



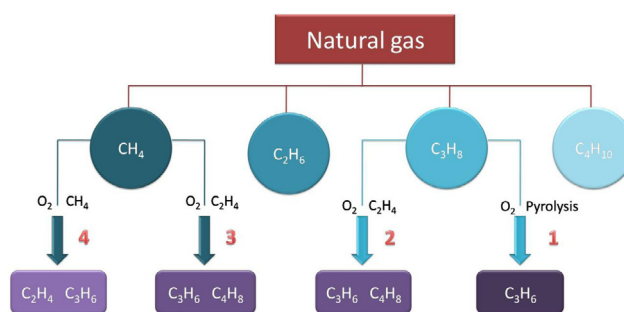
## Production of olefins by the conjugated oxidation of light hydrocarbons

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## HIGHLIGHTS

- New approaches to increase the yield of olefins by oxidative pyrolysis.
- Formation of olefins at the conjugated oxidation of light hydrocarbons.
- Formation of olefins from hydrocarbons in a rich methane flame.

## GRAPHICAL ABSTRACT



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## ABSTRACT

A number of possibilities to increase the yield of propylene in the processing of light gaseous hydrocarbons are considered, including the oxidative pyrolysis of propane, conjugated oxidation of propane and ethylene, conjugated oxidation of ethylene and methane, and introduction of methane into the products of a rich methane flame. The principal possibility of production of olefins in non-catalytic gas-phase processes from light gaseous hydrocarbons, including methane, is demonstrated.

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## 1. Introduction

Lower olefins belong to basic chemicals. It is expected that, in 2016, the global production of ethylene will reach 173 million tons, while that of propylene has already achieved 70 million tons [1]. The ever growing consumption of lower olefins is largely associated with the increase of the production of polyethylene and polypropylene and the expansion of their technological applications. The steady growth of the consumption of olefins needs reli-

able and affordable sources of cheap raw materials for their production and more efficient production technologies.

While the production of ethylene can be increased at the expense of the pyrolysis of ethane extracted from natural or shale gas, the main process for producing propylene remains the pyrolysis of liquid hydrocarbons, more deficient and expensive raw materials, all the more so that this process predominantly yields ethylene. The conventional processes of pyrolysis and catalytic cracking of heavy hydrocarbon feedstock, which make up ~80% of the world production of propylene, yield a wide range of products, but do not fully satisfy the growing demand for propylene [2]. This may lead to a shortage of propylene supply and even the emergence in the future of the so-called “propylene gap”, a serious disparity between the demand for propylene and its

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supply. Therefore, meeting the rapidly growing demand for propylene becomes an increasingly challenging problem.

Currently, special propylene-oriented processes, such as catalytic pyrolysis, deep catalytic cracking [3], propane dehydrogenation [4], and metathesis, are being intensively developed. However, in 2011, the share of propylene-oriented processes was as low as ~13% of the world production, while the proportion of the target processes in 2016 was predicted to be only 20%. The forecasted shortage of supply of propylene and heavier olefins strongly motivates the development of alternative methods for producing lower olefins from cheaper and more accessible gaseous raw materials, ideally from methane, the main component of natural gas.

In recent decades, one of the most popular approaches to solving this problem was the catalytic oxidative coupling of methane (OCM) to ethylene [5]. After more than 30 years of efforts of researchers from many countries, the *Siluria Technologies Company* recently announced performing semi-industrial tests of the OCM process [6]. More tangible results were achieved in developing complex industrial-scale multi-stage processes of natural gas conversion to methanol with its subsequent conversion, using zeolite catalysts, into olefins (MTO process of UOP) or propylene (MTP process of Lurgy) [7], which have already become industrial and are now actively commercialized, notably in China (Fig. 1).

It is also possible to use the conventional route, based on natural gas conversion to syngas, then to Fischer-Tropsch products, with subsequent pyrolysis of thus obtained naphtha to olefins [8]. However, the complexity of these multi-stage routes (Fig. 1) motivates the search for simpler and, therefore, more cost-saving methods for the production of olefins from natural gas.

In the present work, we have examined several alternative approaches to this problem, mainly based on the conjugated oxidation of light hydrocarbons, which seems very promising for the processing of light hydrocarbons. Four different such methods were considered (Fig. 2), more specifically, the oxidative pyrolysis of propane, conjugated oxidation of propane and ethylene, conjugated oxidation of ethylene and methane, and the interaction of methane with the products of a rich methane flame (technological combustion). The latter was demonstrated to provide the principal possibility to produce olefins in non-catalytic gas-phase processes from light gaseous hydrocarbons, including methane.

## 2. Two-section reactor method

The first three approaches to conjugated oxidation of light hydrocarbons were investigated using a two-section flow reactor schematically displayed in Fig. 3. The length and diameter of the first and second reactor sections, made of quartz or stainless steel, were  $L_1 = 16$  cm,  $L_2 = 17$  cm, and  $d_1 = d_2 = 4.5$  cm, respectively. To isolate the processes occurring in the reactor sections from each other, they were separated by a movable partition comprised of small-diameter quartz tubes. The reactor was equipped with end-face inlets for thermocouples, placed in quartz coatings prepassivated with boric acid. The same inlets were used to extract reaction products for analysis. The gas mixture was fed into reactor 5 from gas cylinders 1 through mixer 4. The residence time of the reactants in the reactor was kept constant by means of two valves,

which maintained their flow through flow meters 3 at a constant level. Both sections of the reactor were heated independently.

In the first section, at a lower temperature, the mixture was subjected to a preliminary oxidative activation, while the main reaction occurred in the second section. We can only guess about the mechanism of the activation in the first section because changes in the composition of reagents at the entrance of the second section are below the sensitivity of chromatographic analysis. But without this activation it was necessary to have significantly higher temperatures in the second section to obtain similar conversion at a given time. And at such higher temperatures the yield of products becomes another. In each section, chromel–alumel thermocouples measured the temperatures of the outer surface of the reactor section and of the gas flow at the axis of the reactor. In all the experiments, the pressure was 650–660 Torr, which is atmospheric pressure in Yerevan, at a height of about 900 m above the sea level. The residence time of the mixture in the second section was typically ~2–4 s. Axial temperature gradients in reactor depended on oxygen content, but even at the highest oxygen concentrations they were within 50 °C. The initial reactants and reaction products were analyzed by chromatography with accuracy of about 3%. A more detailed description of the experimental setup is given elsewhere [9].

## 3. Oxidative pyrolysis of propane

At present, the pyrolysis of propane and heavier hydrocarbons is the main industrial source of propylene. The yield of propylene depends on the nature of the feedstock hydrocarbon, being, however, below 14–16 wt%, which is significantly less than that of ethylene. The use of the oxidative pyrolysis of propane, thorough investigated in [10,11], seems to be the most simple and obvious method for enhancing the propylene yield.

The experiments were performed with various propane–oxygen mixtures in a two-section stainless steel reactor. The temperature in the first section was 280 °C, whereas in the second section, it was varied from 530 to 820 °C. The conversion of propane increases sharply with temperature attaining 80–90% at temperatures above 800 °C [12], while the yield of propylene, as can be seen from Fig. 4, passes through a maximum at ~650 °C and then decreases sharply, thereby decreasing the total yield of olefins.

Increasing the  $C_3H_8$ -to- $O_2$  ratio somewhat raises the yield of propylene, but simultaneously decreases that of ethylene. The fact that the contribution of gas-phase reactions increases sharply with temperature leads to a decrease in the yield of  $CO_2$ , which is predominantly formed by heterogeneous processes at the surface of the reactor [11]. That the yield of methane increases monotonically with the temperature while that of CO rises up to 750 °C and then decreases suggests that the contribution from thermal decomposition to the conversion of propane increases.

The addition of oxygen increases the rate of the process, but at the same time increases the conversion of propane to carbon oxides. Note, however, that, at all the investigated ratios of the reagents, rising the temperature sharply increases the ratio  $([C_2H_4] + [C_3H_6])/([CO] + [CO_2])$ . Moreover, the lower the initial oxygen concentration in the mixture, the more sharply this ratio

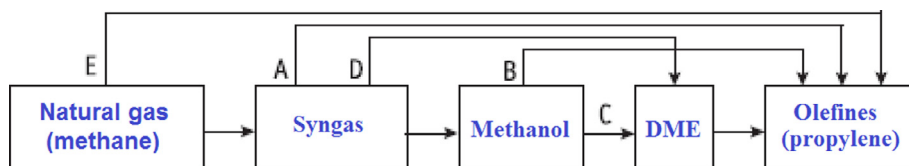


Fig. 1. Possible routes of propylene production from natural gas [2].

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