays of APG-oxygen mixtures exhibit negative or zero temperature coefficients, is determined for the first time. Such a behavior of ignition delays is proved to be a fundamental property of fuel-rich APG mixtures. The range of abnormal temperature dependence of ignition delays is shown to be extended as the initial pressure rises, which makes it possible to significantly increase the reaction rate by increasing the initial working pressure.

DOI: 10.1134/S1070363211120280

INTRODUCTION

Associated petroleum gas (APG) recovery is one of the most important economic and environmental aspects of crude oil production; and the solution of this problem is of special importance for Russia [1]. Thus, the world average APG recovery rate is already at the level of 95%, while Russia has not yet reached such figures. In Resolution of the Government of the Russian Federation no. 7 of January 8, 2009 it is planned to reach such APG recovery rate by 2010. According to the official data, 26% of 55 bln. m^3 of APG extracted in Russia is sent for processing; about 27% of gas is flared and 47% is used by the extracting companies to satisfy field production needs or is written off as process losses [2]. The technology for conversion of natural gas with a relatively low content of methane homologs is well developed and widely used in industry. The companies start to apply this technology at natural gas production sites as well [3]. At the same time, there are no industrial technologies for chemical processing of APG and gases from gas-condensate fields without their preliminary separation into individual components yet [4].

The first stage of natural gas chemical processing is conversion to syngas, which can be performed in a number of ways. The most widely applied methods are steam, steam-oxygen, and autothermal reforming of natural gas with a high methane content; in order to use these methods for APG conversion it is necessary to perform preliminary catalytic transformation of C_2^+ alkanes.

The steam reforming process is characterized by a high metal consumption, significant energy consumption, and high operational costs. The method of gas-phase uncatalyzed partial oxidation in different combustion regimes is free from these disadvantages; moreover, it is an exothermic process [5]. Application of this method makes it possible to convert hydro-

Table 1. Composition of APG from samotlor oil field after separation [9]

Separation stages	Gas composition after separation									
	CO_2	N_2	CH_4	C_2H_6	C_3H_8	*iso*-C_4H_{10}	*n*-C_4H_{10}	*iso*-C_5H_{12}	*n*-C_5H_{12}	$C_6H_{14}^+$
1, wt %	0.84	1.26	62.69	8.07	14.00	2.94	5.81	1.31	1.51	1.57
1, vol %	0.42	1.04	81.67	5.63	6.67	1.04	2.08	0.42	0.42	0.42
2, wt %	0.88	0.31	48.15	11.77	21.22	4.23	8.12	1.68	1.97	1.67
2, vol %	0.48	0.27	71.70	9.85	11.48	1.73	3.34	0.56	0.65	0.44
3, wt %	0.82	0.04	21.06	13.84	33.87	7.06	14.07	2.87	3.49	2.88
3, vol %	0.61	0.05	43.13	15.12	25.22	3.98	7.95	1.32	1.59	1.03

carbon gases with a high C_2^+ content to syngas in one stage. That is exactly why the development of a single-stage technology for APG chemical conversion to syngas is a most crucial task.

This article is dedicated to one of possible options to solve this problem. At the same time, as usual, there are two aspects to this issue: firstly, the scientific aspect related to physicochemical characteristics of the process of APG homogeneous uncatalyzed partial oxidation to syngas in different combustion regimes; secondly, the engineering aspect, i.e. the question of doing it in the best way. We consider both these aspects and provide research results for the conversion process performed in two types of reactors: in a static bypass installation [6, 7] and in a high-temperature flow chemical reactor based on the rocket technology [8].

For adequate representation of the hydrocarbon composition of APG coming for chemical processing, we use a typical composition of APG from the Samotlor oil field after separation as an example (Table 1).

It is evident that in order to obtain syngas it is desirable to use gases of the first and second separation stages, which contain 70–80 vol % of methane and 20–25 vol % of ethane and propane, while the content of C_4^+ hydrocarbons is at the level of 2–5 vol %. At the same time, gases of the third separation stage contain large quantities of heavy hydrocarbons and less than 50 vol % of methane. In chemical processing of such gases it is rational to send them for pyrolysis for production of ethylene and propylene.

The main component of APG after the first and second separation stages that is intended for conversion to syngas is methane. Therefore, at the first stage we examined rich methane mixtures. At the second stage we investigated partial oxidation of APG-simulating mixtures containing methane and lower alkanes.

Obtainment of Syngas from Methane through Partial Oxidation

In the context of the energy industry, methane as the main component of natural gas, which is conventionally combusted for energy production purposes, is thoroughly studied. However, in order to carry out the reaction of methane partial oxidation in combustion regimes, i.e. to achieve the chemical effect but not the energy effect, it is necessary to combust oxygen-deficient mixtures. Unfortunately, the combustion of oxygen- and air-methane mixtures of such non-conventional composition is understudied. Therefore, it was necessary to carry out a series of experimental studies in order to determine some combustion patterns characteristic of rich methane-oxygen mixtures.

A static bypass installation was constructed to carry out experimental research on combustion of rich methane-oxygen mixtures, which enabled us to perform research studies both in laminar and turbulent combustion regimes (forced ignitions) and in the auto-ignition regime. The major objectives of the studies of natural gas and APG partial oxidation in the static bypass installation were to identify the limiting combustion conditions for super-rich mixtures of hydrocarbons with air, oxygen, and enriched air, to select conditions to achieve the maximal yield of the syngas components at minimal concentrations of undesirable substances (soot, unburned hydrocarbon gases, residual oxygen, and CO_2) in the products, and to select a combustion regime for the mixtures (flame or auto-ignition) ensuring the maximal speed of

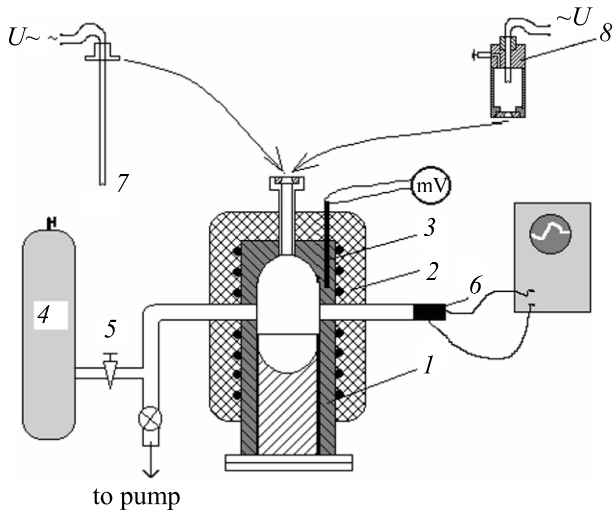

Fig. 1. Experimental installation layout: (*1*) reactor, (*2*) heat insulation, (*3*) thermal couple, (*4*) mixer, (*5*) valve, (*6*) pressure sensor, (*7*) ignition device based on electric burning of the wire (ignition), and (*8*) precombustion chamber.

conversion at thermodynamically equilibrium yield of target products. Although the conditions in the static installation are far from conditions in real industrial units, the results of the experiments can be directly used in piston-engine type installations working under conditions of forced compression of the mixture. They also provide information necessary for the process organization in flow reactors based on the rocket combustion chamber technology.

The main advantage of the installation is its demountable structure, which enabled us to open the installation after every experimental test, take out the soot that had formed, and, therefore, define the yield of the condensation product with certainty. The installation layout is given in Fig. 1.

A method of electric burning of a thin wire was used to ignite the mixture in the course of studies of laminar combustion regimes. The normal flame speed in these combustion regimes was measured on the basis of the spherical bomb method [12] and the composition of combustion products was determined. Pre-combustion chamber ignition was used in order to achieve turbulent combustion regimes. The capacity of the pre-combustion chamber amounted to 5% of the reactor capacity; moreover, the pre-combustion chamber could be filled with mixtures different from the mixtures under investigation in composition. Ignition delay measurements were performed in auto-ignition regimes. Samples of gas-phase combustion products were taken, the soot was weighed, and its specific surface area was measured on the basis of the low-temperature adsorption method for all the abovementioned combustion regimes. The research works were carried out using oxygen-methane mixtures with oxygen excess factors $\alpha = 0.25$, 0.30, and 0.35 within the initial pressure range of 15–40 atm at temperatures ranging from 22 to 600°C.

Ignition delay measurements for rich oxygen-methane mixtures were performed at the initial pressure of 15 at and initial temperatures ranging from 500 to 630°C in mixtures with oxidant excess factors $\alpha = 0.30$ and 0.35. The results demonstrated that auto-ignition delays for two mixtures of different composition were almost identical. Ignition delays for the specified mixtures in Arrhenius coordinates are described with the following Eq. (1):

$$\tau = 5.4\times10^{-12}e^{43500/RT}. \qquad (1)$$

Activation energy of 43 500 cal mol^{-1} is particularly characteristic of methane oxidation in air and oxygen mixtures of the conventional composition.

The normal flame speed for mixtures of three different compositions depending on the initial heating temperature is approximated by the following second-order Eqs. (2)–(4), which is in full compliance with the modern scientific ideas regarding combustion.

For mixtures with the oxygen excess factor α = 0.25:

$$U = 3.82\times10^{-5}T_0^2 - 1.46\times10^{-2}T_0 + 4.26. \qquad (2)$$

For mixtures with the oxygen excess factor α = 0.30:

$$U = 1.14\times10^{-4}T_0^2 - 5.9\times10^{-2}T_0 + 14.42. \qquad (3)$$

For mixtures with the oxygen excess factor α = 0.35:

$$U = 2.2\times10^{-4}T_0^2 - 1.15\times10^{-1}T_0 + 29.7. \qquad (4)$$

The experiments also demonstrated that the normal flame speed in the methane-oxygen mixtures under investigation almost did not depend on the initial pressure.

As could be expected, normal combustion velocities are not high and hardly exceed 40 cm s^{-1} even for the fastest burning mixtures with the oxygen

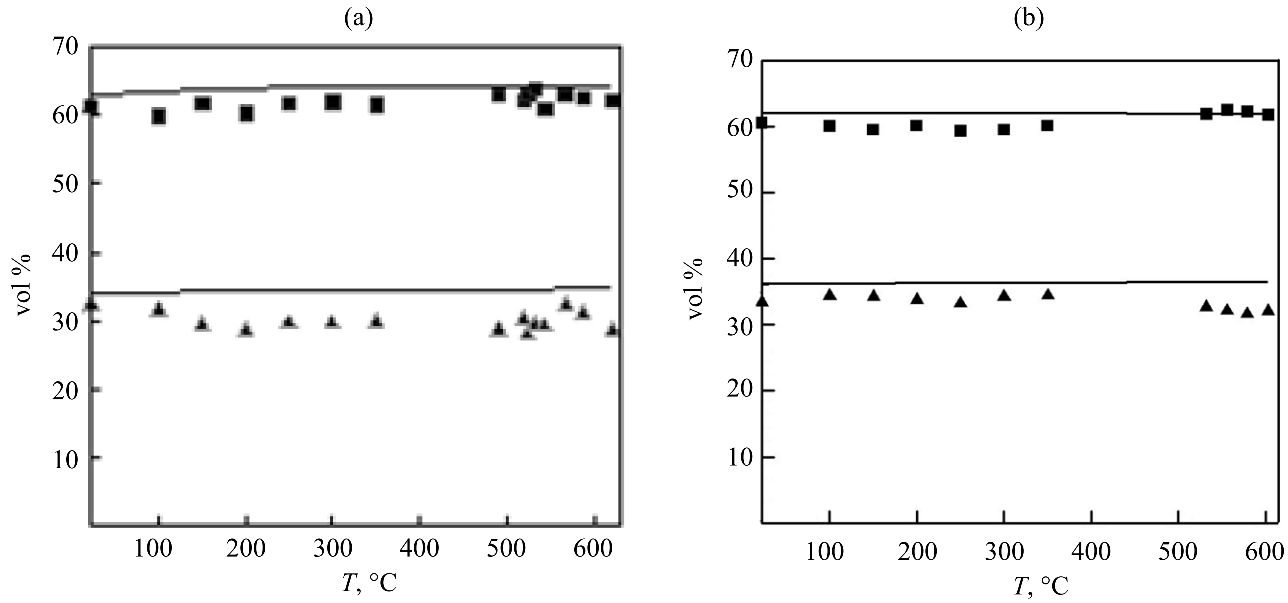

Fig. 2. Comparison of target product yield from combustion of $CH_4 + 2\alpha O_2$ mixtures at forced ignition and auto-ignition ($T_0 > 450$°C) with thermodynamic calculations: $P_0 = 15$ at, $\alpha = 0.30$; (■) H_2, (▲) CO, experiment. (Lines) thermodynamic calculations: (a) for $\alpha = 0.30$ and (b) for $\alpha = 0.35$.

excess factor α = 0.35. Pre-combustion chamber ignition was used in order to accelerate burning of the mixture. It was found that under limited-volume conditions it was possible to reduce the mixture burning time approximately by a factor of 20–30. The combustion velocity for rich mixtures in the turbulent flow can be increased by a factor of 5–7 compared to the normal combustion velocity.

Table 2. Composition of methane partial oxidation products (dry gas)

Component	Static installation		High-temperature flow chemical reactor, 10-minute experiments	
	vol %	wt %	vol %	wt %
H_2	57.6	8.9	56.4	8.2
Ar	0.1	0.3	1.1	3.2
O_2	0.0E+00	0.0E+00	0.02	0.05
N_2	2.0	4.3	0.3	0.6
CH_4	3.9	4.7	2.8	3.2
CO	33.4	71.7	32.6	66.0
CO_2	3.0	10.0	4.4	13.9
C_2H_6	0.01	0.03	0.01	0.01
C_2H_4	7.2E-03	1.6E-02	0.3	0.6
C_2H_2	0.0E+00	0.0E+00	2.0	3.8
Methylacetylene	9.2E-06	2.8E-05	0.007	0.02
1,3-butadiene	4.5E-05	1.9E-04	0.003	0.01
C_5H_{10}	6.8E-05	9.5E-05	0.01	0.05
C_6H_{12}	5.0E-06	8.4E-06	0.005	0.03
C_6H_6	3.0E-03	4.6E-03	0.01	0.07
Total	100.0	100.0	100.0	100.0

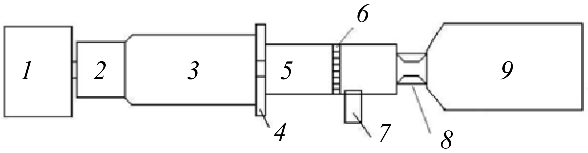

Fig. 3. High-temperature flow reactor layout: (*1*) electropneumatic valve, (*2*) injector, (*3*) pre-mix chamber, (*4*) flame holder, (*5*) reaction zone in combustion chamber, (*6*) turbulator, (*7*) ignition device, (*8*) nozzle, and (*9*) afterburning zone.

As seen, the mixture combustion regimes with forced ignition cannot provide a high speed of conversion of hydrocarbon gases to syngas in industrial reactors. It is possible to solve the problem of raising the partial oxidation rate using the auto-ignition regime, which should improve the combustion conditions in flow reactors due to a sharp (by orders of magnitude) increase in the reaction rate at quite reasonable increase in the initial temperature of the mixture.

Composition of Combustion Products

The composition of combustion products was identified for different combustion regimes in all the experiments. The results of chromatographic analysis were compared with the results of thermodynamic calculations. Figure 2 provides an example of such a comparison for mixtures with oxygen excess factors $\alpha = 0.30$ and 0.35 depending on the initial temperature of the mixture under auto- and forced-ignition conditions in cases of laminar and turbulent combustion. As can be seen from Fig. 2, the composition of combustion products within the range of measurement error does not depend on the ignition method.

A certain divergence with thermodynamic calculations is observed. Although this divergence does not exceed several percent, the richer the mixture is, the more the divergence is. It can be explained by the formation of the condensation product, soot, in combustion of the mixtures under investigation. According to the thermodynamic calculations, the soot content in combustion products of such mixtures should not exceed 0.10–0.08 mole fraction. However, in the experiments the soot yield was quite significant and the richer the mixture was, the higher the soot content was, which can be related to incomplete combustion of the mixture in the boundary layer close to the reactor walls.

The results of the experiments showed that mixtures with the oxygen excess factor $\alpha = 0.25$ were, apparently, quite unpromising as the target product yield did not exceed 86% and the methane content in combustion products reached 11%. Optimal values of the mixture composition, temperature, and pressure, as well as the most feasible ignition regime were defined. Table 2 shows the composition of products of methane partial oxidation with oxygen in a rich mixture with the oxidant excess factor $\alpha = 0.35$. The following ratios were observed in the resulting syngas: $H_2/CO = 1.72$ and $CO/CO_2 = 11.3$.

Formation of the solid carbon phase (soot) in production of syngas in the process of combustion of rich methane mixtures in the static bypass reactor and in the flow reactor based on the rocket technology is described in works [10, 11]. Ways to minimize the soot yield in production of syngas in the combustion process were found. Experiments demonstrated that additions of water vapor (5–10 wt % relative to methane) reduced soot formation in combustion of oxygen-methane mixtures with the oxidant excess factor $\alpha \geq 0.35$, and in case of a 15% addition of water vapor the soot formation was almost completely suppressed. Similar results were obtained when syngas was added to the air-fuel mixture and a 5% addition of syngas almost fully suppressed the soot formation. Studies of the influence of individual syngas components on soot formation demonstrated that the main effect was related to inhibition of the soot formation by hydrogen. The influence of combustion regimes on soot formation was studied and its properties were investigated [10, 11].

Partial oxidation of rich methane mixtures was also investigated using a test facility, the major element of which was a high-temperature flow chemical reactor based on the rocket technology. Unlike the static bypass installation, the process of partial oxidation in a flow of preliminarily unmixed rich mixtures was studied in this reactor.

The reactor was built on the basis of a standard liquid fuel rocket engine of MDTO-123 type (Fig. 3). It consists of an electropneumatic valve (*1*), an injector (*2*), a pre-mix chamber (*3*), a combustion chamber (*5*), a nozzle (*8*), at which supercritical pressure difference is created, and an afterburner (*9*). The volume of the combustion chamber is 1.2 l.

The distinctive feature of the flow chemical reactor that we developed is that the combustion process inside the combustion chamber takes place in the

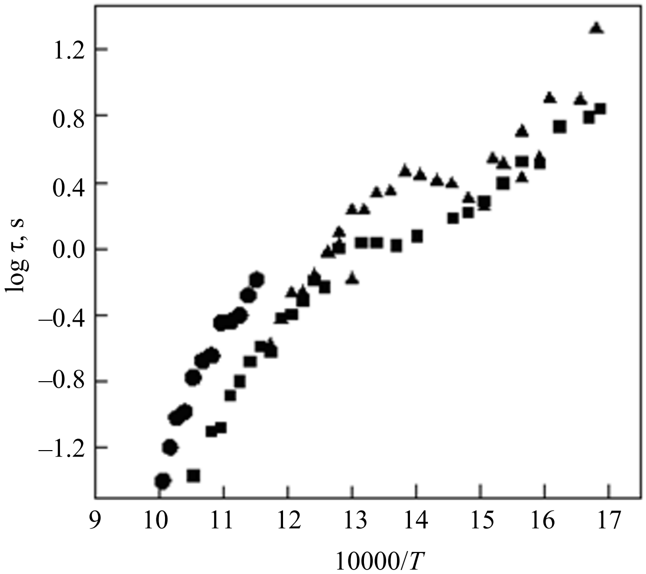

Fig. 4. Temperature dependence of ignition delays in oxygen mixtures of associated petroleum gas ($0.8CH_4 + 0.2C_3H_8$) at different pressures, at: (●) $P_0 = 1$; (■) $P_0 = 3$; (▲) $C_3H_8 + 1.5O_2$; $P_0 = 1$.

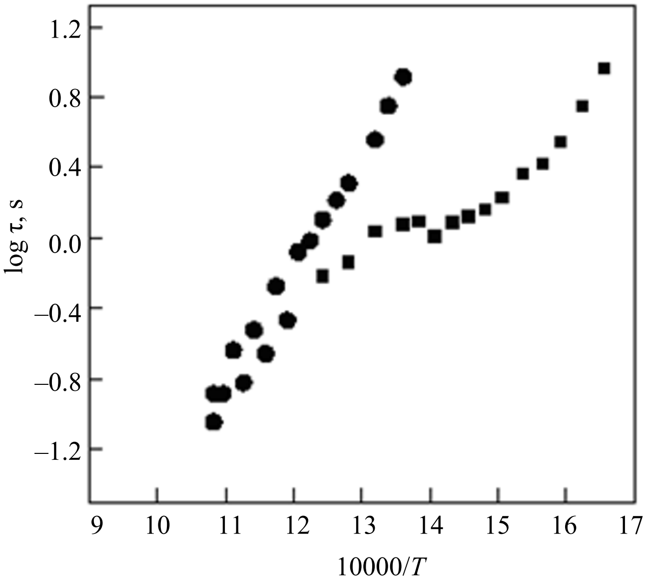

Fig. 5. Temperature dependence of ignition delays in oxygen mixtures of associated petroleum gas ($0.6CH_4 + 0.4C_3H_8$) at different pressures, at: (●) $P_0 = 1$ and (■) $P_0 = 2$.

volume limited by the flame holder (*4*) and the nozzle (*8*) [8]. This construction solution makes it possible to create conditions of elevated combustion intensity inside the combustion chamber, which is reflected on the end product composition.

Inside the combustion chamber there are some details, the geometrical dimensions of which have an impact on formation of the combustion process. Such details include the flame holder, the turbulator, and the nozzle. At present it is almost impossible to carry out theoretical calculations of optimal dimensions of these combustion chamber elements. Therefore, the quantity and optimal ratio of the flow area dimensions in the flame holder, the turbulator, and the nozzle of the combustion chamber were defined by experiment.

Difficulties in ignition of rich mixtures that are always used in syngas production based on the partial oxidation method are well-known. In this connection, different ignition methods were studied at the first stage of the research. It was found out that the best method for ignition of the gas mixture in the flow reactor was to use a liquid fuel rocket micro-engine working on methane-oxygen mixture, the composition of which makes it possible to perform ignition using an electric candle. However, such a technique is not very convenient under production conditions. In this connection, we applied a new method for ignition of rich mixtures in the high-temperature flow chemical reactor using a modern industrial production glow-plug for the first time.

High-temperature glow-plugs, e.g. Bosch Dura-Speed with ceramic heating elements, heat up to 1000°C in less than two seconds and reach the glow temperature of 1300°C. After the reactor is started new glow-plugs maintain long afterglow with a temperature of 1300°C during operation. It reduces formation of the process byproducts before the flow reactor reaches steady thermal conditions.

Combustion products left the chamber through the nozzle with the critical cross-section, which contributed to keeping the working pressure in the combustion chamber at a level of 5–10 atm. The high-temperature flow chemical reactor installed as a part of the testing facility made it possible to carry out flame experiments more than 10 minutes long. In some of the experiments the heat of the partial oxidation reaction was used to heat up the incoming methane flow, which contributed to better mixing and lower soot formation.

The composition of the gas under investigation was as follows (vol %): methane 98.0 and C_2^+ hydrocarbons 2.0. Oxygen was used as an oxidant. The total consumption of the source components amounted to 12 l s^{-1} for short-term and 5 l s^{-1} for longer experiments. Chemical analysis of the initial mixtures and products was performed on the basis of the gas chromatography method.

It was determined experimentally that an increase in the oxygen excess factor α from 0.33 to 0.41 resulted in a reduction in the residual methane content. However, the oxygen content in the products was rising simultaneously. It was demonstrated that in the high-temperature flow chemical reactor under the design of TIPS RAS the best results were achieved within a narrow range of values of the oxygen excess factor α = 0.37–0.39. Table 2 shows the composition of methane partial oxidation products (α = 0.37).

According to the results of the analysis, oxygen conversion reached 99.9% and methane conversion exceeded 91%. The following ratios were achieved: H_2/CO = 1.73 and CO/CO_2 = 7.4. The composition of the process products met the requirements usually set up for syngas in terms of the residual oxygen content and the total of hydrocarbons and CO_2.

Formation of small amounts of soot was detected: during 10 minutes of the reactor operation 0.025 wt % of soot was formed from 1.2 kg of methane. It should be noted that heating of source methane and additions of water vapor reduce the soot yield.

The results obtained in the static bypass installation and in the flow reactor are quite close. In the static reactor the content of C_2^+ hydrocarbons is slightly lower (the greatest divergence is observed for acetylene) and CO/CO_2 ratio is higher.

It should be noted that during partial oxidation of natural gas in the flow reactor C_2–C_5 alkanes present in the gas are converted almost completely. This fact indicates that there is a principal possibility to apply the high-temperature flow chemical reactor for chemical processing of APG into syngas in one stage.

It is also important to note that partial oxidation of methane and APG to syngas is an energy-producing process. The released heat can be used for production of water vapor, which is a highly attractive option if the process is applied at remote fields in northern latitude regions. The amount of heat released in the methane partial oxidation process calculated on the basis of the experimental data that we obtained in the flow reactor reached 1.5 Gcal per 1 t of syngas.

From this perspective, APG is more advantageous than methane as CO/H_2 ratio rises in APG oxidation and, correspondingly, there is an increase in heat liberation in the process of partial oxidation. In this connection, we can agree with the authors of work [5] that it is rational to equip the syngas production installation with a catalytic converter of carbon oxide to hydrogen according to the following conversion reaction: $CO + H_2O \rightarrow CO_2 + H_2$. This reaction does not only increase the yield of hydrogen but it also releases additional heat (approximately 10 kcal mol^{-1}).

We also support the authors of this work [5] with regard to the possibility and advisability to use the produced hydrogen, which can be separated from syngas using the available and technologically proven means (through membranes), for the production of fuel cells, the unit capacity of which has significantly increased in recent years.

Conversion of APG Model Mixtures to Syngas

A possibility to obtain syngas in uncatalyzed auto-ignition regimes of associated petroleum gas of different composition in oxygen was investigated. The performed studies demonstrated that, compared to laminar and turbulent combustion regimes, the composition of APG combustion products in the auto-ignition regime was closer to the composition based on thermodynamic calculations both in terms of the target product content and the residual content of methane and oxygen, while the speed of conversion was many times higher. However, published materials contain no information on the temperature range of APG auto-ignition and on APG ignition delays in oxygen environment, i.e. information that is vital for practical implementation of the APG partial oxidation reaction in industry.

The experiments were carried out in the static bypass installation under limited-volume conditions. Auto-ignition of propane was investigated as propane is the main component of C_3–C_6 heavy fractions, forming a part of associated petroleum gas. Auto-ignition of methane and propane model mixtures containing 40% and 20% of C_3H_8, respectively, in rich mixtures with oxygen was also studied. The oxygen excess factor in all the mixtures under investigation amounted to 0.30. Ignition delays were measured within a temperature range of 600–900 K at pressures of 1 and 3 at.

It was determined that weak stage auto-ignition was characteristic of oxygen-propane mixtures, which was most distinctly manifested in auto-ignition of heavy hydrocarbons found in liquid engine fuels [12]. Figures 4 and 5 provide the results of ignition delay measurements for propane and APG of different composition in Arrhenius coordinates. It is noteworthy that the temperature range of propane auto-ignition is limited by quite a low temperature value $T_0 = 595$ K. Moreover, within a temperature range of 670–830 K a negative temperature coefficient (NTC) for ignition delays is observed, which means that this value increases with rising temperature.

The temperature range of APG auto-ignition in oxygen at a pressure of 1 at is limited below by a higher temperature of $T_0 = 740$ K, while auto-ignition delays themselves do not have any NTC zone. However, the effective activation energy is 36.1 kcal mol^{-1}, which is more characteristic of propane than of methane and speaks for the defining role of propane in the process of APG auto-ignition. It is important that at a pressure of 2.3 at the temperature range of APG auto-ignition is extended and reaches the same limit as for propane. Within a temperature range of 710–830 K the negative temperature coefficient is observed for propane, while APG exhibits abnormal behavior of auto-ignition delays, which remain almost unchanged within the indicated temperature range, i.e. the temperature coefficient assumes a value close to zero or slightly negative. This fact is also indicative of the leading role of propane in APG oxidation.

In model mixtures of APG with a low propane content the NTC zone is found at higher pressures than in APG mixtures with a high propane content. It is possible that the NTC zone appears at a definite absolute content of heavy hydrocarbons in the mixture.

It can be claimed that the NTC effect is a fundamental property characteristic of many APG compositions. It was also established that outside the NTC zone auto-ignition delays comply with general laws and decrease with rising temperature. The distinctive feature of auto-ignition at elevated pressures for rich APG mixtures containing propane is the possibility to significantly reduce (by approximately 150°C) the ignition temperature as compared to natural gas mixtures. According to the preliminary data, the major end products of auto-ignition in the NTC zone are hydrogen and CO; the composition of the products is in compliance with the thermodynamic calculations.

The negative temperature coefficients observed in APG auto-ignition in oxygen were detected for the first time. It is well-known that in the NTC zone, which is characteristic of all heavy hydrocarbons, the ignition delay strongly depends on the initial pressure of the mixture. This fact makes it possible to expect an ignition delay of several milliseconds in rich mixtures of APG with oxygen when the initial pressure of the mixture is increased to 10–15 at, which will drastically reduce the time of the raw material conversion to syngas. Therefore, the limits of the NTC zone should be preliminarily established for typical APG compositions at different separation stages. Thus, the NTC zone for mixtures simulating associated petroleum gas was identified. The presence of C_3–C_6 heavy hydrocarbons in real associated petroleum gases extends the temperature range of their auto-ignition in oxygen and is responsible for the negative temperature coefficient zone.

Table 3. Composition of APG model mixture partial oxidation products (dry gas)

Component	vol %	wt %
H_2	25.5	2.3
Ar	2.3	4.1
O_2	0.49	0.70
N_2	40.5	50.6
CO	20.0	25.0
CO_2	7.0	13.7
CH_4	3.2	2.3
C_2H_6	0.02	0.03
C_2H_4	0.19	0.24
C_2H_2	0.63	0.73
C_3H_8	0.04	0.07
CH_2CCH_2	0.002	0.004
iso-C_4H_{10}	0.005	0.013
n-C_4H_{10}	0.01	0.03
Methylacetylene	0.005	0.009
C_5H_{10}	0.002	0.008
C_6H_{12}	0.002	0.007
C_6H_6	0.01	0.04
Total	100.0	100.0

The practical significance of identification of the NTC zone is that inside this area it is possible to observe a drastic decrease in the reaction time at an increase in the initial pressure; therefore, the limits of the NTC zone should be preliminarily established for typical APG compositions of different separation stages.

The model mixture of APG that was studied in the high-temperature flow chemical reactor had the following composition: 90 vol % of methane, 2.1 vol % of ethane, 5.7 vol % of propane, and 2.2 vol % of butanes. Air enriched with oxygen was used as an oxidant containing 2.8 vol % of Ar, 44.4 vol % of O_2, and 52.8 vol % of N_2 (argon was added as an internal standard). The selection of this oxidant for APG model mixture was dictated by the fact that air enriched with oxygen is the optimal oxidant under APG production and processing conditions [13]. The oxidant excess factor α was measured within a range of 0.35–0.48. The total consumption of source components amounted to 5.8 l s^{-1}. The oxygen content in enriched air of approximately 45 vol % was selected in compliance with the data from companies producing membrane air separation units. The problem of applying oxygen (93–95%) from short-cycle adsorption units as an oxidant requires separate complex (technical and economic) consideration.

It was found that ignition of rich hydrocarbon mixtures was more difficult to perform in enriched air than in oxygen. When the liquid fuel rocket micro-engine was used as an ignition device, it was possible to ignite model gas mixtures with enriched air with $\alpha = 0.39$ and higher. The presence of C_2^+ alkanes in the air-fuel mixture usually contributes to the process initiation; however, in this mixture the alkanes could not compensate for oxygen dilution with nitrogen. The typical composition of the process products after water vapor removal (dry gas, $\alpha = 0.48$) is given in Table 3.

It can be seen from the data presented in Table 3 that conversion of oxygen and methane during partial oxidation of APG model mixtures with enriched air is lower than in the process of oxygen-methane oxidation. It is also evident that propane and butanes are present in trace amounts in the process products. It is noteworthy that acetylene prevails over ethylene in the process products, and their volume ratio is 3.2±0.25. The high content of CO_2 is explained by the air-fuel mixture composition and by the process macro-kinetic factors (the oxidant excess factor here is higher than for the optimal regime of oxygen-methane mixture conversion).

The residual content of methane and the yield of carbon dioxide in the process products exceed the equilibrium values, which is indicative of inefficient mixing of the air-fuel mixture. Thus, superequilibrium methane content in the products corresponds to the presence in the combustion chamber of a zone in which α value is lower than it can be expected based on the ratio of the air-fuel mixture components at the injector inlet. Correspondingly, the process temperature in this zone is also lower.

At the same time, the carbon dioxide content in the products exceeding the equilibrium content corresponds to the presence in the combustion chamber of a zone in which α value is higher than it can be expected based on the ratio of the air-fuel mixture components at the injector inlet. Correspondingly, the process temperature in this zone is also higher. It is evident that changes in the fuel composition, especially with regard to the oxidant, make it necessary to adapt APG, which was previously optimized for partial oxidation of oxygen-methane mixtures in the high-temperature flow chemical reactor, to single-stage processing.

The comparison analysis of the results of the experiments with APG model mixtures in the static bypass installation, in which previously mixed mixtures were used, and in the high-temperature flow chemical reactor demonstrates that the difference in the combustion product composition is primarily explained by differences in fuel-oxidant mixing processes.

CONCLUSIONS

Single-stage conversion of alkane mixtures simulating APG to syngas with the thermodynamically equilibrium yield was experimentally achieved in the static bypass installation and in the flow reactor based on the rocket technology.

The ignition delay zone with a negative temperature coefficient was identified for mixtures simulating associated petroleum gas for the first time. It is a fundamental characteristic of ignition of APG rich mixtures distinguishing it from ignition of rich methane mixtures. The presence of C_3^+ hydrocarbons in real associated petroleum gases extends the temperature range of their auto-ignition with ignition delays at a certain level, which is regulated in a wide range by changes of the initial pressure. The presence of the NTC zone in associated petroleum gases provides a practical possibility to significantly increase the rate of the raw material conversion to syngas by raising the working pressure of the partial oxidation process to 10–15 at.

REFERENCES

1. Knizhnikov, A.Yu. and Pusenkova, N.N., *Problemy i perspektivy ispol'zovaniya neftyanogo poputnogo gaza v Rossii: Ezhegodnyi obzor problemy v ramkakh proekta ekologiya i energetika, mezhdunarodnyi kontekst* (Problems and Prospects of Associated Petroleum Gas Utilization in Russia: Annual Survey of the Problem within the Framework of the Project on Ecology and Energy, International Context), Moscow, 2009, issue 1; *www.wwf.ru/data/pub/ener-gy/po-putnygaz.pdf.*
2. Interview with Natal'ya Komarova, *Governor of Khanty-Mansi Autonomous Region: Yugra, Gazokhimiya*, 2010, no. 1, pp. 12–15.
3. Freide, J.F., *Neftegazovyye Tekhnologii*, 2003, no. 3, pp. 76–78.
4. Novikov, A.A. and Chukhareva, N.V., *Neftegazovyye Tekhnologii*, 2007, no. 1, pp. 2–5.
5. Arutyunov, V.S., Sinev, M.Yu., Shmelev, V.M., and Kiryushin, A.A., *Gazokhimiya*, 2010, no. 1, pp. 16–20.
6. Sister, V.G., Borisov, A.A., Troshin, K.Ya., Bilera, I.V., Bogdanov, V.A., Politenkova, G.G., and Kolbanovskii, Yu.A., *Khim. Fiz.*, 2006, vol. 25, no. 1, pp. 61–68.
7. Borisov, A.A., Karpov, V.P., Politenkova, G.G., Troshin, K.Ya., Bilera, I.V., and Kolbanovskii, Yu.A., *Combustion and Pollution: Environmental Impact*, Roy, G.D., Frolov, S.M., and Starik, A.M., Eds., Moscow: Torus Press Ltd., 2005, p. 87–104.
8. Bilera, I.V., Kolbanovskii, Yu.A., Petrov, S.K., Plate, N.A., and Rossikhin, I.V., RF Patent no. 2320531, Moscow, 2008.
9. *Tekhnologiya pererabotki nefti, v 2 chastyakh, chast' 1: Pervichnaya pererabotka nefti* (Crude Oil Processing Technology, in 2 Parts, Part 1: Primary Crude Oil Processing), Glagoleva, O.F. and Kapustin, V.M., Eds., Moscow: Khimiya, Koloss, 2005, p. 259.
10. Bilera, I.V., Borisov, A.A., Borunova, A.B., Kolbanovskii, Yu.A., Korolev, Yu.M., Rossikhin, I.V., and Troshin, K.Ya., *Neftekhimiya,* 2010, vol. 50, no. 5, pp. 351–354.
11. Bilera, I.V., Borisov, A.A., Borunova, A.B., Kolbanovskii, Yu.A., Korolev, Yu.M., Rossikhin, I.V., and Troshin, K.Ya., *Gazokhimiya*, 2010, no. 3, pp. 72–78.
12. Warnatz, J., Maas, U., and Dibble, R., *Goreniye: fizicheskiye i khimicheskiye aspekty, modelirovaniye, eksperimenty, obrazovaniye zagryaznyayushchikh veshchestv* (Combustion: Physical and Chemical Fundamentals, Modeling and Simulation, Experiments, Pollutant Formation), Moscow: Fizmatlit, 2003, p. 352.
13. Galanov, S.I., Sidorova, O.I., and Kvach, A.E., *Gazokhimiya*, 2010, no. 3, pp. 36–39.