National Research Tomsk Polytechnic University
Institute of Natural Resources
Department of Fuel Engineering and Chemical Cybernetics

# Complex modeling system for optimization of reaction processes of trade gasoline production

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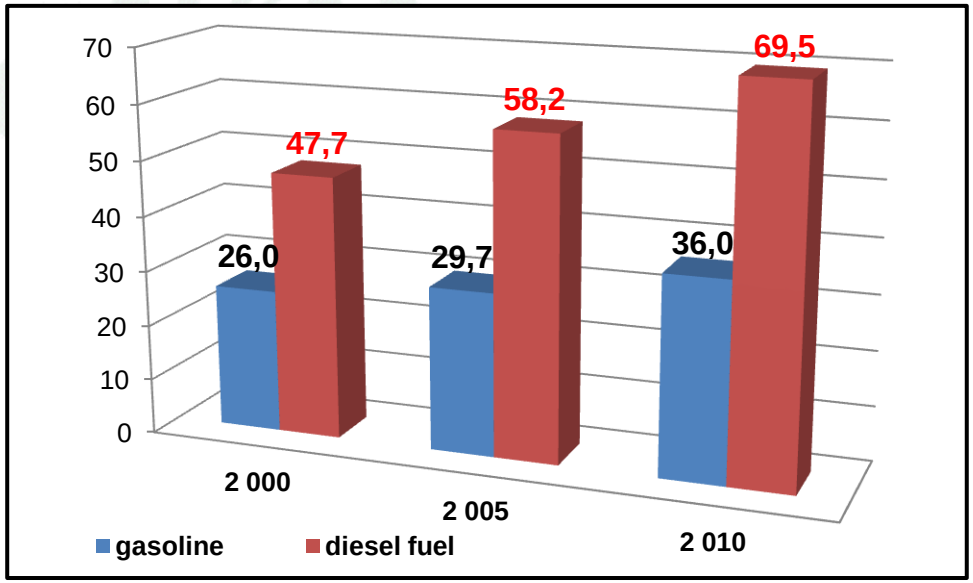
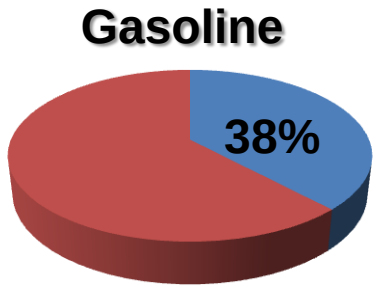
***assistant teacher***

# • Urgency



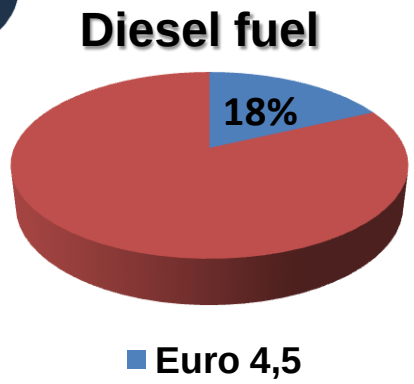




**Fig. 1 Volumes of motor fuels production, million tonnes**

**The main challenge facing the modern oil industry is to improve the resource efficiency of oil refining and the quality of oil products.**

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# Optimization difficulties

**Processes of trade gasoline production is very difficult for optimization!**

***Reasons:***

- **Multistage technology**
- **Changing composition of raw materials**
- **Changing activity of catalysts used during the gasoline components production**
- **Nonadditivity of trade gasoline physicochemical properties**
- **Interconnection of processes and apparatus**

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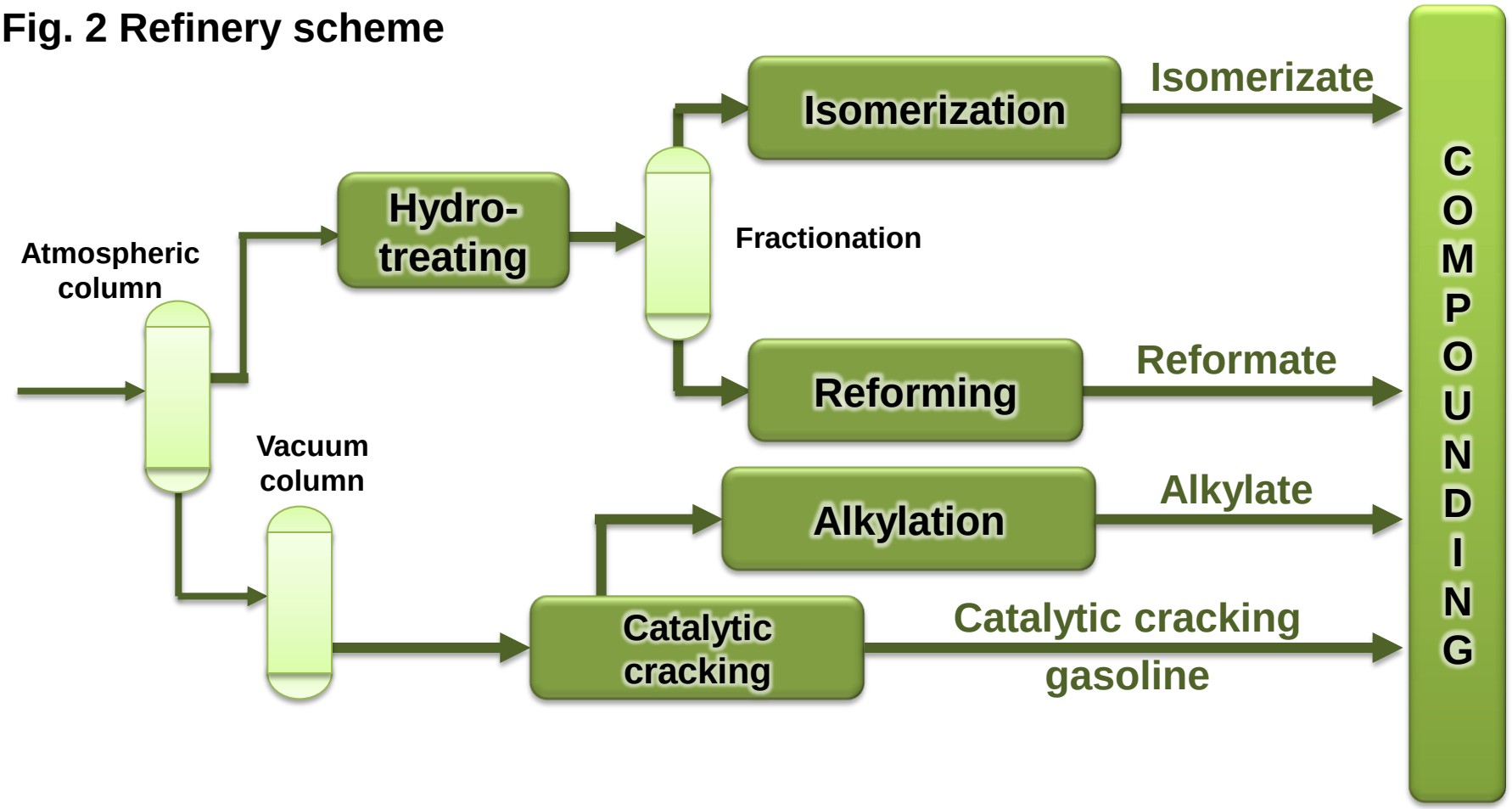
# Optimization difficulties

Fig. 2 Refinery scheme

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# Methods and Solutions

**Mathematical modeling method** is an effective method for solving these multi-factorial and multi-criteria optimization problem.

Optimization of trade gasoline production processes can only be based on a **complex mathematical model** of the preparation, processing and compounding of hydrocarbon streams.

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# Complex modeling system





Fig. 3 The scheme of complex modeling system operation

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# Module of chromatography data systematization

Initial data for calculation – **technological parameters** and the **results of the chromatographic analysis**

**During the process of systematization any chromatogram is reduced to 110 key components (individual hydrocarbons and pseudo-components).**

**Table 1. The structure of the chromatography data systematization**

| Group name | Number of components |
|---|---|
| n-paraffins | 10 |
| isoparaffins | 39 |
| olefins | 32 |
| naphthenes | 15 |
| aromatics | 14 |
| TOTAL | 110 |

**Aggregation of hydrocarbons in pseudo-components based on:**

- **proximity of the molecules structure;**
- **proximity of the octane numbers;**
- **proximity of the reactivity;**

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# Module of chromatography data systematization

| Group | Components | wt. % | Components after chromatography data systematization |
|---|---|---|---|
| A6 | benzene | 0.992 | → benzene (A6) |
| I6 | 2,2-dimethylbutane | 1.805 | → 2,2-dimethylbutane (I6) |
| I6 | 2,3-dimethylbutane | 1.490 | → 2,3-dimethylbutane (I6) |
| A9 | 1,2-methylethylbenzene | 0.270 | → methylethylbenzenes (A9) |
| A9 | 1,3-methylethylbenzene | 0.758 | |
| A9 | 1,4-methylethylbenzene | 0.314 | |
| I9 | 2-methyloctane | 0.246 | → methyloctanes (I9) |
| I9 | 3-methyloctane | 0.292 | |
| I9 | 4-methyloctane | 0.198 | |

**Fig. 4 Example of the chromatography data systematization**

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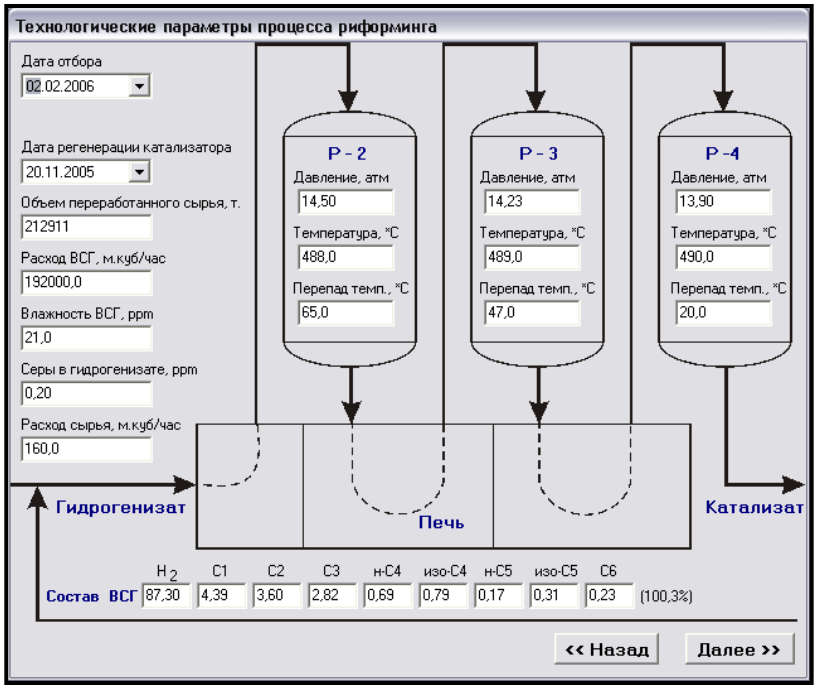
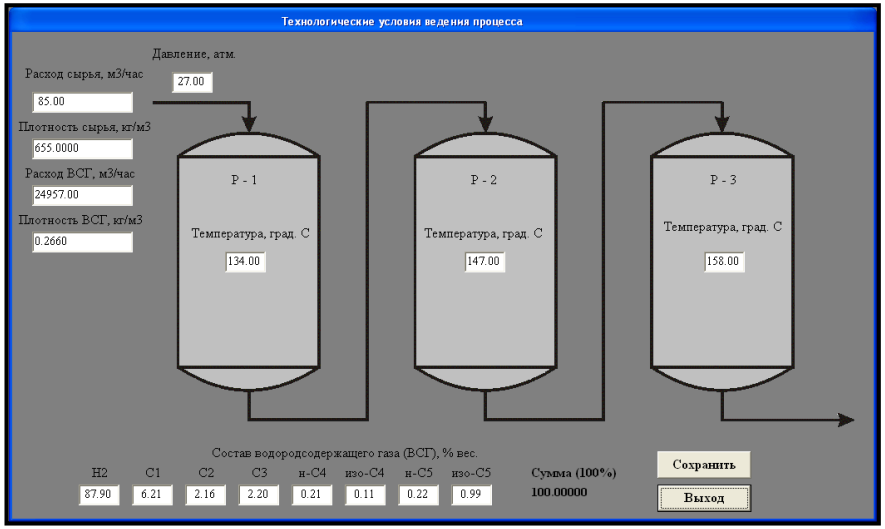
# Modules of isomerization and reforming modeling

Based on the **non stationary kinetic models** of the processes.

Take into account **changes in the composition of raw materials**, and the **activity of the catalysts**.



# Mathematical model of light naphtha isomerization process

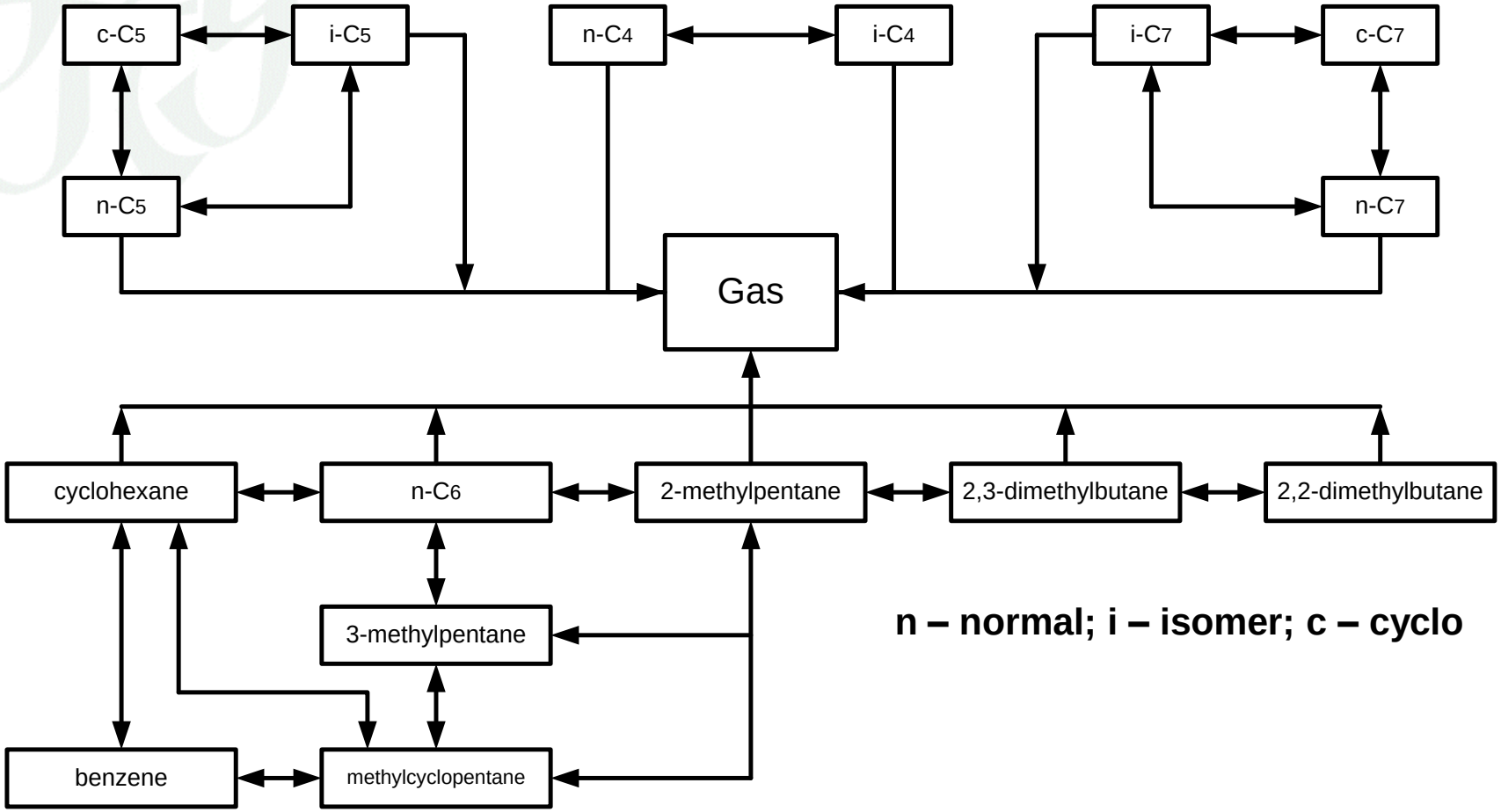



**Fig. 5 Formalized reaction scheme for light naphtha isomerization process**

# Mathematical model of light naphtha isomerization process

***The model of isomerization reactor:***

$$G \cdot \frac{\partial C_i}{\partial z} + G \cdot \frac{\partial C_i}{\partial V} = \sum_{j=1}^{m} a_j \cdot r_j$$

$$G \cdot \frac{\partial T}{\partial z} + G \cdot \frac{\partial T}{\partial V} = \frac{1}{\rho \cdot C_p^{\mathrm{m}}} \sum_{j=1}^{m} Q_j \cdot a_j \cdot r_j$$

at $z = 0\ C_i = C_{i,0}; T = T_{en};$

at $V = 0\ C_i = C_{i,0}; T = T_{en};$

***z*** – volume of raw material processed from the moment when the fresh catalyst was loaded, $m^3$;
***G*** – raw material flow rate, $m^3/h$;
***t*** – time of catalyst work from the new catalyst load, h;
$C_i$ – concentration of i-th component, $mol/m^3$;
***a*** – catalyst activity;
$C_p^m$ – heat capacity of mixture, J/(kg·K);
***T*** – temperature, K;
***V*** – volume of the catalyst layer, $m^3$;
***ρ*** – density of mixture, $kg/m^3$;
$Q_j$ – j-th reaction heat, J/mol;
$r_j$ – j-th reaction rate, $mol/(m^3 \cdot h)$.

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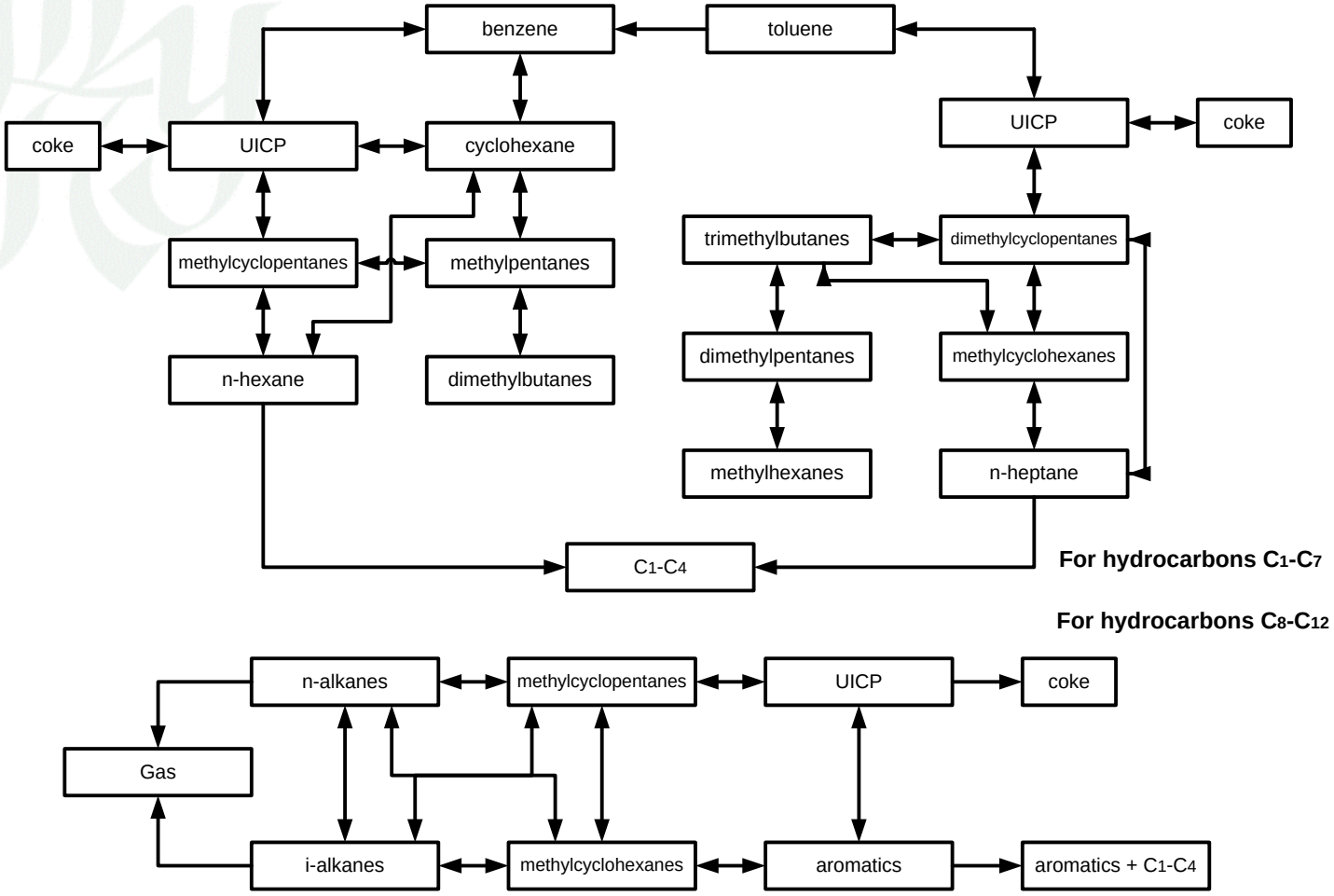
# Mathematical model of catalytic reforming process




**n – normal; i – isomer; UICP – unsaturated intermediate compacting products**

**Fig. 6 Formalized reaction scheme for catalytic reforming process**

# Mathematical model of catalytic reforming process

***The model of reforming reactor:***

$$\begin{cases} G\cdot\dfrac{\partial C_i}{\partial z} = -u\cdot\dfrac{\partial C_i}{\partial R} - \varphi\cdot\dfrac{\partial C_i}{\partial l} + \dfrac{1}{l}\cdot\int_0^l r_j(l)a_j(l)dl \\ \rho^m\cdot C_p^m\cdot G\cdot\dfrac{\partial T}{\partial z} = -u\cdot\rho^m\cdot C_p^m\cdot\dfrac{\partial T}{\partial R} - \varphi\cdot\rho^{cat}\cdot C_p^{cat}\cdot\dfrac{\partial T}{\partial l} + \sum Q_j\cdot\dfrac{1}{l}\cdot\int_0^l r_j(l)a_j(l)dl \end{cases}$$

$$\text{at } z = 0\ C_i = C_{i,0}; T = T_{en};$$

$$\text{at } l = 0\ C_i = C_{i,0}(\text{at the reactor entrance}); T = T_{en};$$

$$\text{at } r = 0\ C_i = C_{i,0}; T = T_{en}.$$

***z*** – volume of raw material processed from the moment when the fresh catalyst was loaded, $m^3$;
***a(l)*** – catalyst activity distribution through the catalyst layer length in the reactor with a moving bed;
$C_p^m$, $C_p^{cat}$ – heat capacity of mixture and catalyst respectively, J/(kg·K);
$\rho^m$, $\rho^{cat}$ – density of mixture and catalyst respectively, kg/$m^3$;
$r_j$ – j-th reaction rate, mol/($m^3$·h);
***t*** – time of catalyst work from the new catalyst load, h;
***u*** – flow rate, m/h;
***r*** – integral reactions rate for component *i*, mol/($m^3$·h);
***T*** – temperature, K;
***G*** – raw material flow rate, $m^3$/h;
$C_i$ – concentration of i-th component, mol/$m^3$;
***R*** – radius of the catalyst layer, m;
***l*** – catalyst layer length in the reactor, m;
***φ*** – catalyst flow rate, m/h;
$Q_j$ – j-th reaction heat, J/mol.

# Modules of isomerization and reforming modeling

***The model the model the isomerization catalyst deactivation:***

$$a_j = \frac{k_{j,current}}{k_{j,initial}}$$

$k_{j,initial}$ – the rate constant of j-th reaction on the fresh catalyst;
$k_{j,current}$ – the rate constant of j-th reaction on the catalyst at present time.

***The model the model the reforming catalyst deactivation:***

$$a_j = A_0 \cdot e^{-\alpha_j \cdot C_{coke} / h_{cir}}$$

$$h_{cir} = u \cdot \rho^m / (\varphi \cdot \rho^{cat})$$

$h_{cir}$ – the catalyst circulating factor;
$C_{coke}$ – mass fraction of coke on the catalyst;
$a$ – catalyst activity;
$A_0$ – linear component determining the number of catalyst active centers;
$\alpha$ – coefficient of catalyst poisoning.

# Nonadditivity of octane numbers

The main characteristic of gasoline – octane number is not subject to the law of additivity


**OB 45…55**

$$ON_{\text{add}} = \sum_{i=1}^{n} ON_i \cdot C_i \neq ON_{\text{exp}}$$

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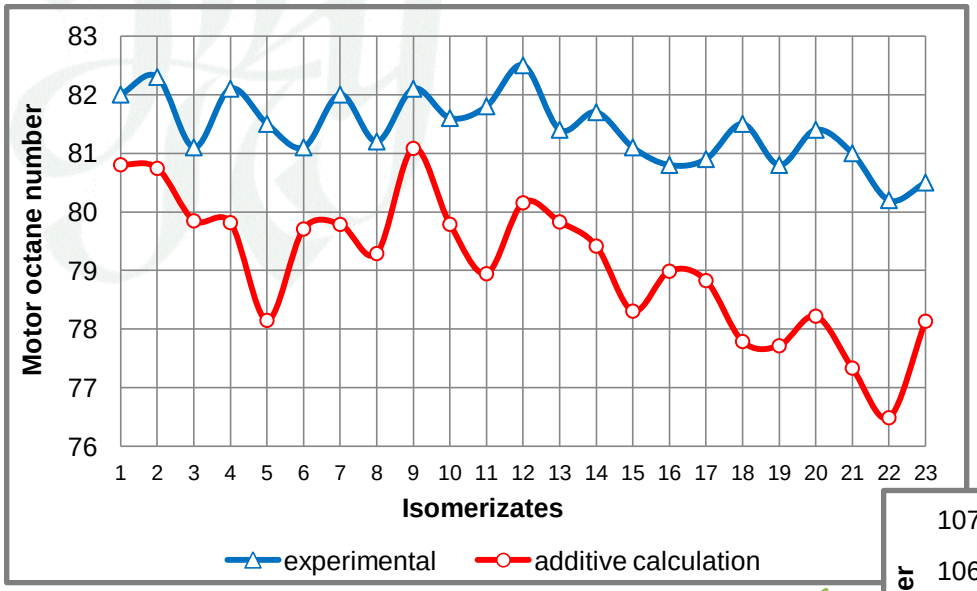
# Nonadditivity of octane numbers

Fig. 7 Isomerization process




**Antagonistic effect:**

deflection: 2 – 3 points

**Synergetic effect:**

deflection: 1 – 2 points

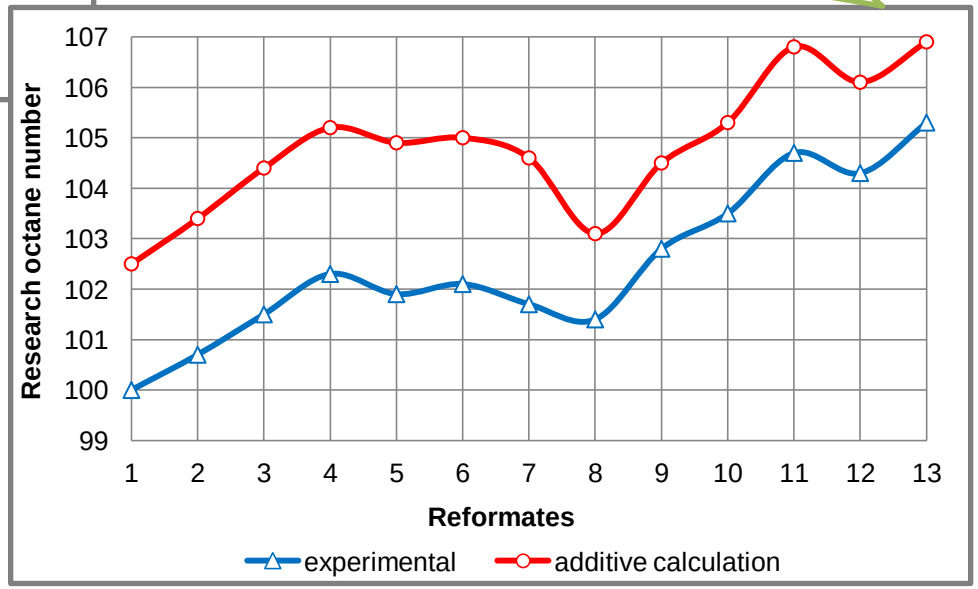



Fig. 8 Reforming process

# Nonadditivity of octane numbers

The reason for octane number nonadditivity is the presence of intermolecular interactions.

Intermolecular interactions forces depend on the polarity of the gasoline mixture components.

Dipole moment is magnitude of the components polarity.

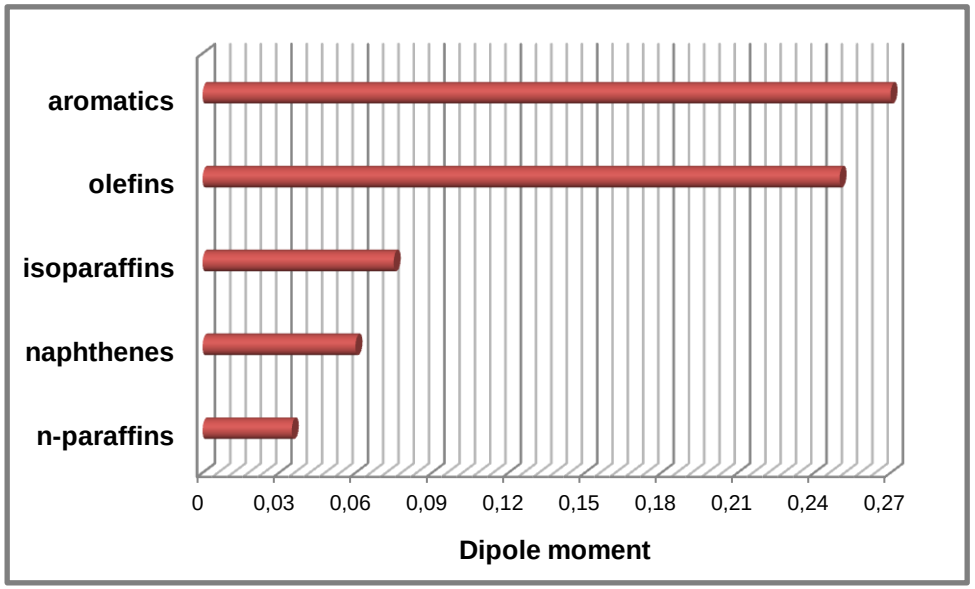
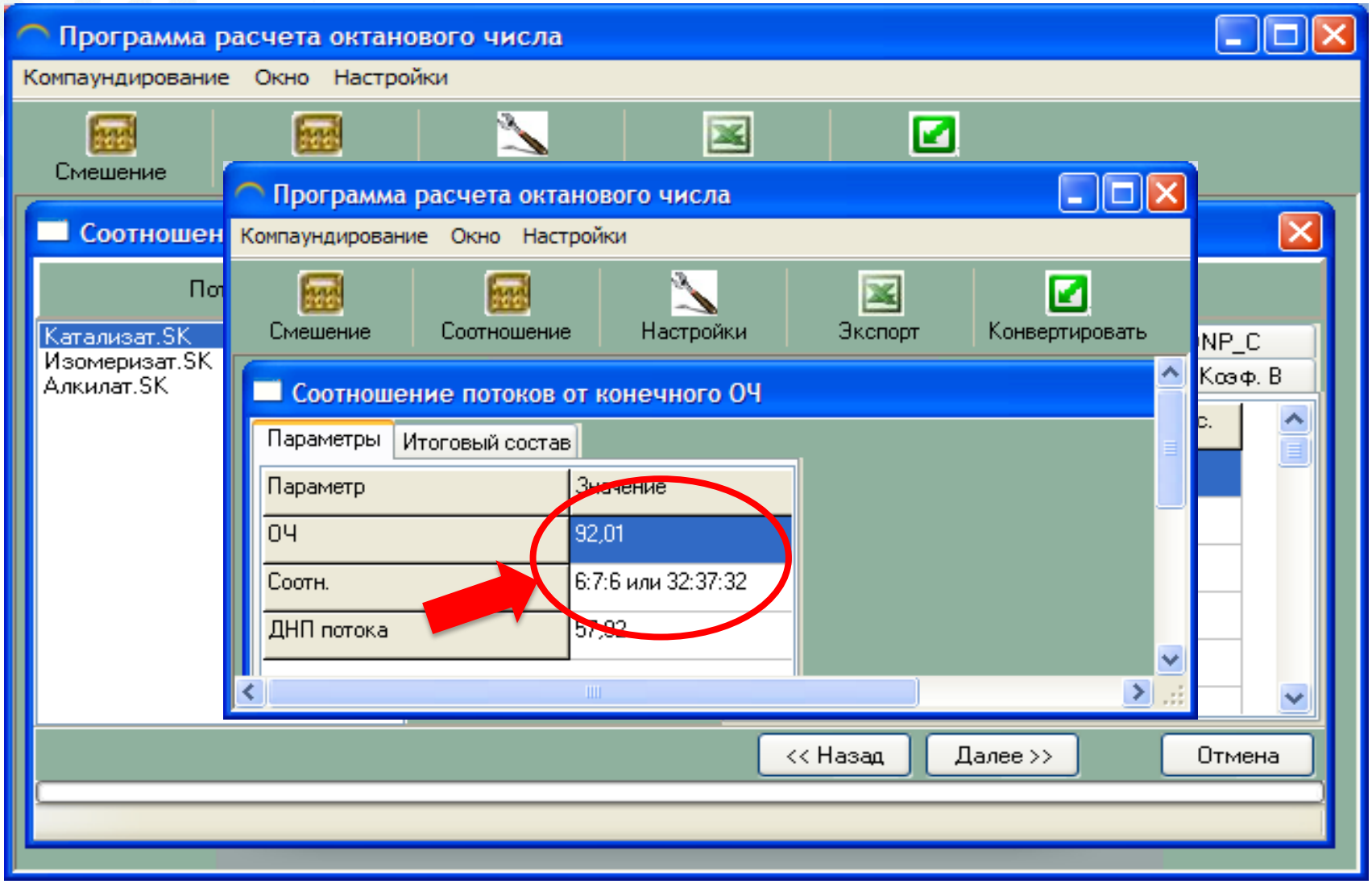



Fig. 9 Average values of the dipole moments in the homologous series of hydrocarbons

# Module of trade gasoline blending recipes calculation



# Octane numbers calculation taking into account the reaction interaction of blend components

$$ON_{mix} = \sum_{i=1}^{n} ON_i \cdot C_i + B$$

***ON*$_{mix}$** – blending octane number;

***ON*$_i$** – octane number of the *i*-th component;

***B*** – rejection of octane number from additivity;

***C*$_i$** – concentration of i-th component, rel. units.

$$B = \frac{1}{100} \sum_{i=1}^{n-1} \sum_{\substack{j=2 \\ i \neq j}}^{n} B_i B_j C_i C_j \quad B_i = \alpha \left( \frac{D_i}{D_{\max}} \right)^{\beta}$$

***D*** – dipole moment;

***Bi, Bj*** – quantities that characterize the tendency of the *i*-th molecule to the intermolecular interaction with *j*-th molecule;

$\alpha$ and ***β*** – the kinetic parameters determined the intensity of intermolecular interactions;

***D*$_{max}$** – the maximum dipole moment of the hydrocarbon molecules.

# Octane numbers calculation taking into account the reaction interaction of blend components

**Table 2. Values of $B_i$ coefficients for certain substances**

| № | Component | $B_i$ | № | Component | $B_i$ |
|---|---|---|---|---|---|
| 1 | propane | 0.09 | 19 | methylcyclopentane | 0.15 |
| 2 | n-butane | 0 | 20 | dimethylcyclopentanes | 0.16 |
| 3 | n-pentane | 0.16 | 21 | cyclohexane | 0 |
| 4 | n-heptane | 0.1 | 22 | 1,2-dimethylcyclohexanes | 0.25 |
| 5 | i-butane | 0.17 | 23 | 1,3-dimethylcyclohexanes | 0.13 |
| 6 | i-pentane | 0.14 | 24 | benzene | 0.98 |
| 7 | 2-methylpentane | 0.2 | 25 | toluene | 0.6 |
| 8 | 3-methylpentane | 0.09 | 26 | ethylbenzene | 1 |
| 9 | 2,2-dimethylbutane | 0.03 | 27 | xylols | -0.57 |
| 10 | 2,3-dimethylbutane | 0.16 | 28 | i-propylbenzene | -0.6 |
| 11 | 2,4-dimethylpentane | 0.29 | 29 | 1,3,5-trimethylbenzene | -0.6 |
| 12 | 2,2,3-trimethylbutane | 0.07 | 30 | tetramethylbenzenes | -0.7 |
| 13 | 3-methylheptane | 0.17 | 31 | butene-1 | 1.08 |
| 14 | 3,3-dimethylhexane | 0.09 | 32 | butene-2 | 0.88 |
| 15 | 2,3,4-trimethylpentane | 0.25 | 33 | cyclopentene | 0.6 |
| 16 | dmethylheptanes | 0.15 | 34 | 2-methylbutene-2 | 1.2 |
| 17 | dimethyloctanes | 0.13 | 35 | methylpentenes-2 | 0.85 |
| 18 | cyclopentane | 0 | 36 | methylhexenes | 1.4 |

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# Octane numbers calculation taking into account the influence of anti-knock additive

$$ON_i = ON_0 + Inj \cdot \Delta ON_{\max} \cdot (1 - e^{-K_{eff} \cdot C_{red}})$$

$$C_{red} = \frac{C_i}{C_{\max}}$$

***ON₀*** – octane number;

***Inj*** – quantity that characterizes different types of fuel anti-knock additives injectivity;

$\Delta$***ON$_{max}$*** – maximum possible increase of octane number;

***K$_{eff}$*** – the coefficient of anti-knock additives efficiency;

***C$_i$*** – additive concentration;

***C$_{max}$*** – maximum permissible concentration of the additive in gasoline.

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# Comparison of the calculated octane number with the experimental data

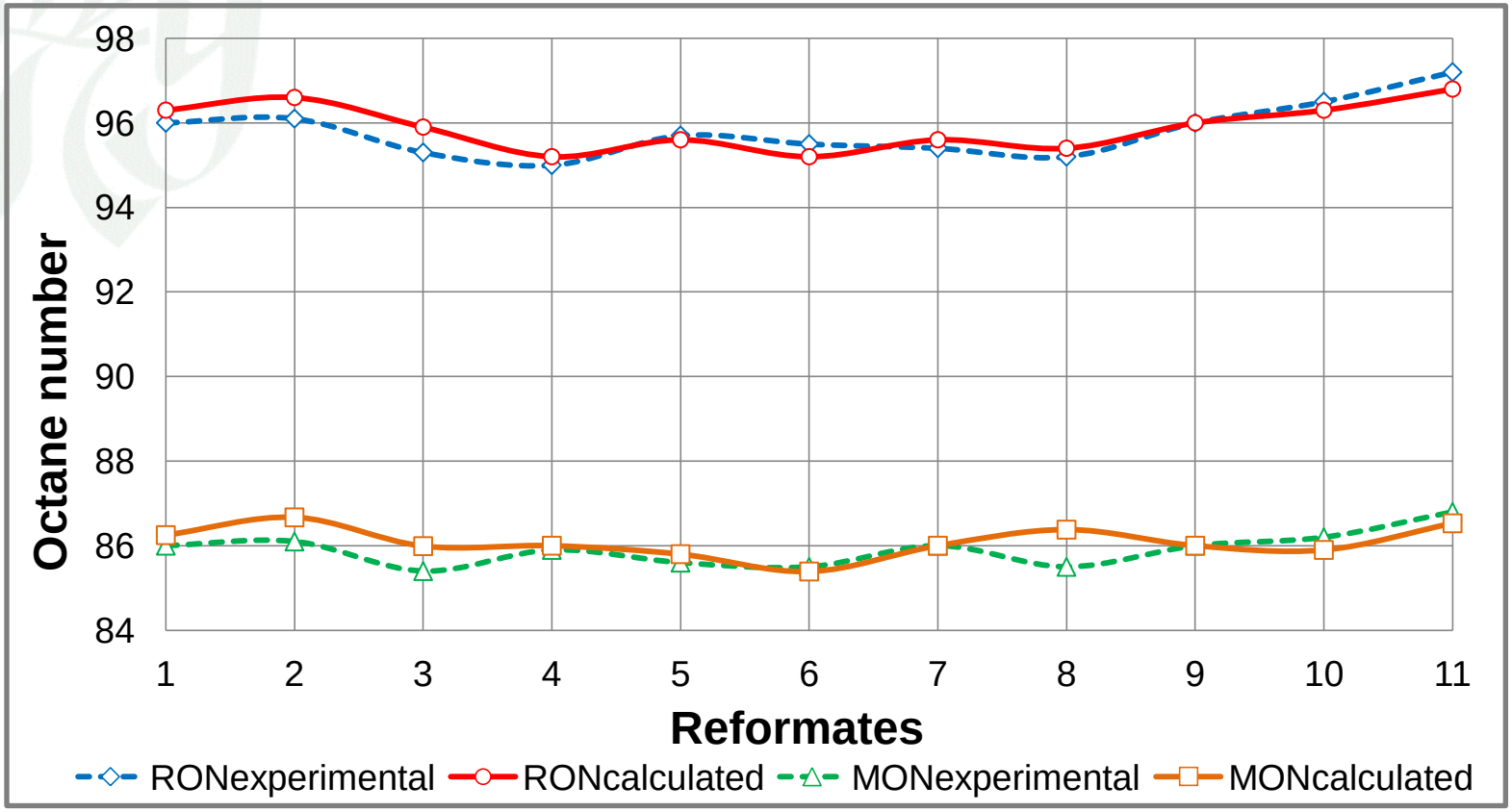



**Fig. 10 Comparison of the calculated octane number of reformates with the experimental data**

**The average absolute error doesn't exceed 1 point.**

# Comparison of the calculated octane number with the experimental data

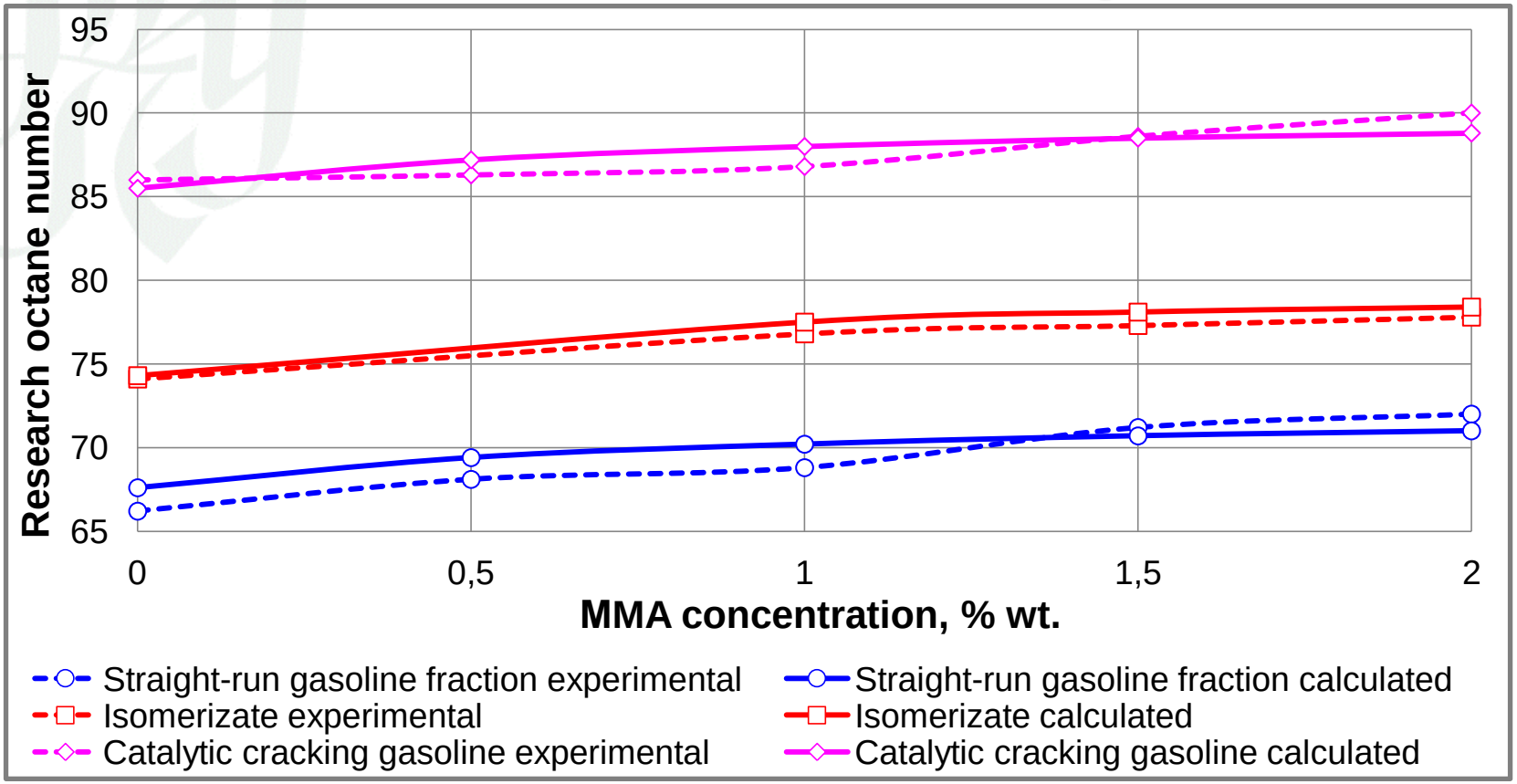



**Fig. 11 Comparison of the calculated octane number with the experimental data with the MMA concentration**

**The average absolute error doesn't exceed 1 point.**

# Development of gasoline blending recipes

**Table 3. Composition of reformates**

| Content, wt.% | Reformate №1 | Reformate №2 | Reformate №3 |
|---|---|---|---|
| benzene | 1.7 | 3.2 | 2 |
| aromatics | 79.9 | 77.2 | 81.4 |
| RON | 104.3 | 101.8 | 105.4 |
| MON | 94.8 | 93.7 | 95.9 |

**Table 4. Composition of Isomerizates**

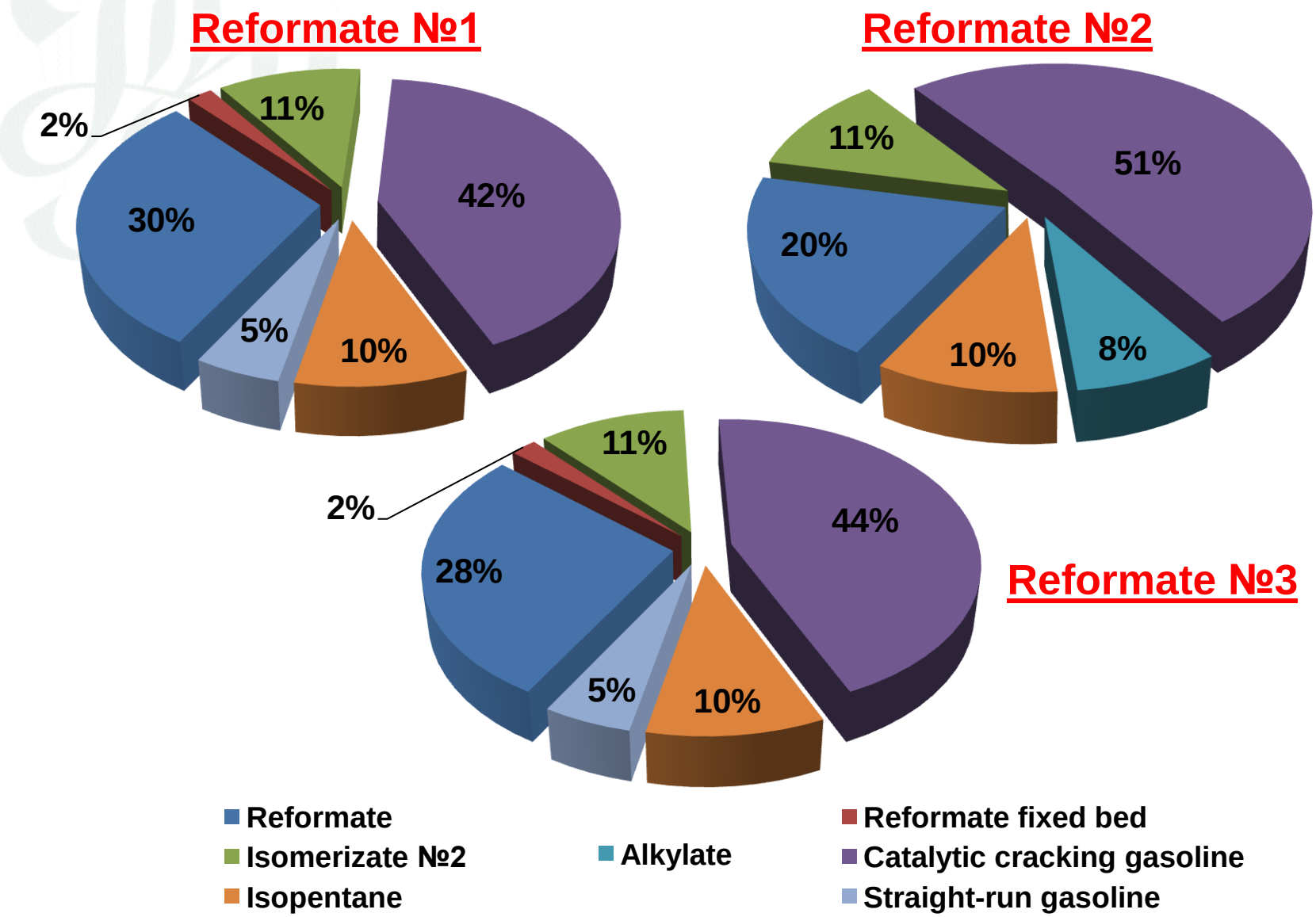
| Content, wt.% | Isomerizate №1 | Isomerizate №2 | Isomerizate №3 |
|---|---|---|---|
| n-pentane | 0.3 | 0.06 | 0.01 |
| n-hexane | 0.25 | 0.03 | 0 |
| dimethylbutanes | 74.6 | 83.16 | 92.32 |
| RON | 89.7 | 92.1 | 93.4 |
| MON | 87.6 | 89.4 | 90.9 |

# Development of gasoline blending recipes

**Table 5. Influence of the catalyst used in the catalytic reforming process on the gasoline blending recipes**

| FLOWS | Regular-92, EURO-5 | | |
|---|---|---|---|
| | I | II | III |
| **Gasoline quality characteristics** | | | |
| RON | 92.3 | 92.1 | 92.6 |
| MON | 84.8 | 84.7 | 85.8 |
| SVP, KPa | 47 | 46 | 50.3 |
| Density, kg/m3 | 730 | 729.5 | 715.6 |
| **Content, wt.%** | | | |
| n-paraffins | 5.42 | 5 | 4.33 |
| isoparaffins | 39 | 39.4 | 46.4 |
| naphthenes | 8.8 | 9 | 7.8 |
| olefins | 11.3 | 11.8 | 13.7 |
| aromatics | 35 | 34.7 | 27.6 |
| benzene | 0.9 | 0.9 | 1 |

# Development of gasoline blending recipes

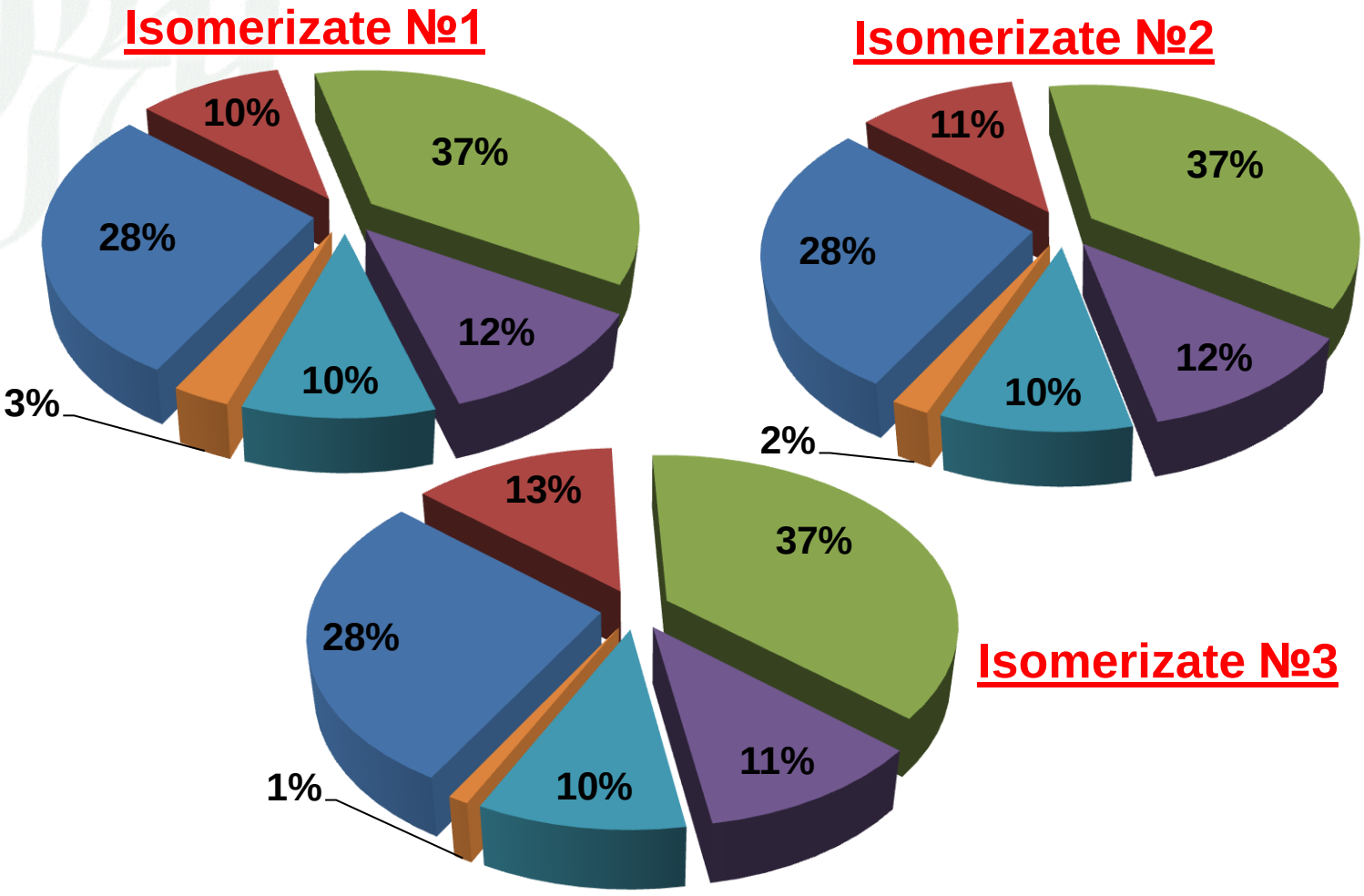


# Development of gasoline blending recipes

**Table 6. Influence of the isomerizates composition on the gasoline blending recipes**

| FLOWS | Premium-95, EURO-5 | | |
|---|---|---|---|
| | I | II | III |
| **Gasoline quality characteristics** | | | |
| RON | 95.4 | 95.3 | 95.1 |
| MON | 88.4 | 88.3 | 88.3 |
| SVP, KPa | 45.6 | 46.1 | 47 |
| Density, kg/m3 | 724.1 | 723.5 | 722 |
| **Content, wt.%** | | | |
| n-paraffins | 3.8 | 3.8 | 3.7 |
| isoparaffins | 45.9 | 46.7 | 47.7 |
| naphthenes | 5.6 | 5.9 | 5.9 |
| olefins | 9.9 | 9.9 | 9.9 |
| aromatics | 31.6 | 31.6 | 31.6 |
| benzene | 0.8 | 0.8 | 0.8 |

# Development of gasoline blending recipes



# Conclusion


**Преимущества комплексной моделирующей системы**

- точный расчет октановых чисел с учетом неаддитивности
- учет состава сырья, технологических параметров процессов и ресурса катализатора

- Точный и оперативный расчет рецептуры приготовления товарного бензина;
- Возможность оптимально распределить сырье между технологическими установками предприятия.

- сокращение выхода некондиционных партий,
- экономия дорогостоящих компонентов,
- повышение эффективности процесса.

# Thanks for attention!

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