Oxidative plasma chemical transformations of C₃-C₄ alkanes

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Abstract. The results of oxidation of a propane-butane mixture (liquefied petroleum gas) with oxygen in a barrier discharge plasma in the presence of liquid octane are presented. The transformation of the initial mixture results in the formation of predominantly hydroxyl and carbonyl compounds of the initial gaseous C₃-C₄ hydrocarbons. The mechanism of hydrocarbon oxidation is similar to that of transformation of liquid hydrocarbons in the barrier discharge plasma. An increase in the initial concentration of the propane-butane mixture in the gas phase results in a decrease in the conversion of gaseous hydrocarbons and octane in one pass through the reactor. Calculations performed using the Bolsig+ program show that a reduction in conversion of gaseous hydrocarbons is due to a decrease in the rate constant of the oxygen dissociation reaction resulted from a decrease in the average electron energy from 4.1 to 3.4 eV. A mathematical expression is proposed, which allows predicting the direction of the plasma-chemical reaction.

1. Introduction
The most efficient and promising method of processing lower alkanes is their oxidative conversion. Currently, more than half of all chemical products produced from natural gas are obtained by oxidizing lower saturated hydrocarbons [1]. Nevertheless, so far only a small percentage of produced natural and associated petroleum gases is used in the processes of direct functionalization of lower saturated hydrocarbons with oxygen, which is due to their high chemical stability. The use of plasma of electrical discharges for the purpose to activate chemical transformations of lower alkanes makes it possible to overcome this problem.

The main areas of study of processing natural and associated petroleum gases in plasma of various discharges are the conversion of methane as their main component into hydrogen and/or synthesis gas [1–5] and the partial oxidation to liquid oxygen-containing compounds [6–9]. However, since the rates of oxidation of methane homologues are higher, it is more profitable to obtain oxygenates from them (mainly from propane, butane or their mixtures) rather than from methane itself. Due to the fact that the propane-butane mixture (PBM) began to be used primarily as a fuel, the studies of the oxidation of C₃-C₄ alkanes in the plasma of electrical discharges have received almost no attention in the literature.

Earlier, the direct oxidation of propylene in a barrier discharge plasma (BD) was reported in [10]. It resulted in the formation of oxygenates, including propylene oxide, which is a valuable petrochemical product. This paper presents the results of experiments on the oxidative conversion of PBM in BD plasma including the formation of predominantly hydroxyl and carbonyl compounds with the same number of carbon atoms as in the initial hydrocarbon.
2. Experiment

For the oxidative functionalization of PBM, a gas-discharge flow reactor of a coaxial design of electrode system was used. The experimental setup is described in detail in [10]. The content of the initial PBM was as follows: methane – 0.9 wt. %, ethane – 2.0 wt. %, propane – 74.3 wt. %, isobutane – 13.5 wt. %, and butane – 9.3 wt. %. The amplitude of high-voltage pulses was ~ 13 kV, their repetition frequency was 400 Hz, and the active discharge power corresponded to ~ 3 W. The length of the discharge zone of the reactor and its volume were 9 and 5.7 cm$^3$, respectively. The volumetric flow rate of the gas mixture (PBM and oxygen) at atmospheric pressure was 60 cm$^3$·min$^{-1}$ and that of octane 0.1 cm$^3$·min$^{-1}$. Analysis of the reaction products was performed using a HP 6890 chromatograph equipped with a thermal conductivity detector, a flame ionization detector, and HP – PoraPlot Q and HP-1 columns.

3. Results and discussion

Oxidation of PBM was carried out in the presence of octane. The presence of a liquid hydrocarbon on the walls of plasma-chemical reactor creates conditions for effective removal of oxidation products from the discharge zone, which helps prevent a deep oxidation of gaseous hydrocarbons [10, 11].

In table 1 is shown the composition of the products of PBM oxidation. As can be seen from the table 1, a rather large set of substances is formed, but the main products are hydroxyl and carbonyl compounds of propane ~ 54 wt. %, butane ~ 11 wt. %, and isobutane ~ 16 wt. %. In addition to oxygen-containing compounds, the formation of a small amount of alkanes, pentanes, and hexanes is observed.

| Product                          | Content (wt. %) |
|---------------------------------|-----------------|
| Ethanol/Methylformate           | 3.6             |
| Acetone/Isopropanol/Propanal    | 39.5            |
| Methylacetate/Acetic acid       | 7.1             |
| Isopentanes                     | 0.4             |
| Propanol                        | 12.2            |
| n-Penthan                       | 0.7             |
| tert-Buthanol/Diethylc Ether    | 5.6             |
| Isobuthanal                     | 2.8             |
| Buthanal/Buthanon               | 2.7             |
| sec-Buthanol/Ethylacetate       | 3.2             |
| i-Hexanes                       | 0.7             |
| i-Buthanol                      | 8.1             |
| Buthanol/n-Hexane               | 7.2             |
| Other                           | 6.2             |

The main primary event that initiates the oxidation reactions of PBM in the BD is the formation of atomic oxygen in a result of electron impact of the oxygen molecule according to the reaction

$$O_2 + e \rightarrow 2O(^3P) + e$$  \hspace{1cm} (1)

and its further interaction with the alkane molecule (RH) by the reaction:

$$O(^3P) + RH \rightarrow R + OH.$$ \hspace{1cm} (2)

The interaction of alkyl radical with oxygen results in the formation of peroxide radical, whose disproportionation results further in the formation of corresponding hydroxyl and carbonyl compounds:

$$R + O_2 \rightarrow ROO.$$ \hspace{1cm} (3)
2ROO → ROH + RCHO + O₂.  \hspace{1cm} (4)

At the same time, the formation of isomers of pentane and hexane is possible as a result of recombination of hydrocarbon radicals with hydroxyl and carbonyl compounds.

As a result of the electron impact of alkane molecules, electronically excited molecules (RH*) are formed, the dissociation of which could be accompanied by both the formation of alkyl radicals with the hydrogen abstraction

\[ \text{RH}^* + e \rightarrow R + H + e \] \hspace{1cm} (5)

and the C-C bond cleavage

\[ \text{RH}^* + e \rightarrow \text{R}_1 + \text{R}_2 + e, \] \hspace{1cm} (6)

\[ \text{R}_1 + \text{R}_2 \rightarrow \text{R}_1\text{R}_2. \] \hspace{1cm} (7)

where R₁ and R₂ are fragments of the alkane molecule.

A further mechanism for the PBM oxidation is similar in general to the mechanism for the oxidation of liquid hydrocarbons in BD [11]. Octane is oxidized along with the components of PBM. Its oxidation products are similar to the products formed during the oxidation of propylene in the BD in the presence of octane under similar conditions [10]. They are represented mainly by the corresponding hydroxyl and carbonyl compounds.

Figure 1 shows the mass of products of conversion of PBM and octane vs the PBM content in oxygen.

![Figure 1. Mass of conversion products: PBM, octane and total mass vs the PBM content in oxygen.](image)

It is evident from figure 1 that octane is oxidized more intensively than PBM for the PBM content in oxygen ranging from 9.5 to ~ 35 vol. %. In this case, the conversion of PBM increases slightly, while the conversion of octane decreases almost 5 times. The change in the mass of products corresponds to their conversion in the range of 4.1–0.9 wt. % for PBM and 2.4–0.3 wt. % for octane.

Intensive oxidation of octane in the presence of PBM is due to the fact that the rate constant of reaction of atomic oxygen with octane (2) is \(1.7 \times 10^{-13} \text{ cm}^3\cdot\text{s}^{-1}\) [12] is significantly higher than with propane \(9.3 \times 10^{-15} \text{ cm}^3\cdot\text{s}^{-1}\) [13], and butane \(2.6 \times 10^{-14} \text{ cm}^3\cdot\text{s}^{-1}\) [13]. It is close to the value for isobutane \(1.2 \times 10^{-13} \text{ cm}^3\cdot\text{s}^{-1}\) [12].

To determine the direction of the process, i.e. what compound is predominately oxidized, octane or PBM, we have used a simple expression:
The value of K characterizes how many times the oxidation rate of octane could be higher or lower than the rate of PBM oxidation. At K > 1, the products of octane oxidation predominate but if K < 1, this is the case of products of PBM oxidation. Under these conditions the initial concentration of octane is constant and corresponds to ~0.7 vol. %. For the initial concentration of PBM 9.5 vol. % K = 1.4, while for the initial concentration of PBM 75 vol. % K = 0.18. Comparison of the values obtained allows us to explain the observed ratio of the products of PBM oxidation and octane (figure 1).

The decrease in the total mass of oxidation products is due to the decrease in the rate of formation of atomic oxygen, which initiates the oxidation of hydrocarbons. Figure 2 shows the dependence of the total mass of the reaction products and the calculated oxygen dissociation rate constant on the content of PBM in oxygen. The calculations were performed using the Bolsig+ program [14], the model gas mixture was propane-oxygen, and the cross sections for electron scattering by molecules were taken from the database [15]. The decrease in the oxygen dissociation rate constant from $6.71 \times 10^{-9}$ cm$^3$·s$^{-1}$ to $1.87 \times 10^{-10}$ cm$^3$·s$^{-1}$ can be explained by a decrease in the calculated average electron energy from 4.1 to 3.4 eV. The change in the oxygen dissociation rate constant (2.8 times) is in good agreement with the change in the mass of the reaction products (2.3 times).

![Figure 2](image-url)

**Figure 2.** Total mass of the products of reaction and the rate constant of oxygen dissociation by electrons vs the content of PBM in oxygen.

Mention should be made of the related similar process of partial oxidation of C$_3$-C$_4$ alkanes. This petrochemical process proceeds at a pressure of 30 atm and a temperature of ~325–375°C with significant fragmentation and deeper oxidation of the initial hydrocarbon and results in the formation of methanol, acetaldehyde, formaldehyde, lower carboxylic acids, and a significant amount of carbon oxides [1]. Comparing the results obtained with the literature data on the partial oxidation of C$_3$-C$_4$ alkanes, we can argue that the effect of BD plasma on PBM occurs under milder conditions and results...
in the formation of predominantly hydroxyl and carbonyl compounds with the same number of carbon atoms in the molecule as in the initial hydrocarbons. This finding can provide a basis for development of effective technologies for processing C₃-C₄ gaseous hydrocarbons.

4. Conclusion
The oxidation of PBM with oxygen in BD in the presence of octane has been studied. It has been found out that the main oxidation products were hydroxyl and carbonyl compounds with the same number of carbon atoms in the molecule as in the initial compounds. The addition of octane to the PBM-O₂ flow has provided an effective removal of oxidation products of gaseous alkanes from the discharge zone, which has permitted a high selectivity of the process. An increase in the oxygen concentration in the gas mixture from 25 to 90 vol. % has resulted in an increase in the mass of formed reaction products by ~ 2 times, while the conversion of PBM has risen from 0.9 to 4.1 wt. %.

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