Involvement of pyrolysis in the Orenburg gas chemical complex

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Abstract. Nowadays, there are no large production facilities to produce unsaturated hydrocarbons in the Orenburg region. Unsaturated hydrocarbons are produced in small quantities by PJSC “Orsknefteorgsintez” at the installation of hydrocracking, but this is not the target product and its quantity is minimal. Relying on this fact, we can assume that, by implementing the pyrolysis plant at the Orenburg gas-chemical complex, it is possible to make a worthy competition to existing enterprises, additional provide the region with the product, and get more profit to the plant, as the cost of olefins is higher than that of the broad fraction of light hydrocarbons or individual components at its separation. The main production of propylene and butadiene is the process of thermal pyrolysis of hydrocarbon materials in tube-type furnaces in the presence of water steam. Unsaturated hydrocarbons can be obtained in other refining processes, but other plants produce unsaturated hydrocarbons in small quantities, which does not meet the demand for olefins. Based on the calculations and the analysis of the background, it can be concluded that the involvement of the NGL pyrolysis plant in the Orenburg gas chemical complex will allow more deeply processing non-targeted products and will be economically beneficial to the enterprise. The amount of produced propylene and butylene is comparable to the leading enterprises producing unsaturated hydrocarbons. These materials can be sold to neighboring regions for further processing and used for their own needs.

1. Introduction
The global polymer market is gaining momentum every year. Demand for them constantly keeps increasing, so it is necessary to build up the production of unsaturated hydrocarbons to supply the market. The best raw material for olefins is a broad fraction of light hydrocarbons, a product derived from gas condensate processing. Propylene and butadiene are valuable materials for a range of products: rubbers, pipelines, fibers, filament, and materials for the chemical, motor-car, and furniture industries. It can be assumed that the involvement of the NGL pyrolysis plant in the Orenburg Gas Chemical Complex is economically reasonable. At the Orenburg Gas Chemical Complex, obtained NGL are the products of natural gas processing at OOGCF [1].

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The main production of propylene and butadiene is the process of thermal pyrolysis of hydrocarbon materials in tube-type furnaces in the presence of water steam. Unsaturated hydrocarbons can be obtained in other refining processes, but other plants produce unsaturated hydrocarbons in small quantities, which does not meet the demand for olefins [2].

Paraffin hydrocarbons of normal structure can be attributed to suitable raw materials to produce unsaturated hydrocarbons. On their basis, one can get the maximum output of unsaturated hydrocarbons. The presence of aromatic hydrocarbons and substituted naphthenetic hydrocarbons should be minimized in the raw materials.

Ethane, propane, butane, petrol, and gas oils are exposed to pyrolysis with varying degrees of conversion. Due to the temperature fracturing of materials, products with less molecular weight get produced at the output.

Selecting the optimal material, the need for the resulting products is taken into account, but one of the main factors is the availability of fractions of oil and gas processing.

Gaseous materials - ethane, propane, n-butane, and their mixtures - are the best saturated hydrocarbons to produce maximum outputs of ethylene, propylene, and iso-butylene [3].

In pyrolysis, hydrocarbons not involved in the reaction most often return to the process, not depending on the used materials. In this case, the degree of transformation can be determined by the specified conditions.

One of the main tasks of any production is to improve the key performance indicators of the plant. To do this, propane together with other olefins gets returned to the process of pyrolysis, in particular propylene and iso-butylene. In plants with absorptive gas separation, recycling propane always contains a certain amount of propylene. Studies of pyrolysis of such raw materials have shown that the content of propylene in the pyrolysis gas is virtually independent of the initial concentration in the raw material, and it quickly converts in the mixture with ethane [4].

The composition of the gas supplied as a power source to the pyrolysis plant is not the same: propane is in the concentration of 50 to 95%, ethane and butane are present in smaller quantities depending on the original composition of raw materials. In industrial conditions, the propane conversion rate reaches 90%. In comparison with ethane, the output of ethylene in pyrolysis of propane is 2 times lower based on the full conversion of raw materials. When propane is converted (table 1), it gives a high yield of propylene, which, at low degrees of conversion, can be in the range of 18 to 21% and can reach 25%, taking into account the recycling. At high degrees of propane conversion, there is a distribution of liquid pyrolysis products: pentane and hexane - about 1.2%, benzene - 2.7, toluene - 0.6, aromatic hydrocarbons - 0.8, non-aromatic hydrocarbons (hexane, heptane, octane, nonane) ≈ 1.3, and heavy resin of pyrolysis ≈ 0.4.

Table 1. Parameters of the process, the product output in propane and n-butane pyrolysis in industry.

| Parameter                    | Propane | n-Butane |
|------------------------------|---------|----------|
| The temperature in the coil (°C) | -       | -        |
| Input                        | 565     | 650      |
| Output                       | 832     | 793      |
| Steam diluting (%)           | 50      | 30       |
| Reaction time (s)            | 0.9     | 0.7      |
| Degree of conversion (%)     | 85      | 89       |

In recent years, there has been a study of the technology for the production of propylene using the plant of liquefied petroleum gas as a power source. But in this case, it is necessary to combine the pyrolysis of materials and the recycling of flows, which somewhat complicates the technology.
2. Materials and methods
There we gained a large range of products on the basis of NGL, which are the main materials of petrochemical enterprises. On the basis of olefins, we conduct the production of rubbers, plastics, ethanol, solvents, and components of high-grade petrol [5].

The output of targeted products, the consumption of materials, the parameters of the process significantly vary, depending on the type of raw materials and the mode of process (table 2).

| Material   | Ethylene | Propylene | Butadiene |
|------------|----------|-----------|-----------|
| Ethane     | 80       | 1         | 2         |
| Propane    | 35.8     | 16.2      | 3.7       |
| n-Butane   | 33.9     | 14.7      | 12        |

Table 2. The output of pyrolysis products (mass fraction, %).

Based on the chemical reactions of possible transformations of saturated hydrocarbons into olefins, Table 3 provides an averaged component composition of a broad fraction of light hydrocarbons produced at the Orenburg Helium Plant.

| No. | Component   | M  | Consumption Di (kg/h) | Consumption (kmole/h) | Mass fraction Xi |
|-----|-------------|----|-----------------------|-----------------------|-----------------|
| 1   | C2H6        | 30 | 6600.0                | 220.00                | 5.50            |
| 2   | C3H8        | 44 | 64680.0               | 1470.00               | 53.90           |
| 3   | C4H10       | 58 | 11280.0               | 194.48                | 9.40            |
| 4   | iso-C4H10   | 58 | 23208.0               | 400.14                | 19.34           |
| 5   | C5H12       | 70 | 5496.0                | 78.51                 | 4.58            |
| 6   | iso-C5H12   | 70 | 4668.0                | 66.69                 | 3.89            |
| 7   | C6H14       | 82 | 4068.0                | 49.61                 | 3.39            |
| TOTAL|             |    | 120000.00             | 2479.43               | 100.00          |

As can be seen in Table 3, the main component of NGL is propane, which makes it possible to get the most important amount of propylene, about 20% of the mass fraction – iso-butane – gives isobutylene at molecule cleavage. There is ethane in small quantities; pentane and hexane form a light resin of pyrolysis. Table 4 presents the reconciliation of the main and side products of pyrolysis.

3. Results and discussion
As a result of conducting the reconciliation of pyrolysis, the maximum amount of propylene and butylene was obtained according to the chemical equations following stoichiometric coefficients. Less ethylene and acetylene were produced. Carbon oxide, hydrogen, and pyrolysis resin were produced as by-products. Since we used a mixture of hydrocarbons without heavy components and impurities, coke was formed in smaller quantities than in the pyrolysis of the petroleum fraction. According to the calculations, materials were in the furnace for 0.105 s. at 1163 °C, and there we observed the maximum selectivity of the process on the main reactions for this type of raw materials.

At the moment, more than 10 Russian companies produce ethylene, propylene, and butadiene. Since 2012, the total productivity of unsaturated hydrocarbons has markedly increased. The growth in the production of unsaturated hydrocarbons is carried out only through the reconstruction and modification of existing plants (table 5). It is necessary to introduce new plants to sell unsaturated hydrocarbons at the domestic market and to export it.
The increase in capacity will allow Russia to rise in the ranking of the countries leading in the production of such valuable raw materials, to approach the world leaders in the production of unsaturated hydrocarbons, and to make a decent competition, which is important with the increased demand for this material [6].

Table 4. Reconciliation of NGL pyrolysis.

| Component     | Income | Expenditure |
|---------------|--------|-------------|
|               | mass fraction | kg/h | kmole/h | mass fraction | kg/h | kmole/h | mass fraction | kg/h | kmole/h |
| H2            | 2      | -    | 2.50    | 2995.43 | 1972.72 |
| CO            | 28     | -    | 0.19    | 228.54  | 8.16   |
| CH4           | 16     | -    | 2.33    | 2798.79 | 174.92 |
| C2H4          | 28     | -    | 1.57    | 1879.57 | 67.13  |
| C2H6          | 30     | 5.50 | 1.93    | 2310.00 | 77.00  |
| C2H2          | 26     | -    | 1.19    | 1430.00 | 55.00  |
| C3H6          | 42     | -    | 39.42   | 47302.14 | 1162.24 |
| C3H8          | 44     | 53.90| 14.55   | 17463.60 | 396.90 |
| C4H8          | 56     | -    | 0.46    | 555.66  | 9.92   |
| iso-C4H8      | 56     | -    | 14.00   | 16805.79 | 300.10 |
| n-C4H10       | 58     | 9.40 | 2.94    | 3523.40 | 60.75  |
| iso-C4H10     | 58     | 19.34| 4.84    | 5802.00 | 100.03 |
| n-C5H12       | 72     | 4.58 | 76.33   | -       | -      |
| iso-C5H12     | 72     | 3.89 | 64.83   | -       | -      |
| C6H14         | 86     | 3.39 | 47.30   | -       | -      |
| Resin of pyrolysis | -    | -    | -14.09  | 16905.08 | 14232.00 |
| TOTAL         | -      | 100.0 | 120000.00 | 2473.09 | 100.00 | 120000.00 | 18105.88 |

Table 5. World production of propylene by the method of propane dehydration.

| Company          | Capacity (kiloton) | Country   | Start      |
|------------------|--------------------|-----------|------------|
| 14 enterprises   | 7500.0             | China     | 2013-2017  |
| Dow              | 750.0              | USA       | 2015       |
| Takreer          | 600.0              | U.A.E.    | 2013       |
| Petrologistics   | 544.0              | USA       | 2010       |
| Al Waha          | 510.0              | Saudi Arabia | 2009   |
| KPI              | 500.0              | Kazakhstan | 2014     |
| Mehr Petro Kimia | 450.0              | Iran      | 2015       |
| Sibur            | 400.0              | Russia    | 2013       |
| EPPC             | 400.0              | Egypt     | 2010       |
| OPC              | 250.0              | Egypt     | 2015       |
| TOTAL            | 11904.0            | -         | -          |
The largest pyrolysis complex is located in SIBUR-ZapSibNefteKhim (Tobolsk) with a capacity of 1.5 million tons per year. The similar plants belong to PJSC Nizhnekamskneftekhim (Nizhnekamsk) and PJSC Kazanorgsintez (Kazan).

The total capacity of all plants is about 4.5 million tons per year for ethylene. In our country, the ethane-propane fraction is mainly used as raw materials.

In SIBUR, propylene is produced on the basis of pyrolysis products and refining gases. Tomskneftekhim, a member of the holding company, uses propylene obtained at the pyrolysis plant as raw materials, which is produced from a broad fraction of hydrocarbons from the gas processing unit of the company, and liquefied gas from Tobolsk-Neftekhim, hydrocarbon raw materials (gaseous petroleum, NGL) from the Surgut condensate stabilization plant of PJSC Gazprom. Also, propylene is obtained by the fractioning of the propane-propylene fraction of cracking gases by SPE Neftekhimiya Ltd. located at the Moscow Oil Refinery (SIBUR owns 50% of the capital stock).

As a result of the implementation of the plan for the development of the petrochemical industry, it is possible to increase pyrolysis capacity from 3.1 million tons in 2012 up to 7.8 million tons in 2017. The capacity should reach 12.8 million tons by 2021 (figure 1) [7].

![Figure 1. The ratio of propylene production and export in Russia for 2012-2030](image)

4. Conclusion

Based on the calculations and the analysis of the background, it can be concluded that the involvement of the NGL pyrolysis plant in the Orenburg gas chemical complex will allow deeper processing of non-targeted products and will be economically beneficial to the enterprise. The amount of produced propylene and butylene is comparable to the leading enterprises producing unsaturated hydrocarbons. These materials can be sold to neighboring regions for further processing and used for their own needs [8-9]. The following advantages and disadvantages of involving the plant in the Orenburg gas chemical complex are summarized below [10].

- **Advantages:** high demand for products coming out from the pyrolysis plant; the versatility of the plant, the ability to use any type of raw materials from lighter to heavier ones to obtain the necessary range of product, which positively affects the challenges of the market in demand for various olefins. By regulating the parameters of the process, it is possible to calculate the necessary conversion of materials and the most optimal time of the reaction, thus the versatility of the pyrolysis process is shown. This process is successfully used at many plants, there is a lot of experience of implementation; one can adopt positive experience and take into account all the nuances.

- **Disadvantages:** the initial high cost of capital expenditure due to the construction and commissioning of a new plant. In the process of work, the formation of coke is possible in the coils of
the furnace and the transfer line exchanger due to high temperatures, but because the raw material is of the light composition, the amount of formed pyrolysis resin is minimal.

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