Open Joint Stock Company "GTL"

AUTOMATED GAS PROCESSING COMPLEX "GTL"

2015

GTL

Open Joint Stock Company "GTL" was established in 2000 to implement the projects for processing of natural and associated gas. To accomplish this task, the "GTL" company developed and patented more than one hundred of innovative technologies. The uniqueness of the production facilities for gas processing, created on the basis of these technologies, is

- high cost-effectiveness and capabilities of processing of any gas composition with separation of the market product (high octane gasoline, diesel fuel, alcohols and aromatic hydrocarbons)

- full automation,

- high ecological performance of the process,

- possibility to work in difficult climatic conditions and infrastructure and low-rate fields.

To implement the projects, the Company organized cooperation with leading international research institutions and universities.

"GTL" COMPANY OFFER:

Maximum use of the expertise and technologies, available in the "GTL"'s arsenal.

Technology solutions that are fully adapted to the specific climatic conditions of future construction sites. Major decisions are taken in accordance with the requirements specification.

Compliance with all aspects of integrated security.

Avoiding expensive buildings and facilities of the high fire and explosion hazards degree.

Usage of integrated unit equipment, manufactured and tested at manufacturing plants.

Maximum automation of the process.

Involvement of construction organizations that have experience in implementing large international projects.

KEY POINTS

1. Cost-effective technology for converting of natural and associated gas into liquid fuels.

2. Does not require prior fractionation of associated gas.

3. Absence of liquid effluents and emissions.

4. Moderate capital and operating costs.

5. Technology and catalysts are developed and delivered by a single supplier - the "GTL" company.

6. All stages of the technology have been successfully tested.

7. GTL plant technology allows a subsequent increase in production capacity by the commissioning of additional modules.

Introduction of the participants

Presentation of the consortium

Purpose of the project

Technological chain:

1. Gas conditioning section;
2. Alcohols direct synthesis section;
3. Alkanes direct synthesis section;
4. Section of high octane gasoline synthesis from alcohols;
5. Section of co-processing of alkanes and alcohols to produce high octane gasoline;
6. Diesel fuel production section;
7. Aromatization section;
8. Power generation section;
9. Finished products warehouse.

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Scientific Project Manager - Prof. Valeriy Yazev, Doctor of Engineering

Scientific Project Manager - Prof. Vitaliy Guzeev, Doctor of Engineering

Research group

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Group of environmental control
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Group of works on visual communication - Aigul Kadyrova, director.

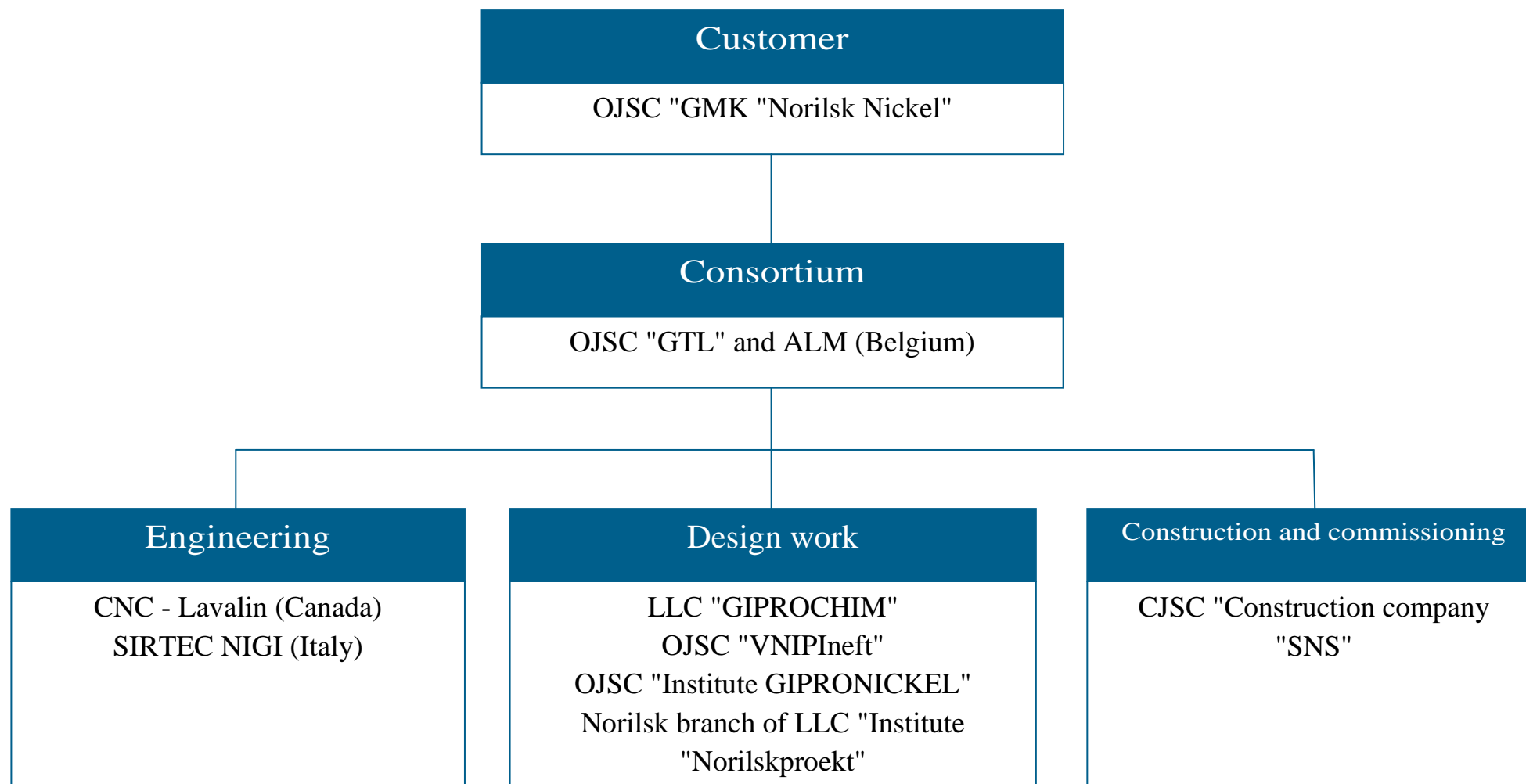## "GTL" COMPANY EXPERIENCE ON ESTABLISHMENT OF CONSORTIUM

For implementation of new projects, the "GTL" Company creates a **consortium with the leading international engineering companies and Russian design institutes** to maximize the effectiveness of economic and technological results.

For example, for the project of reconstruction of sulfur production at the Medniy and Nadezhdinskiy Metallurgical Plants of the OJSC "GMK "Norilsk Nickel" the OJSC"GTL" created a consortium with the Belgian company Ateliers de la Meuse (ALM), combining advanced domestic and foreign developments in the field of recycling waste gases of metallurgical manufactures and invaluable experience in the implementation of such large-scale projects.

"GTL" COMPANY has experience in the creation of consortium for the implementation of highly **complex technology projects.**

THANKS TO THE JOINT EFFORTS OF the members of the consortium, it was possible to develop and implement technical and design solutions, providing production of elemental sulfur from waste gases of Medniy and Nadezhdinskiy Metallurgical Plants of the OJSC "GMK "Norilsk Nickel" and reducing sulfur air emissions **to the maximum possible level above the established statutory provisions, taking into account complex security requirements.**

CONSORTIUM STRUCTURE FOR THE "GMK" NORILSK NICKEL" PROJECT

Customer

OJSC "GMK "Norilsk Nickel"

Consortium

OJSC "GTL" and ALM (Belgium)

Engineering

CNC - Lavalin (Canada)
SIRTEC NIGI (Italy)

Design work

LLC "GIPROCHIM"
OJSC "VNIPIneft"
OJSC "Institute GIPRONICKEL"
Norilsk branch of LLC "Institute "Norilskproekt"

Construction and commissioning

CJSC "Construction company "SNS"

CONSORTIUM STRUCTURE FOR THE AGPS "GTL" PROJECT

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┌─────────────────────────────┐
│          Customer           │
├─────────────────────────────┤
│                             │
└─────────────────────────────┘
               │
┌─────────────────────────────┐
│         Consortium          │
├─────────────────────────────┤
│         OJSC "GTL"          │
└─────────────────────────────┘
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│  Engineering │ │  Design work │ │ Construction and commissioning │
├──────────────┤ ├──────────────┤ ├──────────────────────────────┤
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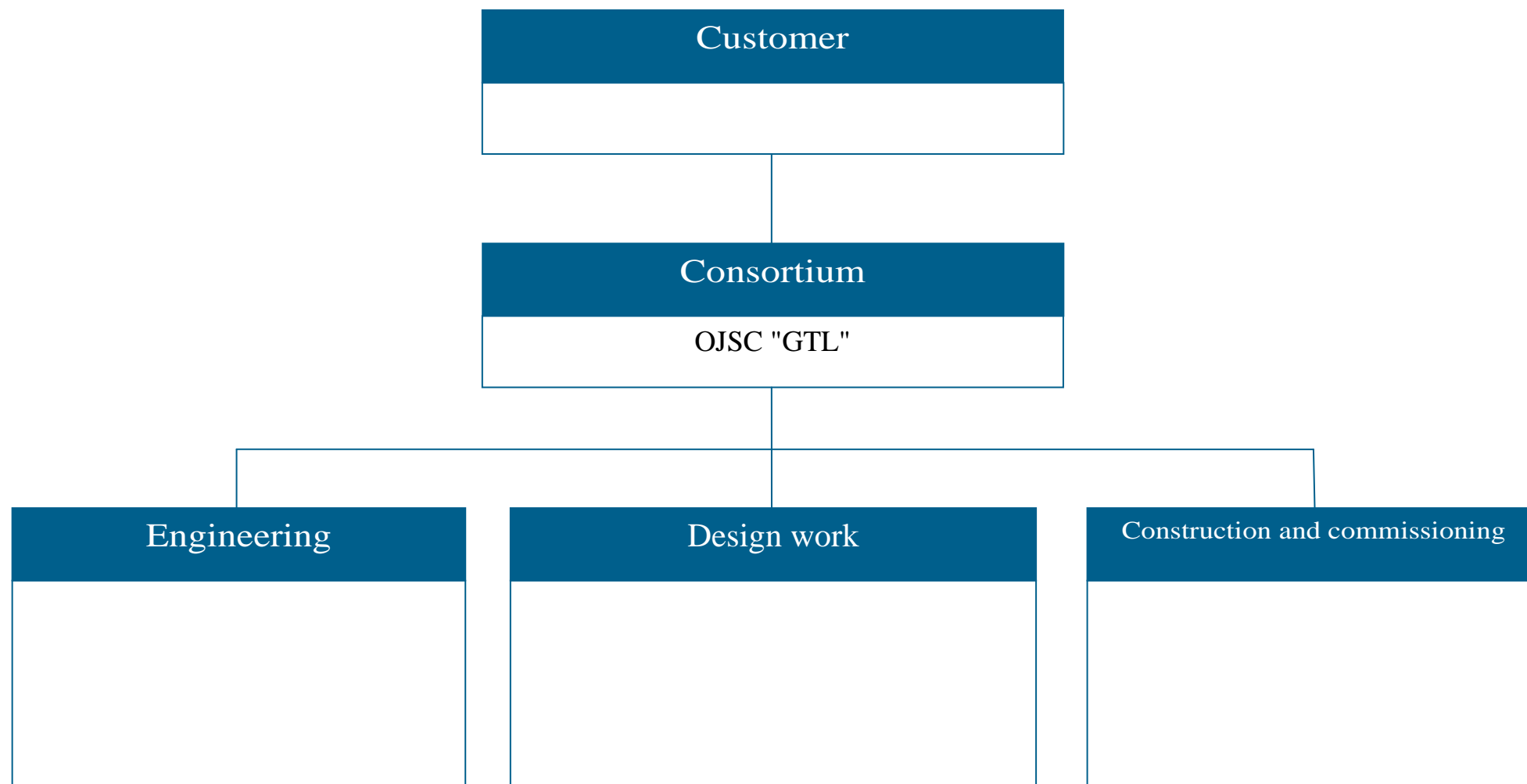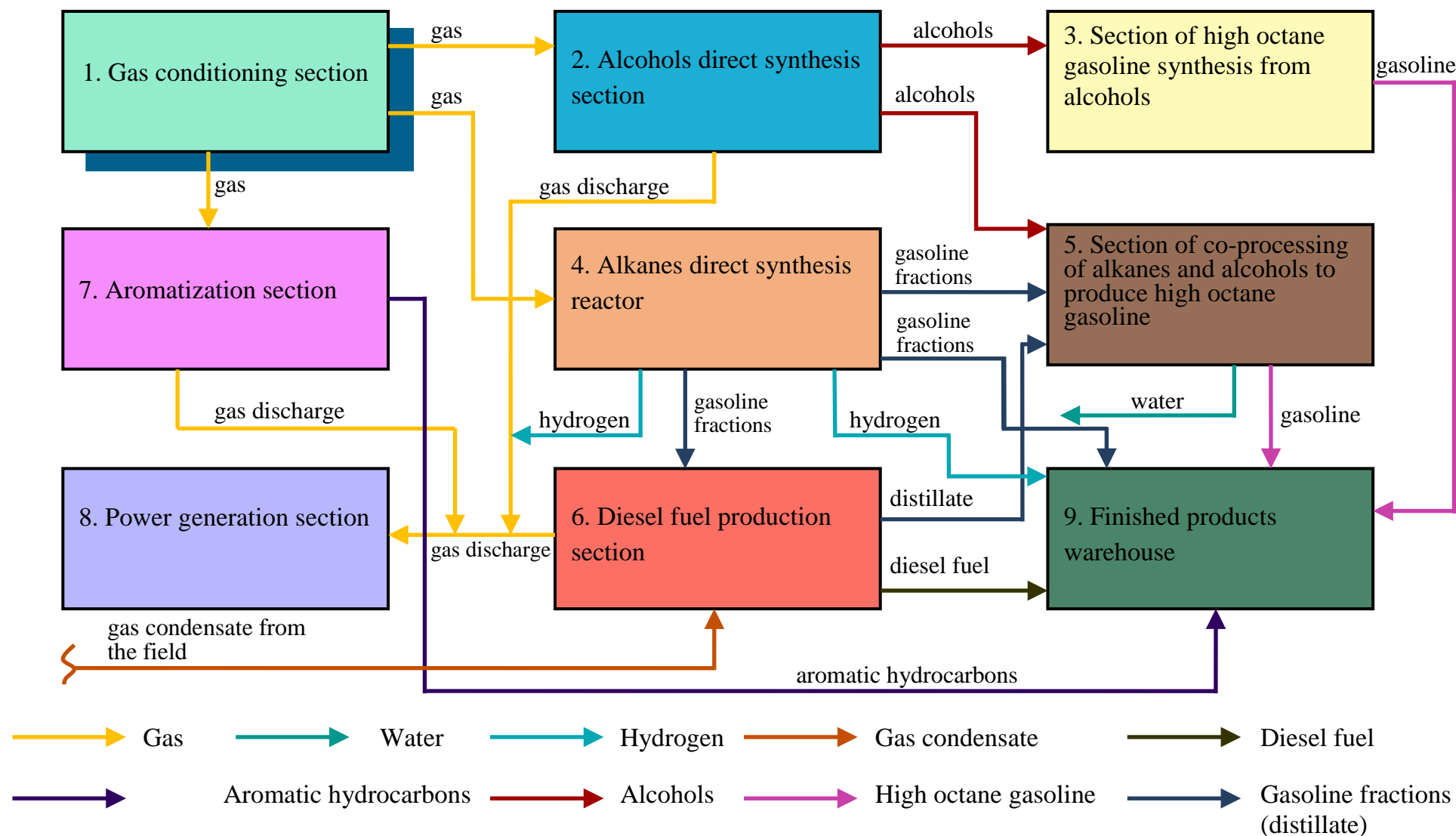
PURPOSE OF THE PROJECT

Development and implementation of technical and design solutions, providing the construction of a plant for processing of natural and associated gas, taking into account peculiarities of oil and gas field.

PROJECT BASIS

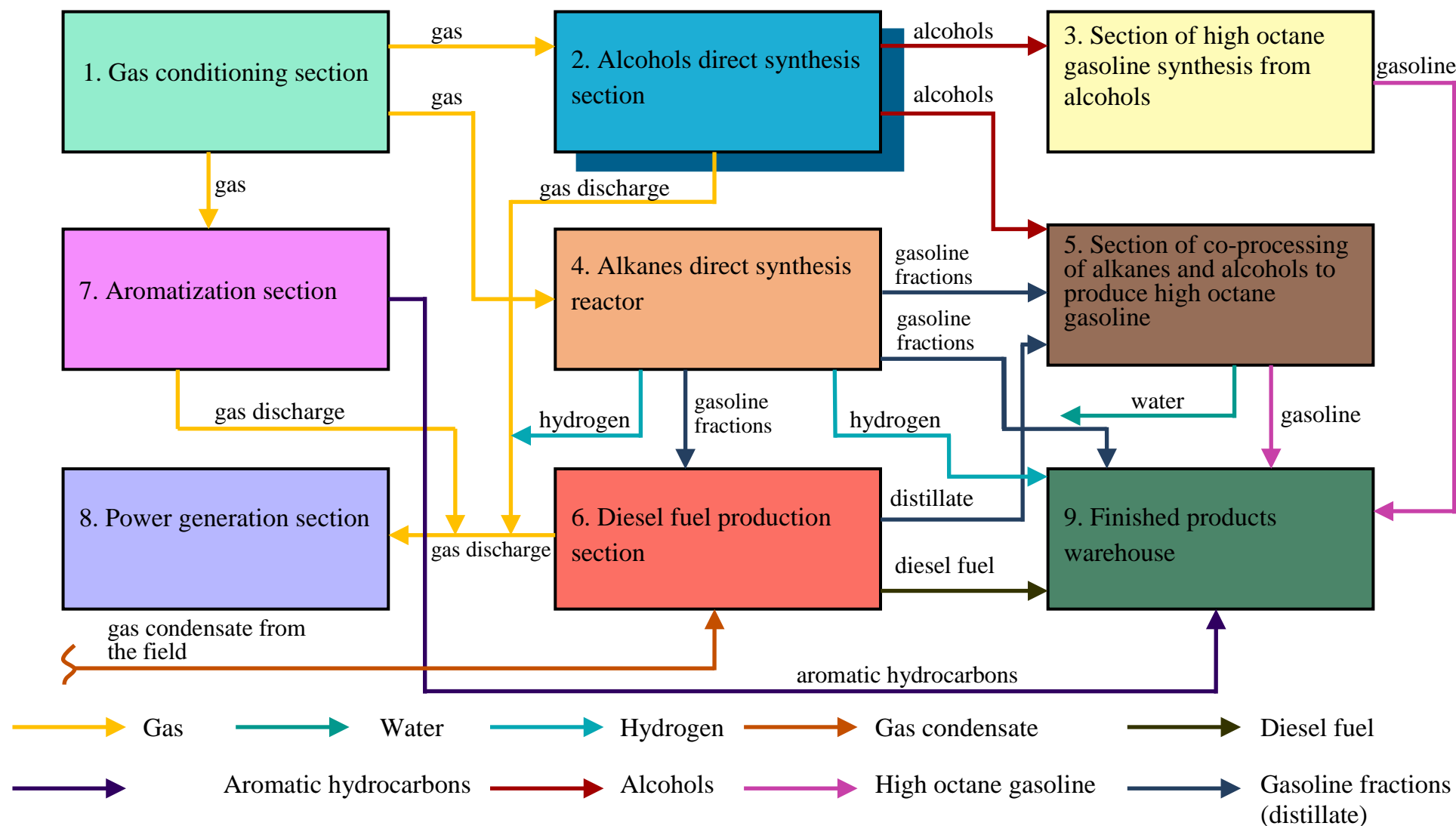The agreement on construction of the plant between the "GTL" Company and the Customer.

PLAN OF GAS CONDITIONING SECTION

Gas into the HTR

Gas for own needs

Original gas

C-1
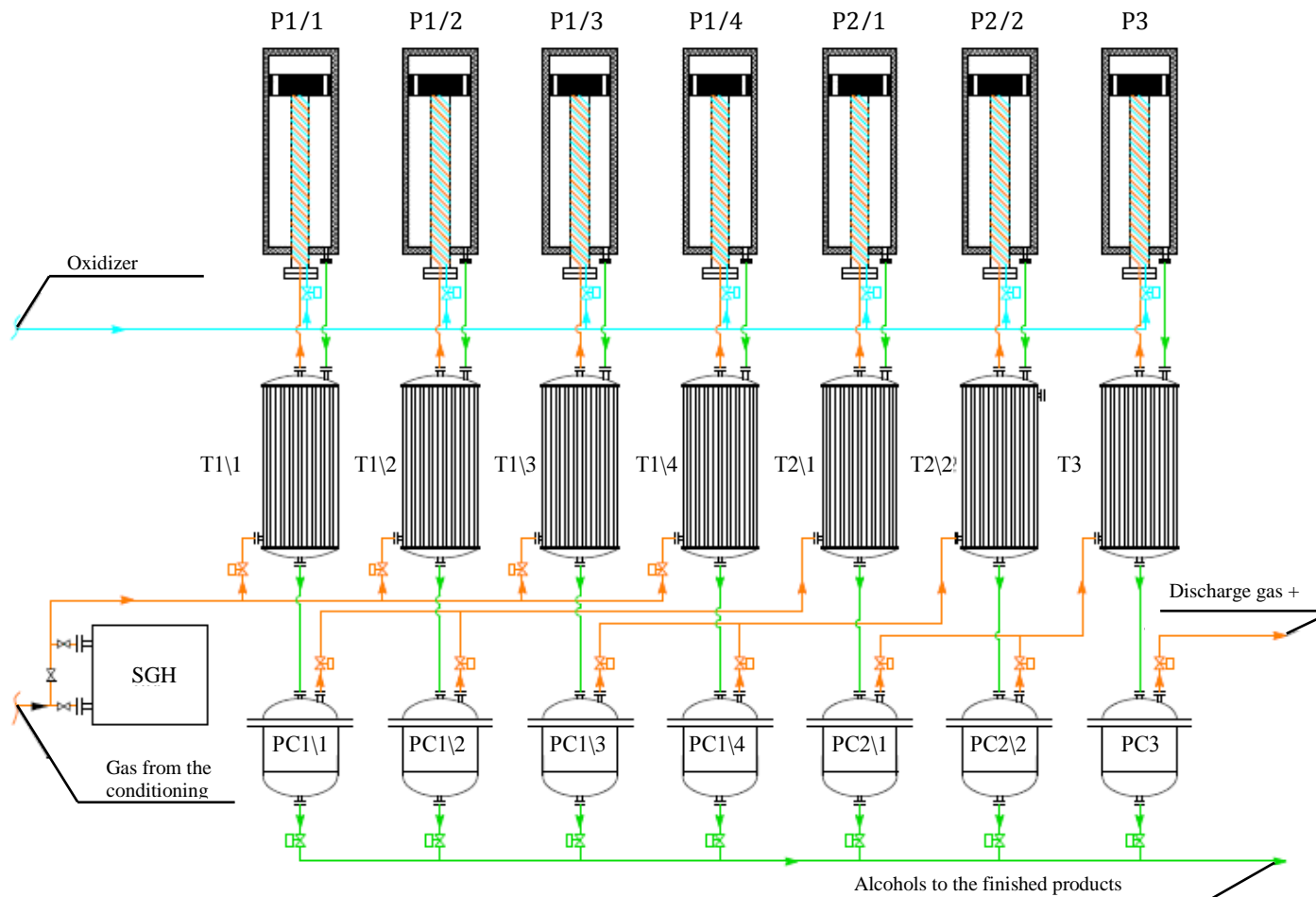
C-2

K-1

Water

Stable condensate
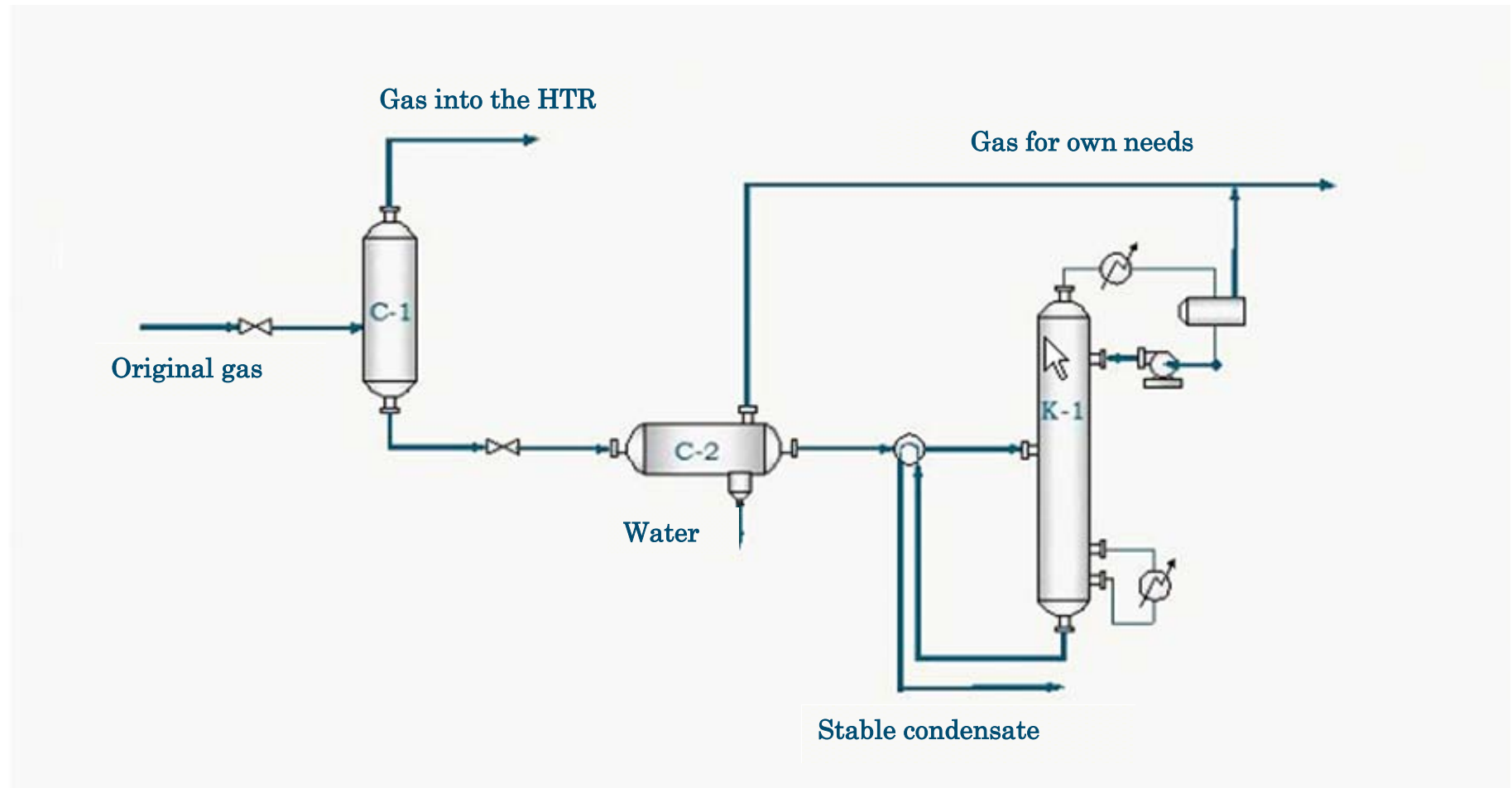
GAS CONDITIONING SECTION is a complex of process equipment and ancillary systems, providing collection, treatment, removal of condensed moisture, mechanical impurities and processing of natural gas and gas condensate.
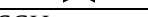
STAGES OF THE PROCESS and equipment-specific design are determined by engineering calculations taking into account features and deposits of hydrocarbons.

1. Gas conditioning section — gas → **2. Alcohols direct synthesis section**

2. Alcohols direct synthesis section — alcohols → **3. Section of high octane gasoline synthesis from alcohols**

2. Alcohols direct synthesis section — alcohols → **5. Section of co-processing of alkanes and alcohols to produce high octane gasoline**

1. Gas conditioning section — gas → **7. Aromatization section**

1. Gas conditioning section — gas → **4. Alkanes direct synthesis reactor**

2. Alcohols direct synthesis section — gas discharge

4. Alkanes direct synthesis reactor — gasoline fractions → **5. Section of co-processing of alkanes and alcohols to produce high octane gasoline**

4. Alkanes direct synthesis reactor — gasoline fractions

4. Alkanes direct synthesis reactor — gasoline fractions → **6. Diesel fuel production section**

4. Alkanes direct synthesis reactor — hydrogen

hydrogen

water

3. Section of high octane gasoline synthesis from alcohols — gasoline

5. Section of co-processing of alkanes and alcohols to produce high octane gasoline — gasoline → **9. Finished products warehouse**

7. Aromatization section — gas discharge

6. Diesel fuel production section — distillate → **9. Finished products warehouse**

6. Diesel fuel production section — diesel fuel → **9. Finished products warehouse**

gas discharge → **8. Power generation section**

gas condensate from the field

aromatic hydrocarbons

8. Power generation section

6. Diesel fuel production section

9. Finished products warehouse

Legend:
- Gas
- Water
- Hydrogen
- Gas condensate
- Diesel fuel
- Aromatic hydrocarbons
- Alcohols
- High octane gasoline
- Gasoline fractions (distillate)

PLAN OF ALCOHOLS DIRECT SYNTHESIS SECTION

Symbols

Symbol	Name
	Oxidizer
	Gas
	Alcohols
	Flow direction
	Valve
SGH	Starting gas heater
P	Reactor
T	Heat exchanger
PC	Rotary separator

Natural gas from the gas conditioning section is supplied to four parallel "gas-gas" heat exchangers. Heated gas is supplied to the tube space, heating is carried out by the heat, generated during the gas reaction in four parallel rectors of the first order, entering the tube space (housing). In the heat exchangers, the gas entering the reactor is heated to start the reaction, gas cooling after the reaction area of the reactor and the condensation of resulting product. For the start mode and turning the reactors into the operating modes for several minutes, a heat exchanger is used with a possibility of heating the additional gas, supplied thereto from the conditioning unit. (Used technologies are protected by the patent for invention no. 2181622.)

The gas, heated in the heat exchanger, then enters the reactor through the central tube, which is also the inner electrode of the reactor. Inside the tube there are two channels in the form of mutually interwoven springs, tightly contacting with the inner wall of the tube, which serve to guide the gas and the oxidant gas into the reaction zone, achieving the highest possible level of heat exchange and additional heat exchange in the reaction zone of the reactor. This allows additional control of the heat balance in the reaction zone of the reactor. (Used technologies are protected by the patent for invention no. 2199366.)

The upper end of the reactor has an apparatus which creates swirling of gas and oxidant gas, entering the reaction zone , creating a maximum fast mixing of gas and oxidant gas, heated to the temperature, required to initiate the reaction. (Used technologies are protected by the patent for invention no. 2426715.)

After the reaction, the mixture of obtained products and unreacted gas residue, leaving the reactor, enters the heat exchanger where it is cooled to the desired temperature by cold gas, supplied from the gas conditioning section, and then goes to the block for separating the liquid products from the residual gas. Isolated liquid products are sent to the finished products warehouse or for further processing in the following sections of the plant for conversion of natural and associated gas.
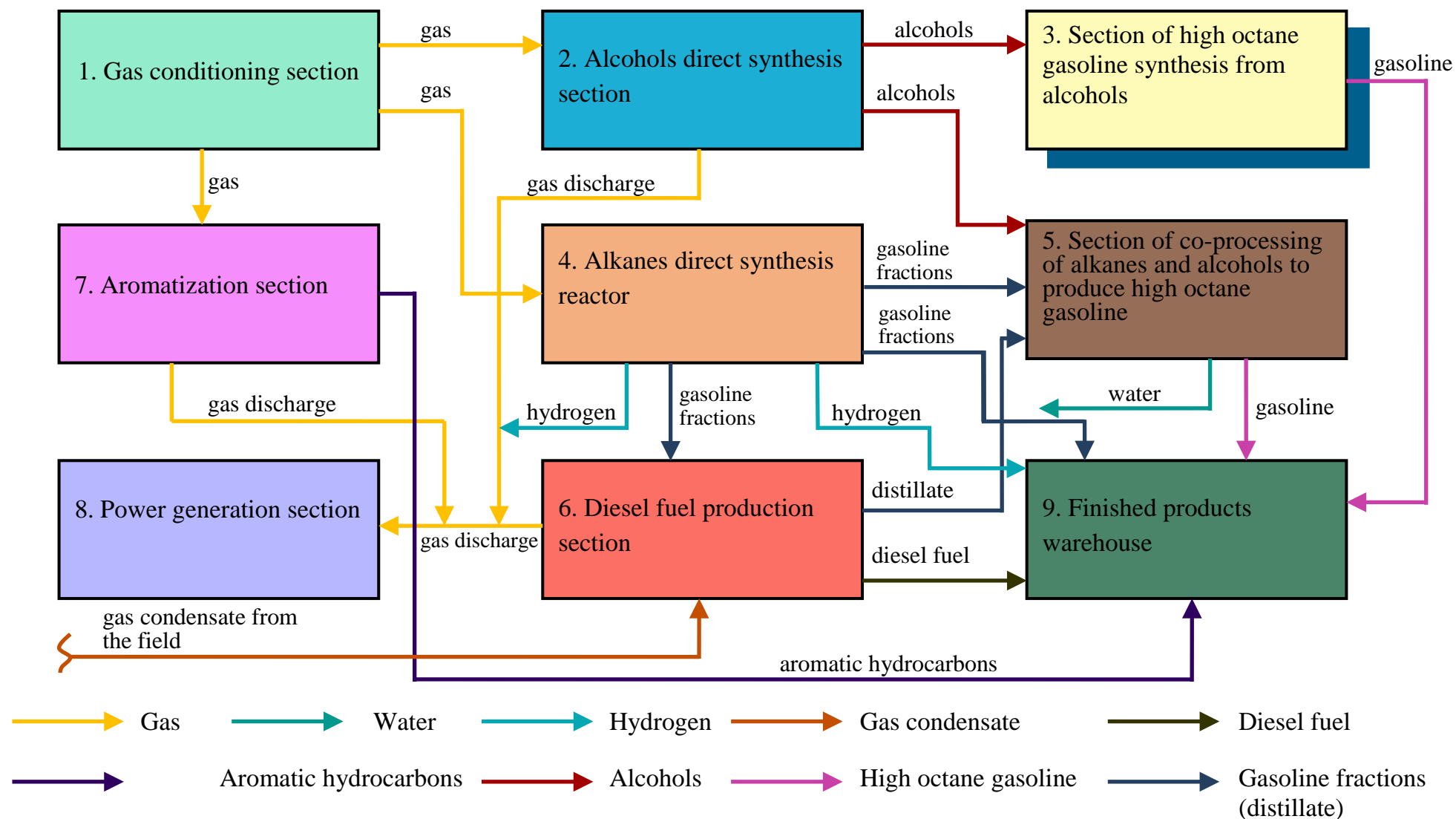
Secondary gas, obtained from two reactors of the first order, after separation from the depleted liquid product in sections of gas-liquid separation, according to the technical requirements during the designing, may be sent to the section for isolation of the formed hydrogen, as a commodity product or for further use in fuel elements in the plant power unit; if there is helium in gas composition, then to extract helium as a commodity product. (Used technologies are protected by the patent for invention no. 2513917.)

Two streams of gas from the reactors are combined into a single stream and sent as cooled gas to the fifth heat exchanger to heat it before processing in the next reactor of the second order, if the technical design specification does not provide for the allocation of helium and hydrogen. Heating of the gas is carried out by the heat flow from this reactor. Also the gas flows are sent from the second pair of parallel reactors of the first order.
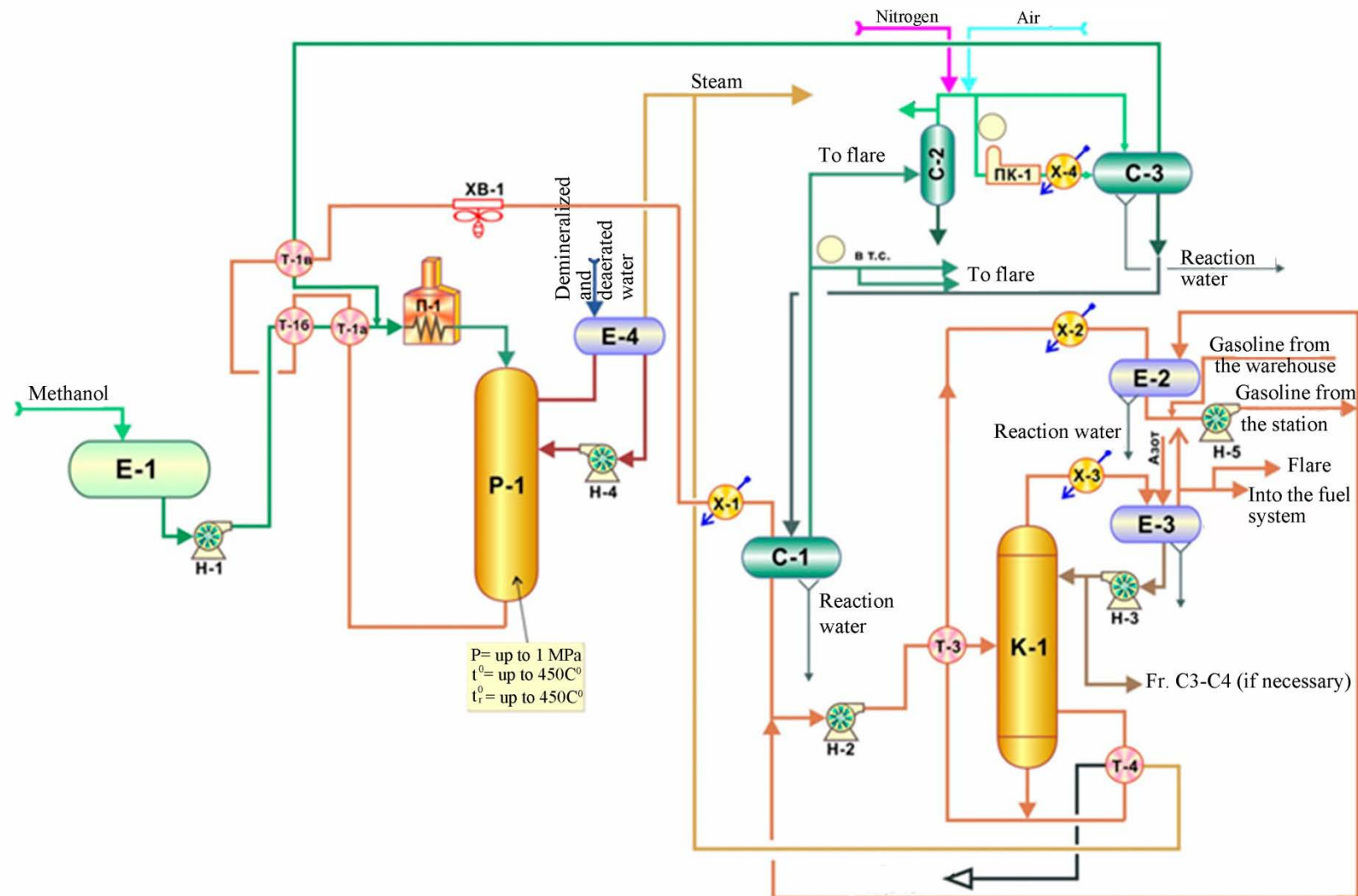
The produced products in the reactors of the second order, as in reactors of the first order, are isolated in sections of gas-liquid separation, and cooled gas of two streams is combined into the single stream and sent to the heat exchanger, serving the following reactor of the third order. The product obtained from the reactor after cooling in the heat exchanger is isolated in the unit of gas and liquid products separation.

Liquid products are sent to the finished products warehouse or for further processing in the following sections of the plant for conversion of natural and associated gas, and isolated gas in the composition of the discharge gas is sent to the power section of the plant, where, if it is necessary, additional associated products, including hydrogen, are possible to be produced.

1. Gas conditioning section

2. Alcohols direct synthesis section

3. Section of high octane gasoline synthesis from alcohols

7. Aromatization section

4. Alkanes direct synthesis reactor

5. Section of co-processing of alkanes and alcohols to produce high octane gasoline

8. Power generation section

6. Diesel fuel production section

9. Finished products warehouse

gas · gas · gas · alcohols · alcohols · gasoline · gas discharge · gas discharge · gasoline fractions · gasoline fractions · gasoline fractions · hydrogen · hydrogen · water · gasoline · distillate · diesel fuel · gas discharge · gas condensate from the field · aromatic hydrocarbons

Legend:
— Gas — Water — Hydrogen — Gas condensate — Diesel fuel
— Aromatic hydrocarbons — Alcohols — High octane gasoline — Gasoline fractions (distillate)

PLAN OF SECTION OF HIGH OCTANE GASOLINE SYNTHESIS FROM ALCOHOLS

Section of high octane gasoline synthesis from alcohols with low durene and benzene content is characterized by the fact, that the catalyst for the production of high octane gasoline is heated in an isothermal reactor with heat pipes to a temperature of 280-320 °C. The process of contacting the raw material with a catalyst, heated in the isothermal reactor with heat pipes, is carried out at a pressure of 0.1-1 MPa, fed into the reactor of raw material with volumetric feed rate of 1-5 h^{-1} (for fluid) and inert gas with volumetric feed rate of 1000 -10000 h^{-1} after evaporation of the raw material in the preheater. Alcohols are used as raw materials. (Used technologies are protected by the patent for invention no. 2440189.)

PROCESS CONDITIONS

T=360-420°C; P=1.0 MPa; W (for raw materials) = 1.0-2.0 h^{-1}

EQUIPMENT-SPECIFIC DESIGN

Tray reactor using a cold quench.

PROCESS INDICATORS

- Output of gasoline - 95-105% on the initial fraction C_5-C_{11}.
- Conversion of methanol - 99-100%.
- Performance ≈ 0.6 tons of gasoline/1t of catalyst per hour.
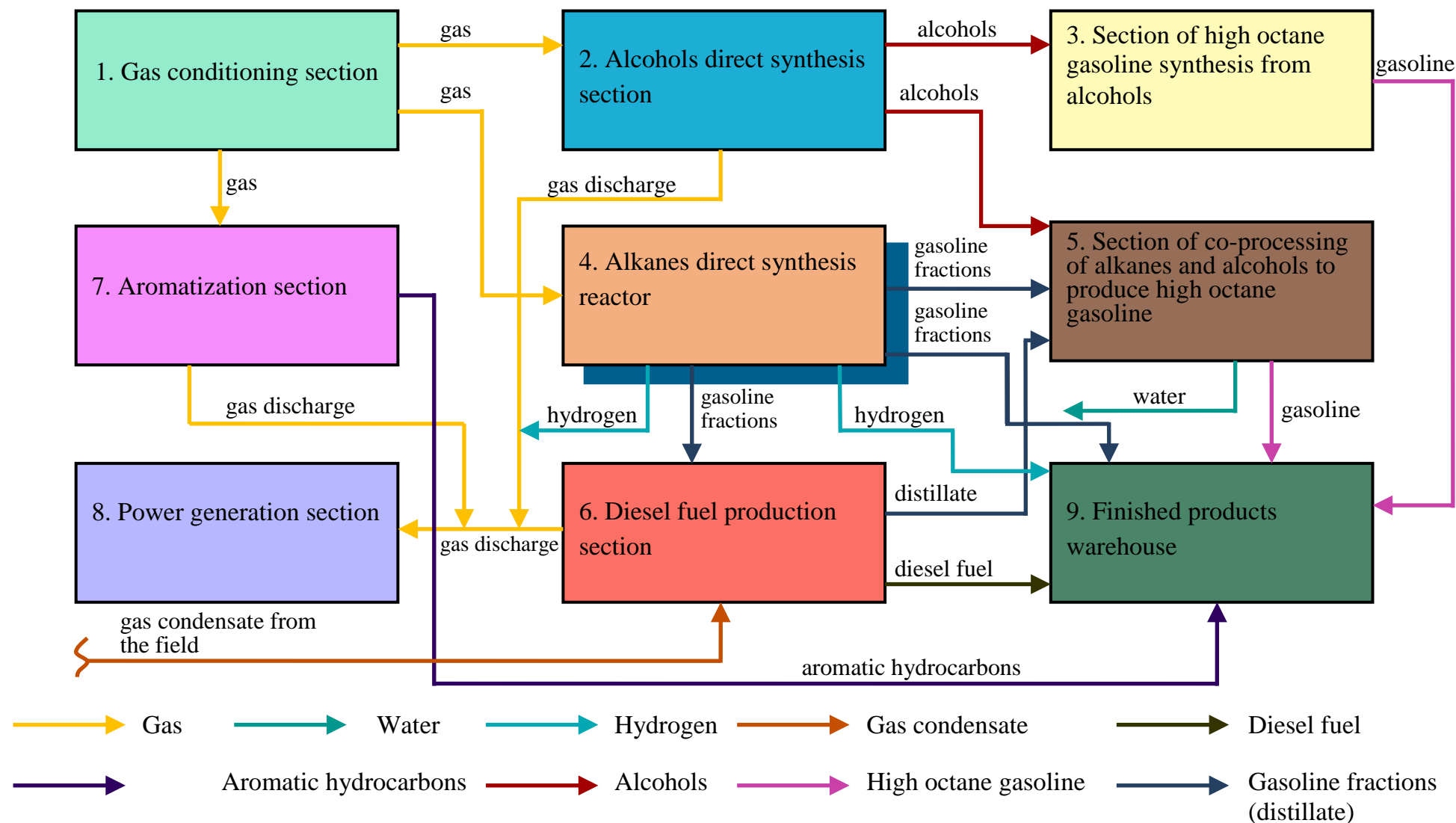
ZEOLITIC CATALYST

- Cycle length of at least 500 hours.
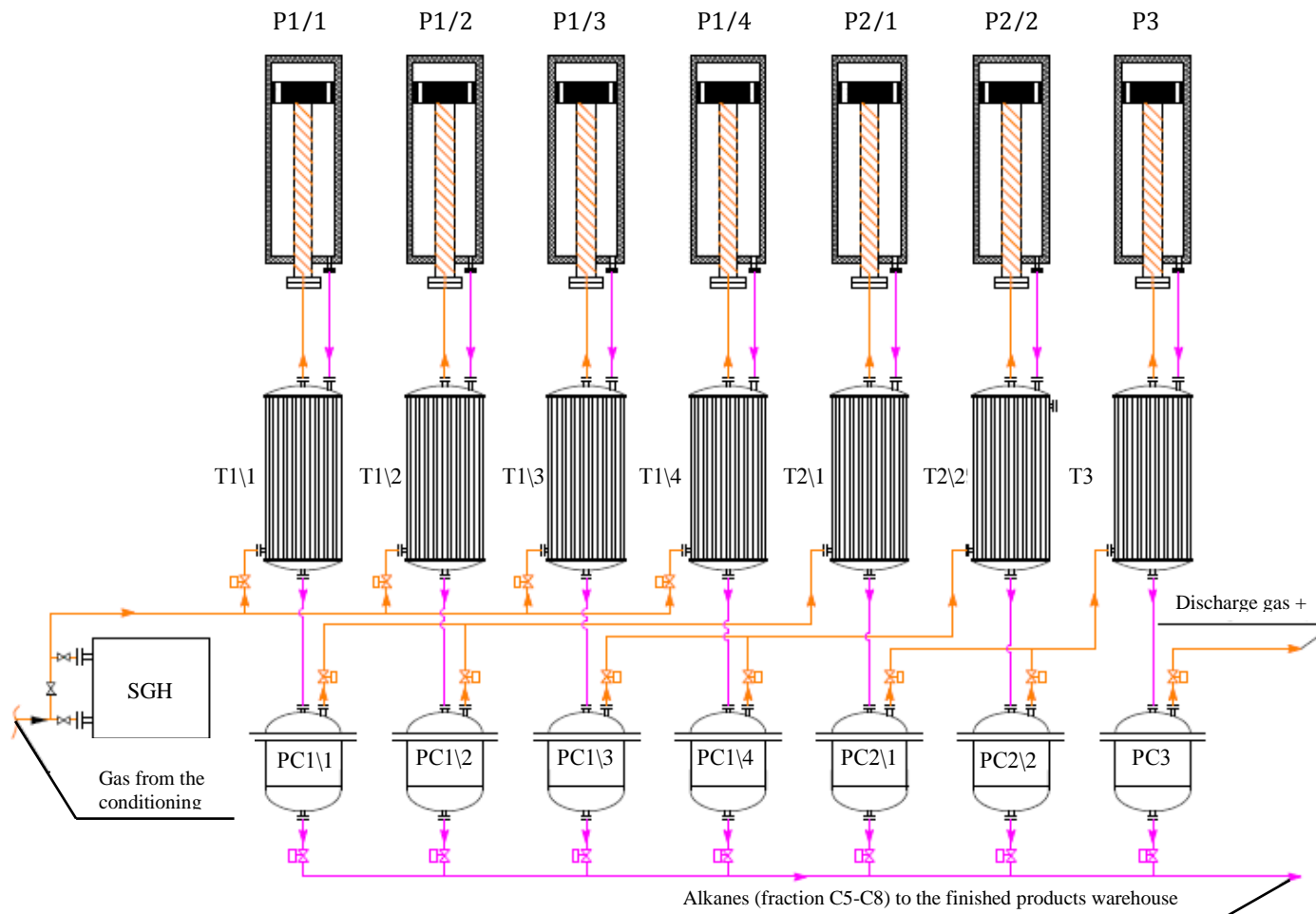- Total lifetime of at least 2 years.

FEATURES OF THE PRODUCED GASOLINE

Gasoline with RON 92-93 with the following composition:

Components:	% by weight.
Aromatic hydrocarbons	*38-40*
Olefins	*2-3*
Naphthenes	*12-15*
Iso-paraffins	*28-30*
Paraffins	*15-20*

Plant of gas conversion into gasoline and diesel fuel

PLAN OF ALKANES DIRECT SYNTHESIS REACTOR

P1/1   P1/2   P1/3   P1/4   P2/1   P2/2   P3

T1\1   T1\2   T1\3   T1\4   T2\1   T2\2   T3

SGH

Gas from the conditioning

PC1\1   PC1\2   PC1\3   PC1\4   PC2\1   PC2\2   PC3

Discharge gas +

Alkanes (fraction C5-C8) to the finished products warehouse

Symbols

Symbol	Name
	Gas
	Alkanes (C5-C8 fraction)
	Flow direction
	Valve
SGH	Starting gas heater
R	Reactor
H	Heat exchanger
RS	Rotary separator

PROCESS OF INTERACTION OF THE GAS MOLECULES in the alkanes direct synthesis reactors.

The kinetic energy of the molecules is expressed by the formula:

$$E = mv^2/2$$

During the movement of the molecules, the collisions occur; resulting in the momenta exchange, the speed of one group of molecules increases, and the speed of the other decreases. In this case, the law of conservation of momentum is satisfied, i.e., sum of the momenta before the collision is equal to the sum before and after the collision. If we write the equation of exchange of momentum between two molecules, it becomes obvious.

$$m_1 v_1 + m_2 v_2 = m_1 v'_1 + m_2 v'_2$$

After the collision the speeds of molecules changes, the speed of one of molecules increases, and the speed of the other decreases. As a result of these collisions in the gas, there is a separation of molecules by the velocity. Maxwell specified this separation, and it depends on the temperature. The higher the gas temperature, the greater the molecular motion at high speed.

This confirms the Boltzmann equation, which relates the temperature of the gas with a rate of gas molecules, and consequently, the kinetic energy.

$$E = 3/2kT = mv^2/2;$$

where k- Boltzmann's constant;

T is the temperature of the gas.

But in this case, a certain average velocity of the gas molecules is assumed, and gas molecules undergo elastic collisions, i.e. the molecule is not deformed, and inside it the state of the electrons is not changed.

This shows that the velocity of gas molecules is dependent on temperature.

The higher the gas temperature, the higher the velocity of the gas molecules.

If you raise the gas temperature , then a moment occurs, when the molecules will undergo inelastic collisions, i.e., they will begin to firstly deform each other, and then destroy them.

A fact that confirms the inelastic collisions is glowing of gas when heated.

The source of glowing is the excitation of the outer electrons of the gas molecules.

When the electron returns from the excited state to the normal state, a quantum of light is emitted. Quantum energy:

$$E=h\gamma$$

h- Planck's constant;

γ- frequency of the emitted light.

For the methane molecule, the destruction of the molecule is a hydrogen atom removal.

The energy, expended in this removal, is called the binding energy. This energy must be expended to destroy this binding . After hydrogen atom removal, there are two options:

1. Two molecules without hydrogen atom (radicals) can connect and form a molecule of ethane.

2. The molecule without hydrogen atom (radical) is connected to a hydrogen atom and again becomes methane molecule.

It can be assumed that these processes are equally probable. Then there are the reaction products of ethane and hydrogen.

$$2CH_4 = C_2H_6 + H_2$$

Practice has shown that the implementation of such reaction needs a minimum temperature of 2000 °C and high pressure, which will depend on the reaction outcome.

Further, if the ethane molecules will collide, they can form molecules of butane or propane, but these processes are very unlikely.

Thus, the thermal activation of molecules with a very low probability can lead to the formation of more complex molecules than ethane.

This will happen if the formed molecule is rapidly removed from the zone of transformation, i.e., cooling.

Hence, in order to carry out the reaction and obtain the products, the gas molecules need to be converted into an excited state.

BARRIER DISCHARGE

The best way to do this is the gas discharge.

There are many types of gas discharges, but to implement the technology of chemical reactions, the barrier discharge is most suitable.

Barrier gas discharge exists between the two electrodes, and one electrode is separated from the other by a dielectric barrier.

This barrier is any material with poor electrical conductivity.

In the interelectrode space the gas molecules commit disorderly, chaotic motion, which is called Brownian motion.

When voltage is applied to the electrodes, it produces an electric field, and the electric current should appear. By increasing the voltage, at the beginning there is a polarization of the gas molecules and the dielectric barrier. Polarized molecules in an electric field will move to the electrodes and will transfer the charge, i.e. there is a weak electrical current. According to Ohm's law, the current is:

$$I = U/R;$$

where U - voltage in volts;
R- Electrical resistance of the polarized gas barrier.
In turn, voltage is:

$$U = Ed;$$

E- Electric field strength;
d- Distance between the electrodes.

E=Fq

F - Force of the electric field, acting on a charge in the interelectrode space;

q - Charge in the interelectrode space.

Strength is a force of the electric field, and the voltage is the force multiplied by the distance, work on charge transfer between the electrodes. Work is energy, then the electric field is the energy that is transferred to the charges. Charge is an ion or electron.

With an increase in voltage, the time occurs when the electrons in the central electrode (cathode) begin to leave it and go into the interelectrode space. This process is called the electron emission. On their leaving the electrode, it is necessary to expend energy. This energy is called the work function of the electron and is 4-5 eV.

Once entering the interelectrode space, the electron is accelerated under the action of electric field, as in the electron accelerator, the kinetic energy increases. However, it will inevitably collides the gas molecules. If its energy is greater than the binding energy between the atoms of carbon and hydrogen, it will destroy this binding.

As a result of this destruction, there will occur two radicals: hydrogen atom and methane moiety without hydrogen. If its energy is high, then it can free the electrons from the radicals. They are called secondary electrons.

Thus, in the interelectrode space by the impact of the electric field, the hydrogen ions and methane molecule residues appear. In addition, there are at least two secondary electrons, which are accelerated and in the collision can free four electrons, four - eight electrons, etc.

Avalanche process will occur as long as the electric field energy is sufficient to ionize a number of molecules in the interelectrode space.

As a result of these processes, the current is generated, which characterizes the flowing process capacity and therefore, the number of transformations undergone by the gas molecules located between the electrodes.

$$P=UI - \text{power of the gas discharge.}$$

Power multiplied by time shows the energy expended in the gas discharge to the chemical conversion in the gas reactor.

$$E=P\tau=UI\tau \text{ (kilowatt hours)}$$

IN GAS DISCHARGE:

1. Activation of the gas molecules occurs.

2. It results from the impact of the electrons on the gas molecules more efficiently than in heating.

3. The degree of activation depends on the voltage of the electric field, and so the process is controlled.

As practice has shown, the reactor temperature does not rise above 250 °C.

The reaction products can optionally include a wide range of substances, and selectively at high output.

Power consumption for various substances is between 0.2 and 5 kilowatt hours per kilogram of product.

Dielectric barrier may play a catalytic role and determine the yield and quality of products.

The process can be carried out at any pressure.

CALCULATION OF ENERGY CONSUMPTION on the formation of alkanes (liquid state) of molecules of methane, ethane, propane, butane.

Methane, ethane, propane and butane, constituting the main part of the natural gas and associated oil, gas, under normal conditions, are in a gaseous state.

Next in the homologous series of saturated hydrocarbons (alkanes), pentane has a boiling point (condensation) 35 ℃, and it is different from gaseous alkanes by the molecule length.

In pentane, five carbon atoms are connected in the carbon chain.

Hydrocarbon molecules with a chain length of 5 or more carbon atoms are liquid hydrocarbons.

In order to combine the molecules of methane, ethane, propane, butane and receive hydrocarbons, molecules length of which increases to five atoms and more, some energy must be expended.

The effective way of introducing energy in gases is a gas discharge in an electric field. Gas discharge is a stream of electrons that ionize gas molecules. As a result of ionization at the reactors with a gas barrier discharge, methane loses one hydrogen atom. Two ionized methane molecules are combined into the ethane molecule, wherein hydrogen is obtained.

$$2CH_4 = C_2H_6 + H_2$$

This endothermic reaction takes place with heat absorption. $\Delta H = 15.54$ kcal/mol - the heat result of the reaction. In this case, it is necessary to spend 15.54 kcal (kilocalories) on formation of 30 g of ethane (gram moles).

The energy of the electric field is calculated by the formula:
Eout = UIt, kilowatt-hour (kW/h)
where U - voltage, volts (V)
I -current, amperes (A)
t -time of electric field impact on the gas, (h).

ACTIVATION OF GAS MOLECULES in the interelectrode space of the gas discharge.

The electrons are emitted from the cathode under the impact of the electric field (electron emission). The electron emission requires energy. This energy is called the "electron work function". Its level is about 3-5 eV and depends on the type of material, from which the electrode is made. Since the electrodes are made of metal, "electron work function" is ~ 4 eV.

The electrons, released from the electrodes and trapped in the electrode space, by the action of the electric field are accelerated and acquire energy capable tear hydrogen atoms in a molecule of methane, i.e. exceed the ionization energy of the gas molecules. This ionization energy is about 6000-8000 electronvolts (eV). In this case, a molecule of methane in the moment of collision with an electron can have low kinetic energy (cold gas). After separation of the hydrogen atoms, the remaining parts are combined into a molecule of ethane.

The process of activation and association of molecules can occur almost without heating the gas at room temperature, so the reaction in the gas discharge does not require to warm up the gas. But after a collision with an electron, the part of the energy is transferred to the gas molecules.

Gas molecule or formed ion begin to move faster. This increase in velocity of the gas molecules and ions is recorded by the thermometer as an increase in the gas temperature. In the process of turning the gas temperature does not rise above 250 °C.

In order to the reverse process of ion recombination does not occur promptly, the optimum temperature is required. By adjusting the flow of energy in the gas discharge it is possible to manage the process of association of molecules into the long chain molecules.

Let's make a calculation of the energy consumption for the formation of ethane from 1000 m ^{3} or 714.286 kg of methane. Ethane output - 669.851 kg. The formation of ethane from methane requires 0.34 x 106 kcal or 395.3 kW/h. Further, transmitting the electrical current through the gas, methane is formed from formed ethane and propane:

$$CH_4 + C_2H_6 = C_3H_8 + H_2$$
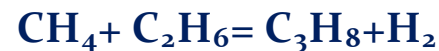
Thus H = 13.31 kcal/mole is absorbed.

And butane is formed from two molecules of ethane:

$$2C_2H_6 = C_4H_{10} + H_2$$

H=8.33 kcal/mol

On the connection of two molecules of ethane, almost twice less energy is required then for the connection of methane molecules. Thereafter, the gaseous medium contains molecules of methane, ethane, propane, and the number of options for the formation of molecules is increasing.

If we look at how the hydrocarbon chain elongation takes place, we get a series of parallel reactions:

$$2CH_4 = C_2H_6 + H_2$$

H=15.54 kcal/mol

$$CH_4 + C_2H_6 = C_3H_8 + H_2$$

H=13.31 kcal/mol

$$CH_4 + C_3H_8 = C_4H_{10} + H_2$$

H=10 kcal/mol

$$CH_4 + C_4H_{10} = C_5H_{12} + 4H_2$$
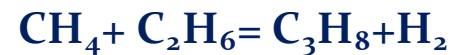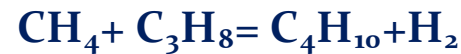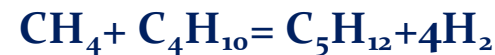
H=15,06 kcal/mol

During the reaction of pentane formation of methane, pentane and four hydrogen molecules are obtained.

$$5CH_4 = C_5H_{12} + 4H_2$$

Energy costs amount to H = 54.45 kcal/mol.

On obtaining of pentane in reaction (5) at one time, there would be required to expend H = 54.45 kcal/mole. If this process is carried out in stages (reactions 1-4), each step takes less energy. It does not require immediate entering large amounts of energy. In a gas discharge, the self-regulation, stepwise conversion of methane into liquid pentane occur.

This chain extension process will continue to form solid or tarry substances. To avoid this, it is required to cool the gas after some time. Thus, liquid substances, formed in the process, are condensed and converted into liquid hydrocarbons.

The process of burning of the produced hydrogen:

$$H_2 + 2O_2 = H_2O$$

H=57.79 kcal/mol

Since four moles of hydrogen are burned, it emits 231.16 kcal, i.e. 4 times more than spent. Reaction with methane indicates that, the bigger molecules are, the less energy is needed for their association. This means that in general, the system selects the path where it meet less resistance. This corresponds to the well-known principle of least action.

If we write the general formula to form a hydrocarbon chain of any length, it is evident that the result is a hydrocarbon and hydrogen in an amount of (n-1), where n - is the length of the hydrocarbon chain.

$$nCH_4 = CnH_2n+2 \ + (n-1)H_2$$

Energy consumption for the formation of octane, n = 8

$$8CH_4 = C_8H_{18} \ + 7 \ H_2$$

Heat of reaction (spent): H=93.32 kcal/mol (1 mole 114 g).

Combustion of 7 moles of hydrogen, formed during this, allocates 404.6 kcal, 4.3 times more than spent.

1 kW/h = 8,598,400 cal = 36,000,000 J.

Let's make a calculation of the energy consumption in accordance with the thermodynamic parameters for formation of octane (liquid state) from methane at 1000 m ^{3} or 714.286 kg. We will obtain 636.16 kg of octane. Generation of octane from 1,000 m^3 of methane consumes 61 kW/h of electric energy. The longer produced hydrocarbons, the lower the unit cost.

CALCULATION OF THE CHAIN LENGTH

The first part shows, the hydrocarbon chain elongation is possible, and energy expenditure are calculated. It is important to know what determines the length of the chain, which hydrocarbons and under what parameters hydrocarbons of the desired length can be obtained.

The general formula of hydrocarbon formation.

$$nCH_4 = CnH_2n+2 + (n-1)H_2,$$

where n is a number of atoms in the hydrocarbon.

It is assumed that for the hydrocarbon chain elongation, the methane must lose one hydrogen atom and be transformed into a radical. This occurs under the influence of an electric field. When this energy is supplied from the outside - Eout. = UIt. For the calculation, it is assumed, that at cleavage the energy is consumed - the endothermic reaction, at formation the energy is released - an exothermic reaction.

The hydrogen atom release in methane and hydrocarbons with an increase in the chain length requires energy - $e_1 = e_3 = 99$ kcal/g-atom. In case of formation of connection at elongation C-C $e_2 = 85$ kcal/g-atom and the H-H $e_4 = 104$ kcal/g-atom energy is released, respectively, e_2 and e_4. The change of the total energy of the system is represented by formula (1).

For methane the total binding energy Emet is four connections

$$\text{C-H} \quad E_{met} = 4ne_1.$$

For hydrocarbon the total amount of connections C-C will be (n-1), so the total binding energy will be

$$E_{c-c} = (n-1)e_2.$$

Number of C-H connections in the resulting hydrocarbon amounts to $(2n + 2)$, so the total binding energy is

$$E_{c-н} = (2n+2)e_3.$$

When extending the chain, hydrogen is formed and connection H-H, the number of molecules of hydrogen connection H-H will be (n-1), and the binding energy of hydrogen atoms is equal to

$$E_{H-H}=(n-1)e_4.$$

The total energy of the system is:

$$E\ total=E_{out}- N_0\ 4ne_1+ N_0/n[(n-1)e_2+(2n+2)e_3]+ N_0(n-1)/n\ (n-1)e_4+ N_0\ 3/2kT+n(Q_a-Q_d)\ (1)$$

After simplification we get the formula for calculating the length of the chain:

$$n= 1+ (E_{out.}\ /2e_1- e_2-e_4)\ (2)$$

From the equation it follows that the length of the chain depends on the gas discharge electric power and the ratio of the binding energy between carbon and hydrogen atoms e_2, e_4.

If Eout. = 0; energy is not supplied, then n = 1. This means that the methane remained unchanged. To form octane n=8, necessary amount of the applied electric energy is calculated by the formula (2).

$$n= 8=1+ (Eout. /198-85-104)=1+ Eout. /9$$

Eout. = 63 kcal or 0.007 kW/h of electricity to obtain 114 grams of octane or 0.0614 kW/h to obtain 1 kg of octane. The greater applying electric energy, the greater the length of the carbon chain.

Calculation of energy consumption for formation of octane (liquid state) of from per 1000 m ^{3} or 714.286 kg: 636.16 kg of octane. Generation of octane from 1,000 m^3 of methane consumes 39 kW/h of electric energy. The longer produced hydrocarbons, the lower the unit cost. Use of catalyst also reduces energy costs.

Plant of gas conversion into gasoline and diesel fuel

The diagram shows the following sections and flows:

- **1. Gas conditioning section** → gas → **2. Alcohols direct synthesis section**
- **1. Gas conditioning section** → gas → **4. Alkanes direct synthesis reactor**
- **1. Gas conditioning section** → gas → **7. Aromatization section**
- **2. Alcohols direct synthesis section** → alcohols → **3. Section of high octane gasoline synthesis from alcohols**
- **2. Alcohols direct synthesis section** → alcohols → **5. Section of co-processing of alkanes and alcohols to produce high octane gasoline**
- **2. Alcohols direct synthesis section** → gas discharge
- **3. Section of high octane gasoline synthesis from alcohols** → gasoline → **9. Finished products warehouse**
- **4. Alkanes direct synthesis reactor** → gasoline fractions → **5. Section of co-processing of alkanes and alcohols to produce high octane gasoline**
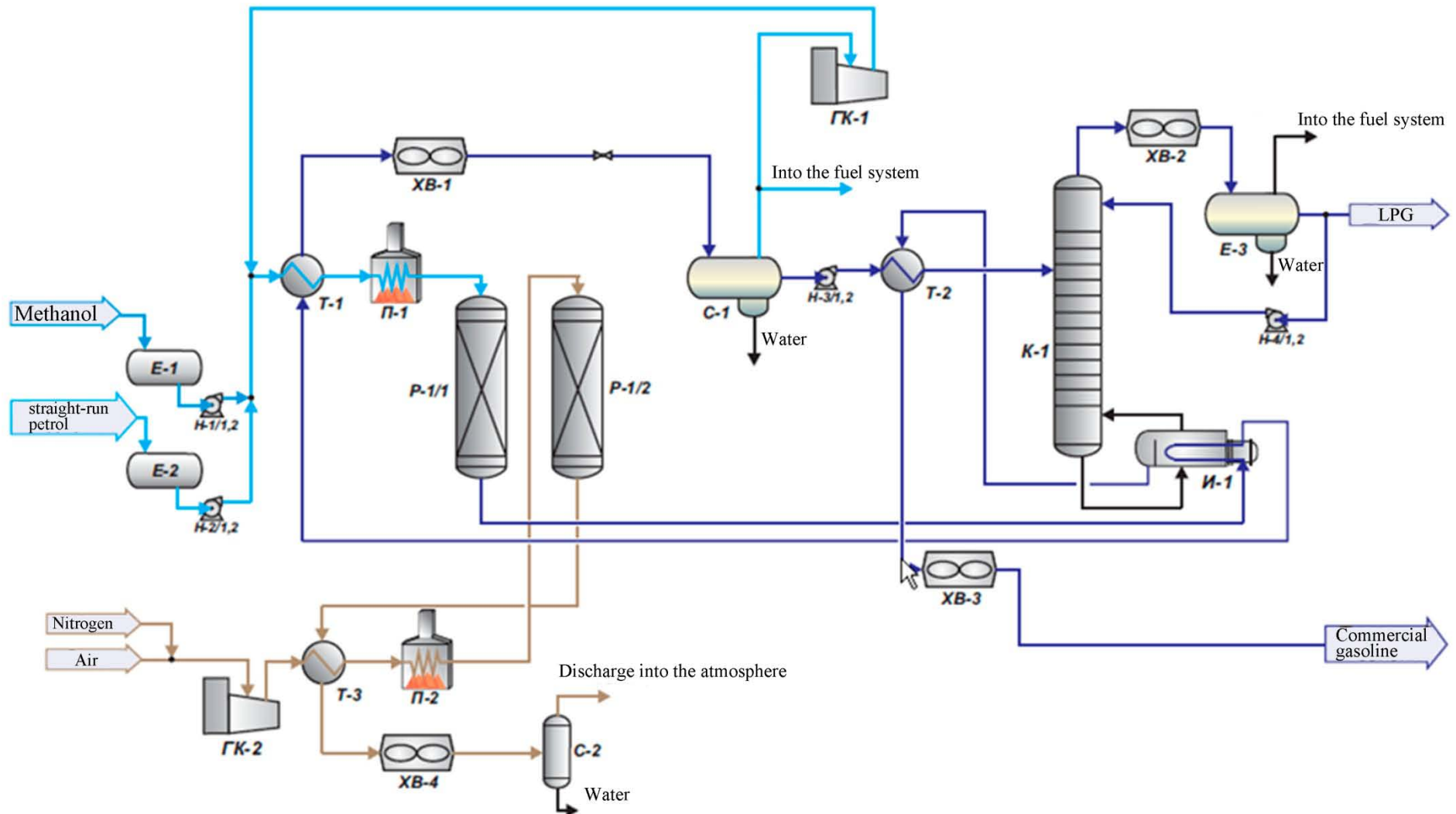- **4. Alkanes direct synthesis reactor** → hydrogen
- **4. Alkanes direct synthesis reactor** → gasoline fractions → **6. Diesel fuel production section**
- **5. Section of co-processing of alkanes and alcohols to produce high octane gasoline** → gasoline → **9. Finished products warehouse**
- **5. Section of co-processing...** → water
- **5...** → distillate → **9. Finished products warehouse**
- **6. Diesel fuel production section** → hydrogen
- **6. Diesel fuel production section** → diesel fuel → **9. Finished products warehouse**
- **7. Aromatization section** → gas discharge → **8. Power generation section**
- **7. Aromatization section** → aromatic hydrocarbons → **9. Finished products warehouse**
- gas condensate from the field → **6. Diesel fuel production section**

Legend

- → Gas
- → Water
- → Hydrogen
- → Gas condensate
- → Diesel fuel
- → Aromatic hydrocarbons
- → Alcohols
- → High octane gasoline
- → Gasoline fractions (distillate)

PLAN OF SECTION OF CO-PROCESSING OF ALKANES AND ALCOHOLS

Technology of production of high-octane gasoline by co-processing of hydrocarbon fractions and oxygen-containing raw material.

A new technology of production of high octane gasoline is proposed, which consists of co-processing of hydrocarbon fractions and oxygen-containing raw materials, which has obvious advantages in comparison with conventional technologies.

Reforming is the most common method of catalytic upgrading of straight-run gasoline. Catalytic reforming units are located almost in all domestic and foreign refineries. But at the same time, this process has several disadvantages, the need to increase the reformate octane number leads to a decrease in liquid yield with an increase in the proportion of undesirable gaseous products: high content of aromatic hydrocarbons in the catalytic reforming gasolines; the use of expensive platinum catalysts; narrow hydrocarbon fraction 85-180 °C is served in processing.
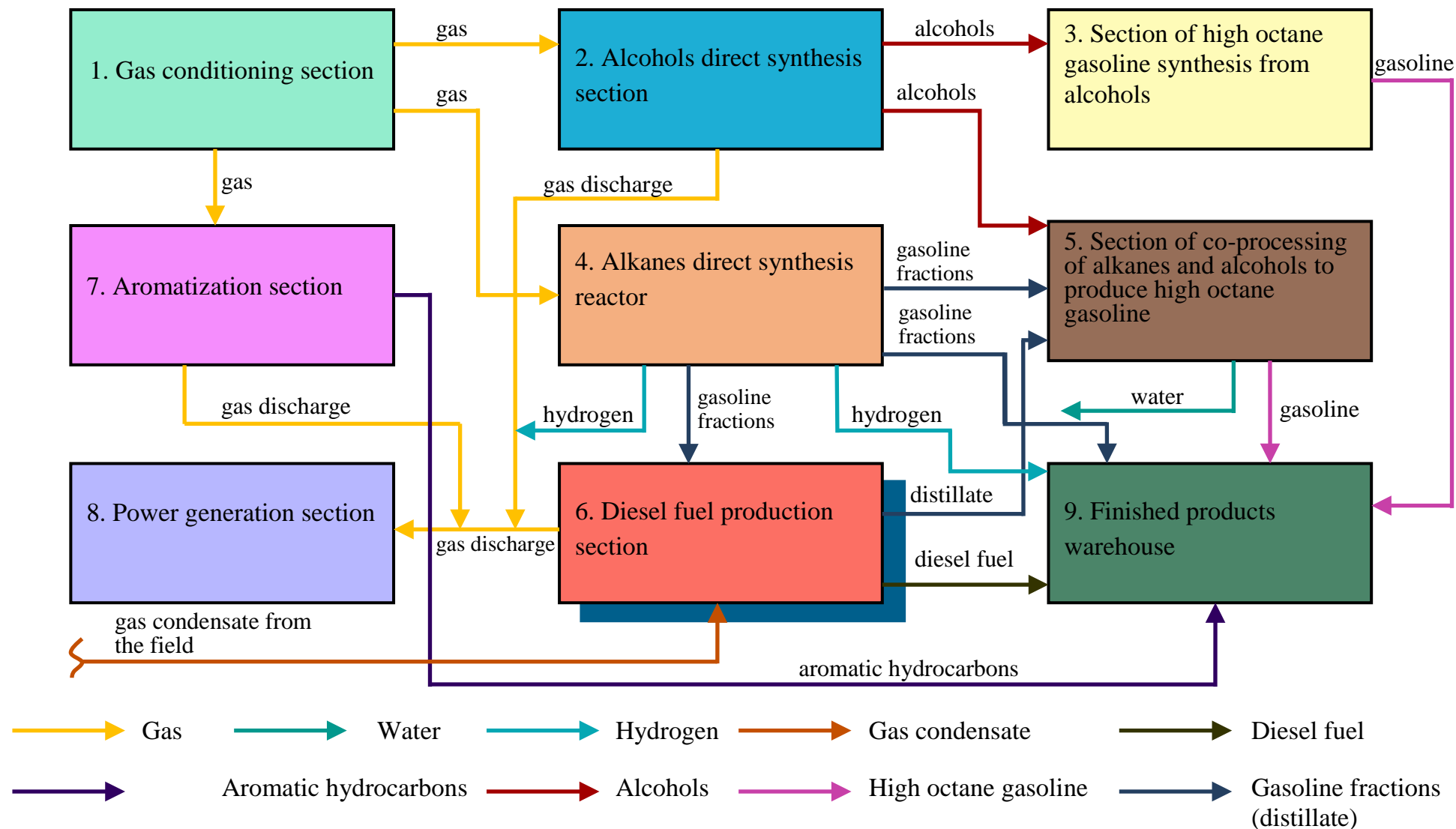
To eliminate these reforming shortcomings, there were developed the technologies of one-step upgrading of low-grade (straight-run) gasolines without usage of hydrogen and expensive platinum catalysts: BIMT type and Zeoforming (SEC "Zeosit" of the Russian Academy of Sciences, Novosibirsk). However, the disadvantage of these technologies is the low yield of gasoline compared to the process of reforming (80-85% for AI-80, 60-75% for AI-92 and only 55-60% for AI-95), the dependence of the output of gasoline with fixed octane number on the feed composition and high content of benzene in the final product (from 4 to 10%).

These problems are solved by the technology, which consists of co-processing of wide hydrocarbon fractions and oxygen-containing raw materials, which, in contrast to the reforming and "Zeoforming"/BIMT, allows to bring the output of commercial high octane gasoline to 98-100% on taking the initial hydrocarbon fraction i.b.p. -140/180 degrees. This technology does not use hydrogen and expensive catalysts containing precious metals, and gassing is minimized.

The principal difference of the proposed technology - the use of two types of raw materials. Wide hydrocarbon fractions i.b.p. -140/180 degrees undergo processing (straight-run gasoline, stable gasoline etc.) together with the oxygen-containing compounds: C_1-C_4 alcohols (methanol, crude methanol, ethanol, crude ethanol, propanol, butanol, alcohol production waste etc.) ethers etc. Process conditions: temperature - 350-450 ° C, pressure - 0.5-1.5 MPa. Service cycle of the catalyst - at least 500 hours, regeneration - oxidant, with air to 550 °C, catalyst life - 2 years, catalyst - zeolite-containing.

The process was tested in experimental units, gasolines, produced by this technology, have been tested in the Test laboratory of oil products"Lukoil-Nizhegorodnefteorgsintez" and OJSC "VNII NP". As can be seen from the scheme, in order to increase the yield of the desired fraction - a component of high octane gasoline - the reforming unit is complemented with the aromatization unit of discharged gas of decontamination and stabilization, containing more than 40% of unsaturated hydrocarbons.

This technology can be applied both to produce high octane gasoline Euro-5, and for the production of short supplied in Russia aviation fuel B-92 with an additional compounding of gasoline with lead and high-octane additives (e.g. toluene).

1. Gas conditioning section

2. Alcohols direct synthesis section

3. Section of high octane gasoline synthesis from alcohols

7. Aromatization section

4. Alkanes direct synthesis reactor

5. Section of co-processing of alkanes and alcohols to produce high octane gasoline

8. Power generation section

6. Diesel fuel production section

9. Finished products warehouse

gas · gas · alcohols · alcohols · gasoline · gas · gas discharge · gasoline fractions · gasoline fractions · water · gasoline · gas discharge · hydrogen · gasoline fractions · hydrogen · distillate · gas discharge · diesel fuel · gas condensate from the field · aromatic hydrocarbons

Legend:

| → Gas | → Water | → Hydrogen | → Gas condensate | → Diesel fuel |
| → Aromatic hydrocarbons | → Alcohols | → High octane gasoline | → Gasoline fractions (distillate) | |

In the production of diesel fuel, the "GTL" company applies a widespread scheme of two-column distillation of hydrocarbon fractions. The process is carried out at temperatures of 400-450 ^{o}C and pressure of 2-2.2 MPa.

PRINCIPAL DIFFERENCES of the "GTL" Company technology consist of:

Application of the special design of column equipment, providing maximum mass transfer at the optimum resistance of contacting media;

Maximum automation of the process using up to 10 algorithms of automatic emergency stop of the equipment to enhance technological safety of the process;

High energy efficiency of the process by the design of column equipment.

Plant of gas conversion into gasoline and diesel fuel
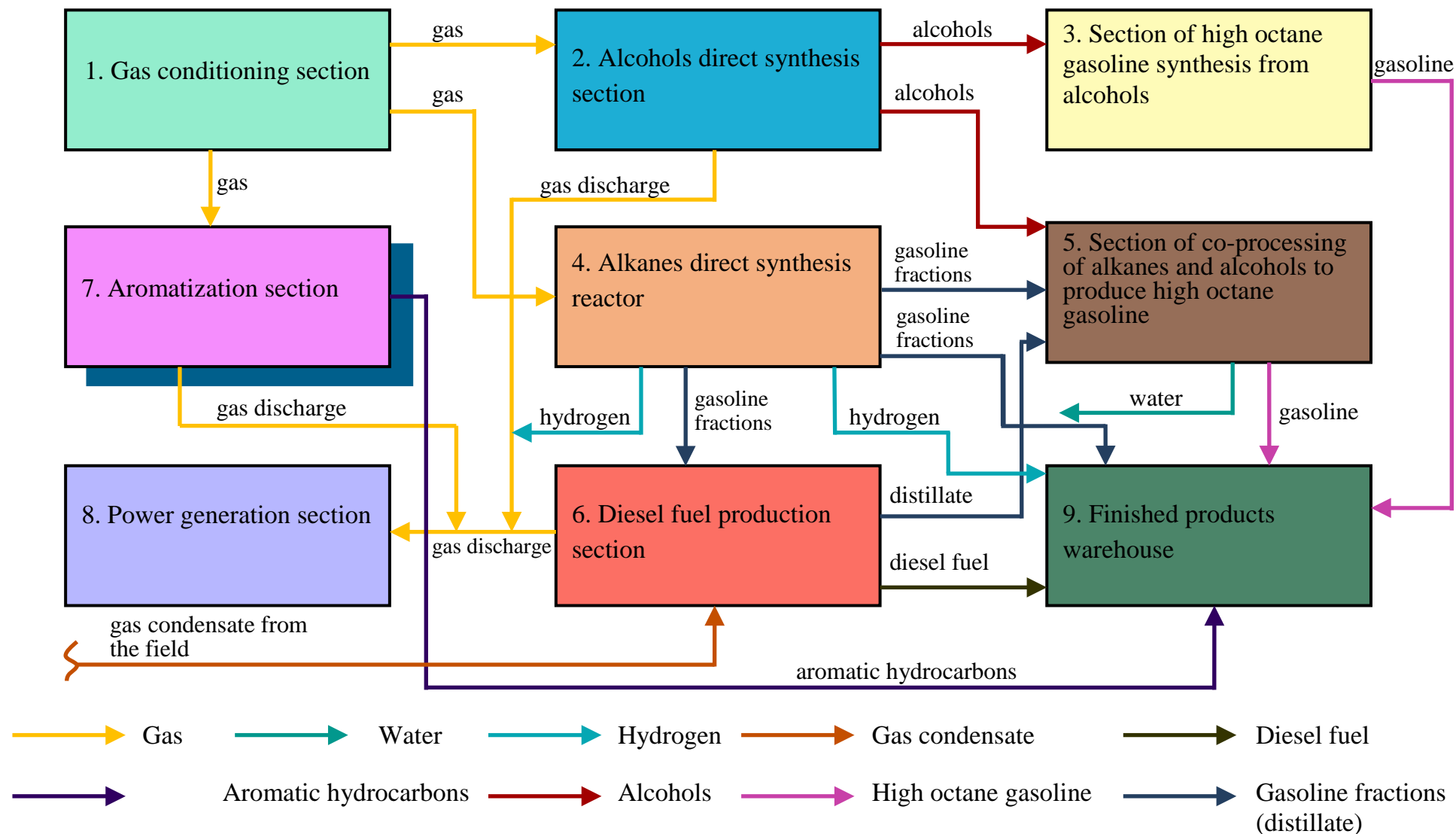
PLAN OF THE AROMATIZATION SECTION
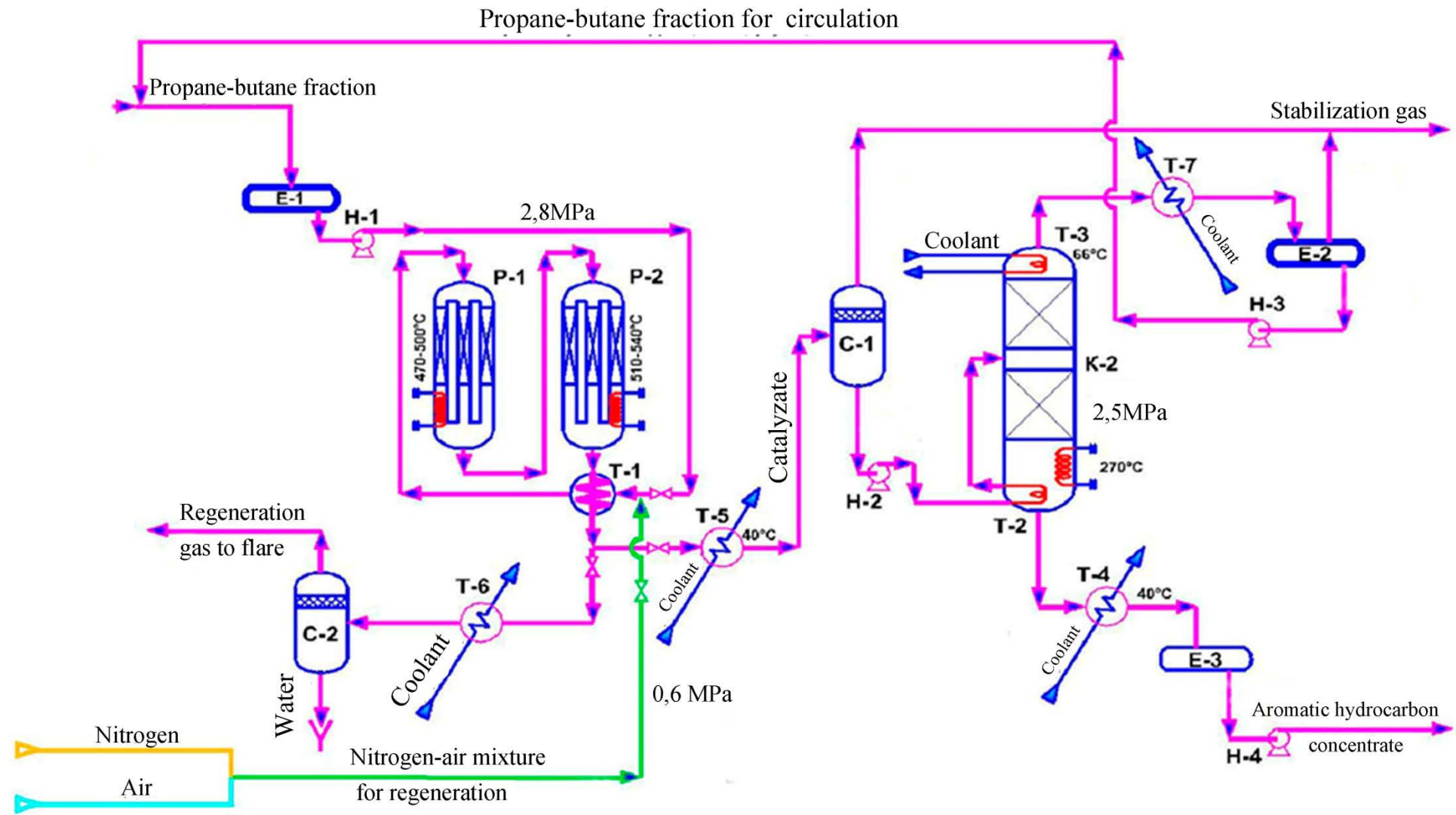
Technology for producing a mixture of hydrocarbons of the aromatic series from propane-butane fraction or associated gas

In connection with the ban on burning of associated gas in flaring (Act of the government of the Russian Federation dated 08.01.2009 no. 7 "On measures to stimulate the reduction of air pollution by products of associated gas flaring"), as well as taking into account the complexity of storage and transportation (under pressure of 2 MPa) of liquefied propane-butane fraction (PBF) at sites with severe climatic conditions away from consumers and the absence of an established system of export, it is appropriate to process associated gas and PBF in highly liquid stable product, easy to store and implement.

For this purpose, a process of catalytic aromatization (dehydrocyclodimerization) is proposed, allowing recycling of the associated gas in PBF into the aromatic hydrocarbons concentrate (benzene-toluene-xylene fraction - BTX).

The process is carried out on zeolite-containing.catalysts at a reaction temperature of 47-540 ° C under a pressure of 2-3 MPa.

The most important element of the proposed facility is reactors with heat pipes. Their use provides a constant temperature throughout the length of the pipe-vaporizers and prevents overheating of the catalyst at any sites. Due to the isothermal process, the catalyst life increases by about 1.5 times compared with conventional reactors (3-4 years). Moreover, product yield is increased by 10-20%. Another important factor is the significant reduction in weight and size characteristics of the reactor-furnace equipment in comparison with the classical layout.
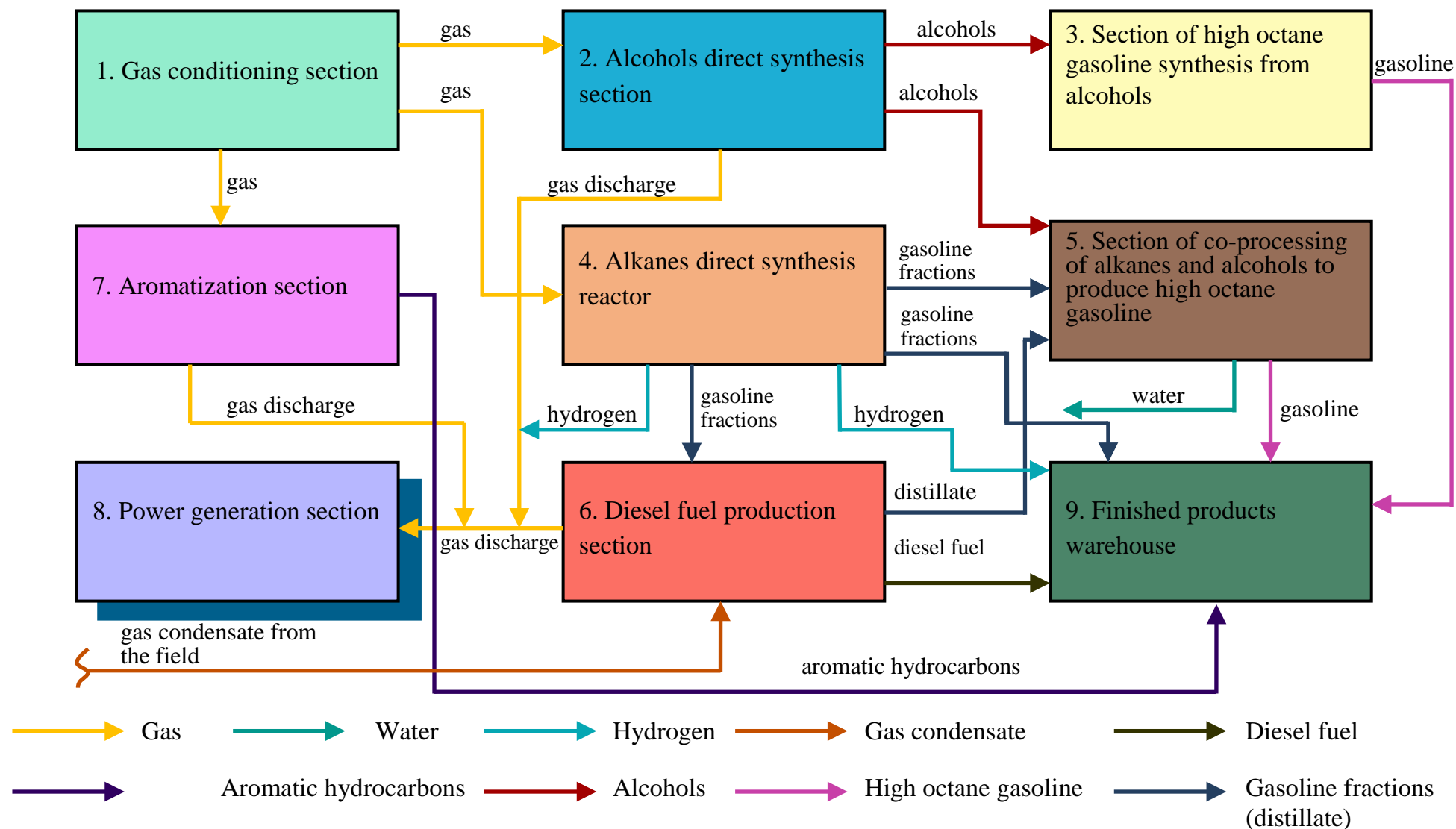
Potassium is used as coolant in the reactor tubes.

The first reactor is intended for converting mainly C_4+ fractions.

The second reactor, operating at higher temperatures, allows to involve propane into the reaction.

Regeneration of the catalyst is carried out by the nitrogen-air mixture after 250-300 hours at a temperature of 550 °C.

Output of the BTX fraction to the contained in the feed fraction C_{3+} is 55-60% by weight.

1. Gas conditioning section

2. Alcohols direct synthesis section

3. Section of high octane gasoline synthesis from alcohols

7. Aromatization section

4. Alkanes direct synthesis reactor

5. Section of co-processing of alkanes and alcohols to produce high octane gasoline

8. Power generation section

6. Diesel fuel production section

9. Finished products warehouse

gas — gas — alcohols — alcohols — gasoline — gas — gas discharge — gasoline fractions — gasoline fractions — water — gas discharge — hydrogen — gasoline fractions — hydrogen — gasoline — distillate — gas discharge — diesel fuel — gas condensate from the field — aromatic hydrocarbons

Legend:
- Gas
- Water
- Hydrogen
- Gas condensate
- Diesel fuel
- Aromatic hydrocarbons
- Alcohols
- High octane gasoline
- Gasoline fractions (distillate)

REST OF GAS, leaving the reactor of the third order is sent to the power block of the plant, where it is used to generate electricity and provide electricity needs of industrial, administrative and residential areas.

COMPLETING OF THE POWER EQUIPMENT, designed to generate electricity, as well as suppliers of construction of the power generation section in each project are determined individually taking into account local conditions and needs in electricity in order to achieve maximum reliability and profitability of operating equipment.
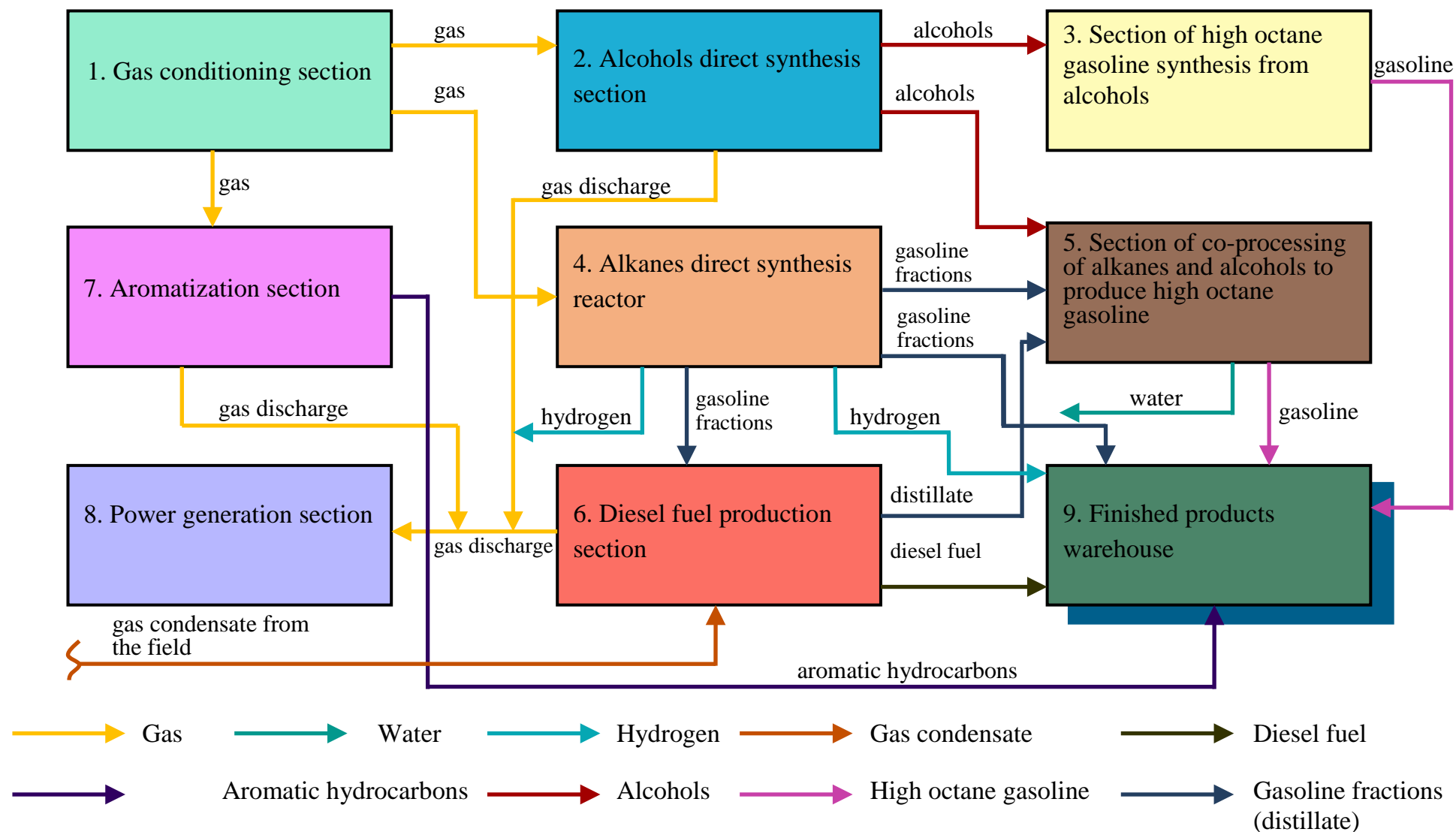
In developing the technology for storage and shipment of finished products, the "GTL" company applies:

Sealed system to prevent evaporation of the finished product and air pollution;

Automated leaks control system;

Modular pumping stations;

Construction of automated platforms for loading of liquid petroleum products.

TECHNOLOGIES OF THE "GTL" COMPANY make it possible to effectively address issues related to the processing of natural and associated gas.

OPPORTUNITY of production of motor fuels from gas reduces the cost of shipping the motor fuels to distant fields and satisfy domestic demand of the commercial vehicles in motor fuel.

COMPREHENSIVE APPROACH to addressing the issues of natural and associated gas reduces the negative impact on the environment and increases the economic efficiency of oil and gas production.

THANK YOU FOR YOUR ATTENTION!