

Optimization of Multistage Gasoline Production in Hydrocracking, Catalytic Cracking, Reforming and Compounding Processes

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Introduction

The purpose of this work is to develop the digital technology scientific basis based on the consideration of the chemical interaction of motor fuel components both at the stages of catalytic conversion of hydrocarbons and at the stage of compounding.

Research Theoretical Background

Basic reactions of the hydrocracking process:

- Paraffins hydrocracking to form n - C_nH_{2n+2} : $C_nH_{2n+2} + H_2 \rightarrow 2C_{n/2}H_{n+2}$
- Paraffins hydrocracking to form i - C_nH_{2n+2} : $C_nH_{2n+2} + H_2 \rightarrow 2C_{n/2}H_{n+2}$
- Aromatic compounds hydrogenation: $C_nH_{2n-6} + 3H_2 \rightleftharpoons C_nH_{2n}$
- Coke formation reaction: $C_nH_{2n-6} \rightleftharpoons Coke$

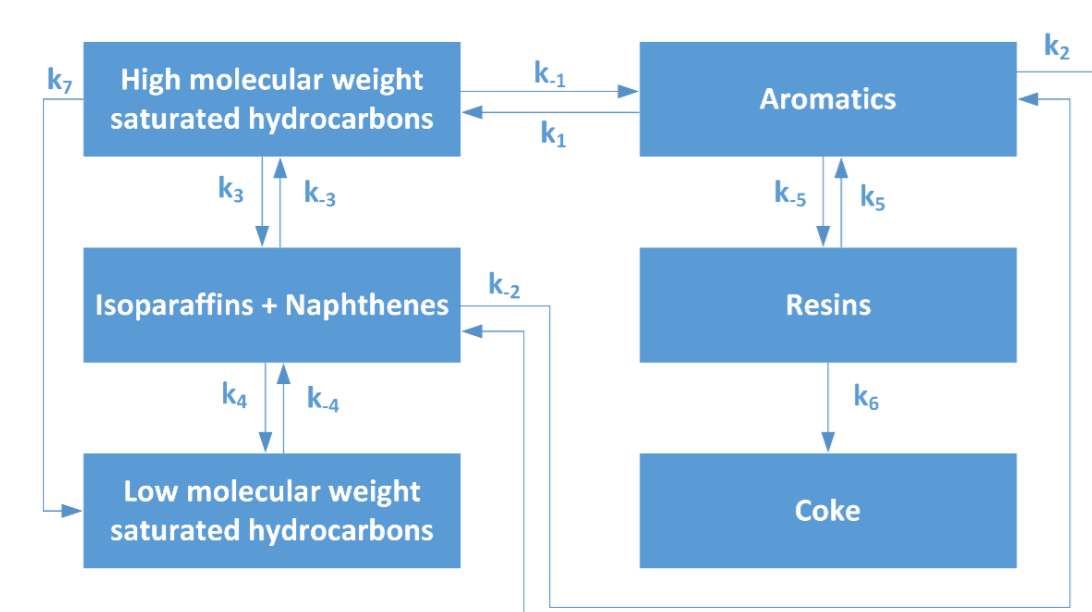


Figure 1: Reaction network of the hydrocracking process

An important step in modeling the processes of multi-stage production of motor fuels is to choose the level of formalization of the reaction mechanism or drawing up a scheme for converting hydrocarbon raw materials. For deep processing of vacuum gas oil (hydrocracking and catalytic cracking), the grouping of hydrocarbons by homologous groups (n-paraffins C_1 - C_{42} , i-paraffins + naphthenes, monoaromatic hydrocarbons, polyaromatic hydrocarbons, resins) is valid.

For the processes of processing naphtha fraction up to 180 °C in the technology of reforming and

isomerization, it is necessary to consider the transformation of individual hydrocarbons.

General view of the equations of material and heat balance

Despite the different level of formalization of the mechanism of reactions in hydrogenation processes (hydrocracking and reforming), the system of equations of material and thermal balances has a general form.

The new gasoline production optimization method was proposed, implemented and introduced into industrial plant as a result of the research. The method essence is to optimize the manufacturing processes of mixture components, such as the hydrocracking and catalytic cracking gasoline, reformate, isomerizate, alkylate.

$$\begin{cases} G \cdot \frac{\partial C_i(x)}{\partial V} + G \cdot \frac{\partial C_i(x)}{\partial Z} = \sum_{j=1}^n k_j(x) \cdot C_i(x) + \sum_{j=1}^n k_j(x) \cdot C_i(x) \cdot C_{H_2} + \\ \quad + \sum_s C_{H_2} \sum_x k_s(x') \cdot v(x, x') \cdot C_i(x, x') \\ G \cdot \frac{\partial T}{\partial V} + G \cdot \frac{\partial T}{\partial Z} = -\frac{1}{C_p^m} \cdot \sum_{i=1}^n \sum_{x=1}^m \pm \Delta H_i(x) \cdot w_i(x) \\ Z = 0, V = 0, C_i = C_{i0}, T = T_{en} \end{cases}$$

$C_i(x)$, $k_j(x)$, $k_s(x')$ – distribution of concentrations and rate constants of reactions; $v(x, x')$ – probability distribution functions of the paraffin hydrocarbons bond breaking in hydrocracking; V – catalyst load volume, m^3 ; T – the process temperature gradient, K; C_p^m – the mixture heat capacity, kJ/mol·K; ΔH_i – the reaction enthalpy change, kJ/mol; x, x' – the carbon atoms number in a hydrocarbon molecule; j – the hydrocarbon groups number (paraffins, isoparaffins, naphthenes, aromatic, resins, coke); n, m – number of group reactions; s – number of hydrocracking reactions.

To control the catalyst decontamination process, considering the changing consumption and composition of raw materials, the mathematical model of the hydrocracking process was supplemented with the decontamination function. The activity of a catalyst can be defined as the ratio of the rate constant at some point in time to the rate constant at the initial time when a fresh catalyst was loaded into the reactor:

$$a_j = A_j \cdot e^{-\alpha_j \cdot C_{coke}}$$

Where A_j , α_j – coefficients of deactivation; C_{coke} – coke concentration, wt.%.

To determine the numerical value a_j , thermogravimetric analysis of samples of the catalyst discharged from the reactor was performed. To determine the function of decontamination of the hydrocracking catalyst by coke, studies were conducted on a mathematical model. The dynamics of coke accumulation on the catalyst surface is determined depending on the volume of processed raw materials.

The concentration of coke on the catalyst was 6 wt.%. In the period from 2014 to 2017, there was a gradual decrease in the yield of diesel fractions with a simultaneous increase in the yield of gasoline fractions from 8 to 14%.

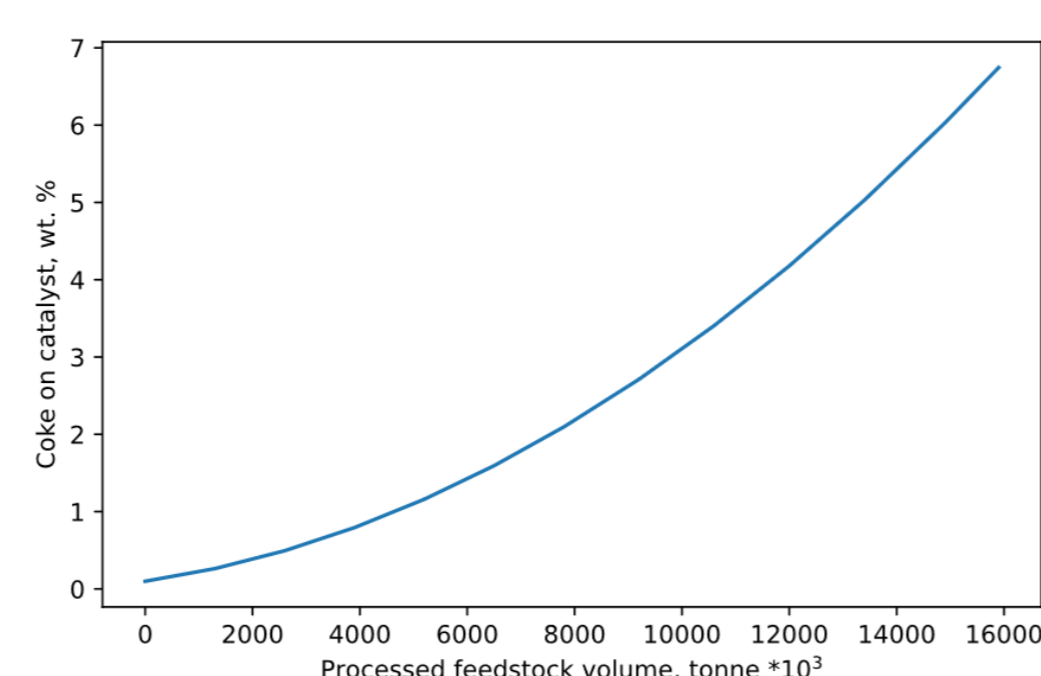


Figure 2: Dynamics of coke accumulation on the catalyst from the volume of processed raw materials

Mathematical modeling of the reforming of naphtha

In order to study the quality of the resulting product LCH-35-11/1000, when using hydrocracking gasoline as a raw material, the group composition of heavy naphtha was analyzed, fraction 85-180°C and mixed feedstock.

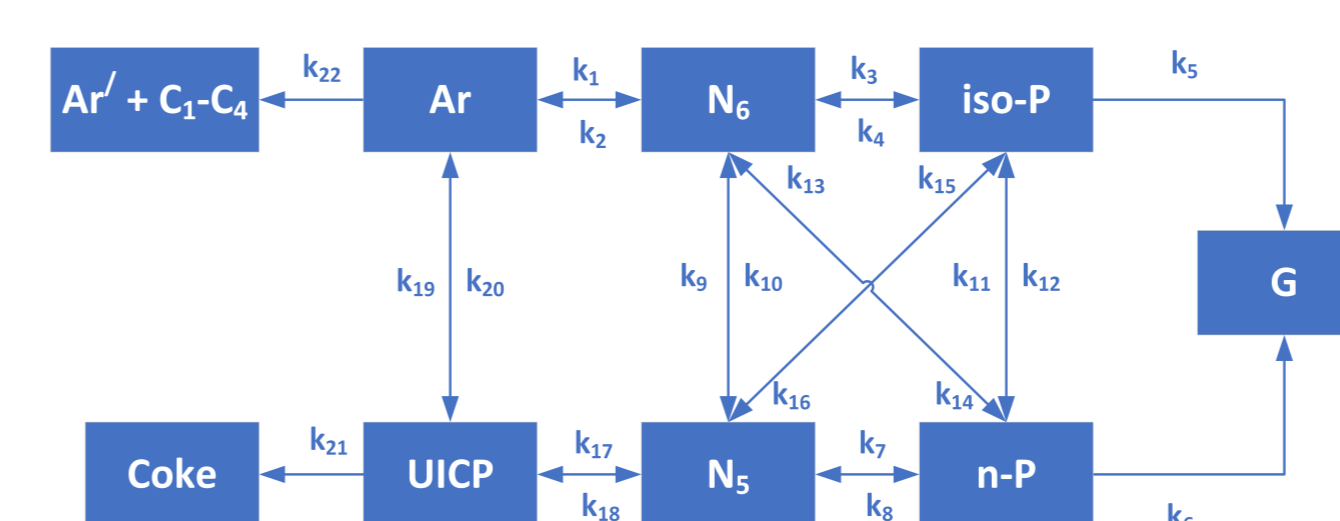


Figure 3: Formalized reaction scheme of naphtha reforming: n-P, iso-P – normal and iso-alkanes; N-5, N-6 – methylcyclopentanes and methylcyclohexanes; Ar – aromatic hydrocarbons; UICP – unsaturated immediate compacting products; G – gas

The content of paraffin hydrocarbons in the heavy naphtha less than in straight-run FR. 85-180°C (8-9 wt.%, in the naphtha and 22-23% wt., in straight-run FR. 85-180°C), at the same time, the content of naphthenic hydrocarbons is higher in the heavy naphtha, straight-run than in fr 85-180°C (46-47 wt.%, and, accordingly, 29-30 wt.%).

As a result, in reforming product mixed raw materials with fr 85-180°C there is a decrease in the content of paraffins (up to 2% by weight) and a slight increase in

the content of naphthenic hydrocarbons. The content of isoparaffinic hydrocarbons also increases. Calculation of the octane number and yield of the target product during the reforming process were performed using the kinetic model of reforming. The initial parameters for calculation in the program were data on the component composition of raw materials and catalyze (chromatograms of raw materials and catalyze), temperature and pressure for reactors, raw material consumption and HCG.

Mathematical modeling of the catalytic cracking process

The kinetic description of process is based on the reactions scheme for converting raw materials into a product.

Digital technology for the production of commercial gasoline allows you to reduce the percentage of expensive components (additives, alkylates) by increasing the share of reformate and catalytic cracking gasoline in the composition of commercial gasoline, which makes it possible to significantly increase economic efficiency.

It is possible to predict the composition of gasoline with the specified properties when using components for which the characteristics are known: octane numbers, yield, content of aromatic hydrocarbons and benzene, olefins and sulfur.

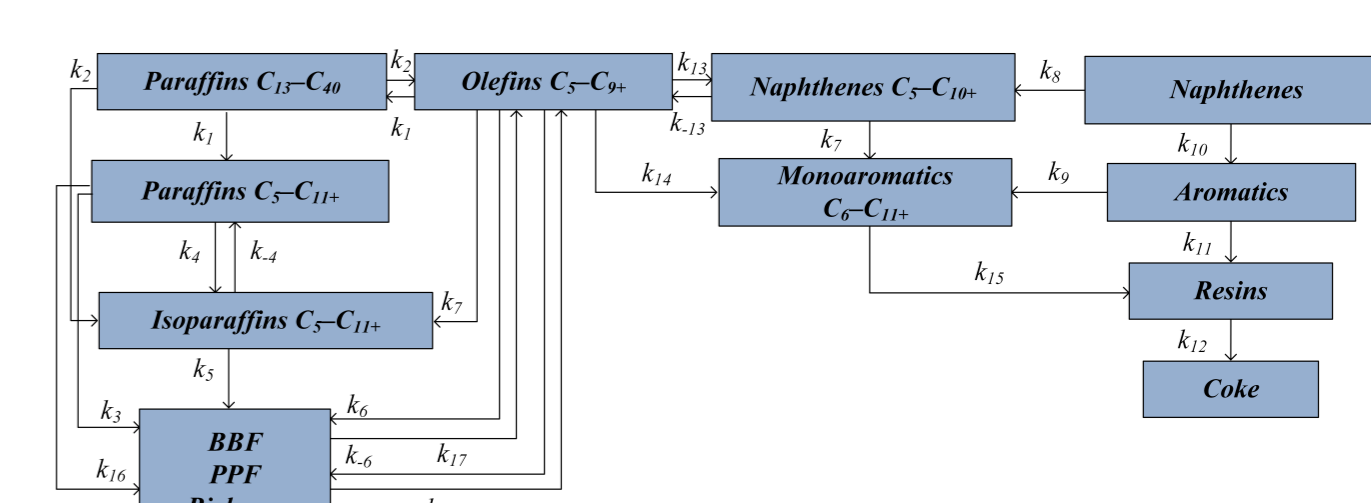


Figure 4: The reactions scheme for converting feedstock into product

Results

Calculation of commercial gasoline formulations using predictive models, taking into account changes in the composition of processed raw materials and the activity of the catalyst in the production of gasoline components, allows us to obtain motor fuels that fully comply with modern environmental standards. According to preliminary calculations, the cost of finished products can be reduced by 10-12 % due to savings in the consumption of expensive flows, as well as a reduction in the quality reserve (octane number of gasoline, the content of sulfur and aromatic hydrocarbons in their composition).

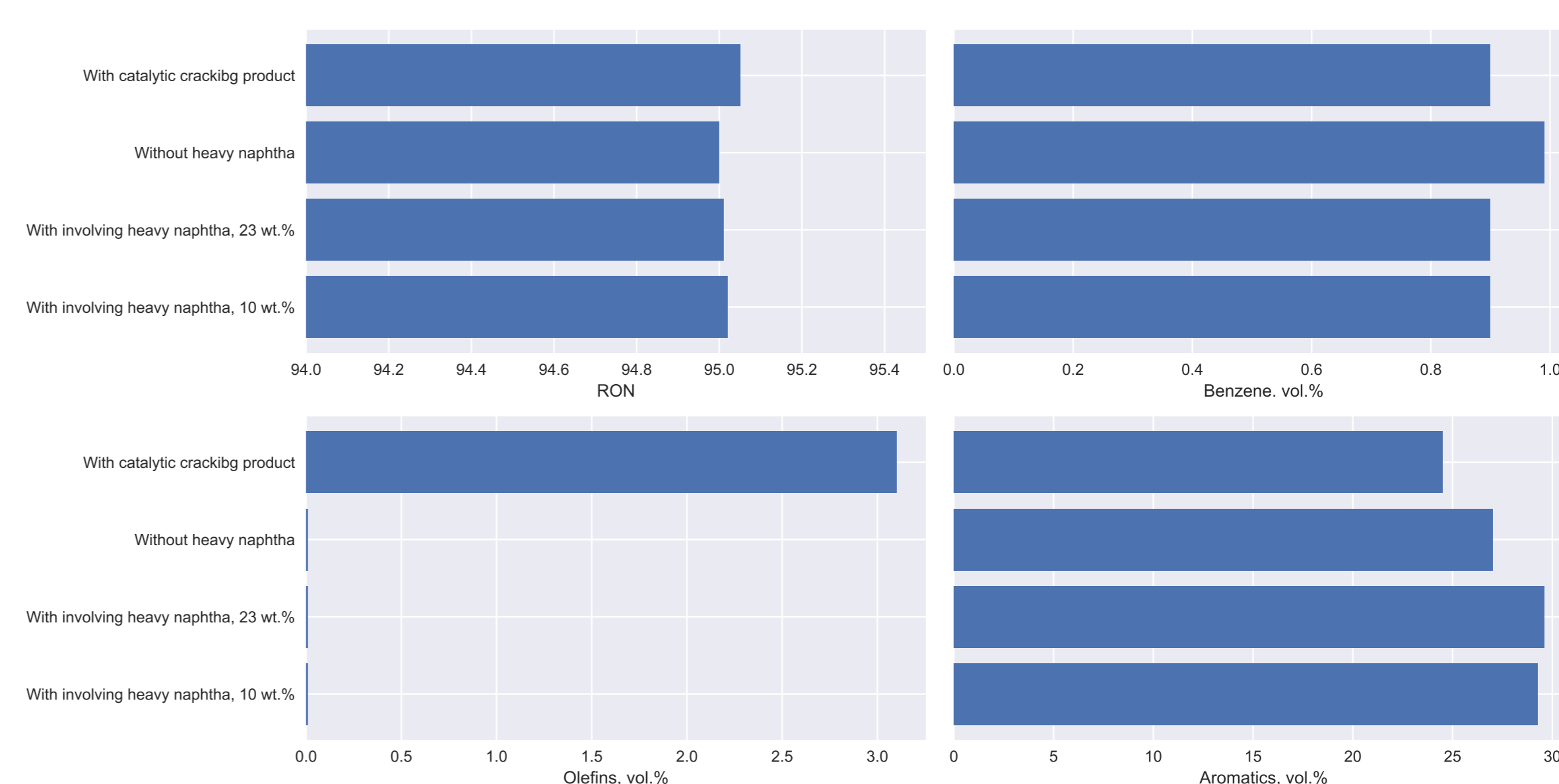


Figure 5: Calculation of AI 95 gasoline (properties of the mixture)

The new method allows to reduce the cost of the quality of commercial gasoline by regulating the gasoline formulation in accordance with the requirements. The principle of the proposed method is to perform successive stages of calculation and optimization of the manufacturing processes of mixed components.