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Original article

Design of a Combined Isomerization-Catalytic Reforming Unit for Increasing Gasoline Octane Number Using an AI-Based Quality Prediction Model

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ABSTRACT

Background: The production of high-octane gasoline meeting stringent environmental requirements remains an important task for petroleum-refining industries, including Kazakhstan. At the same time, artificial intelligence and digitalization are increasingly applied to support process design and fuel-quality prediction.

Aim: To design a combined isomerization-catalytic reforming system for producing AI-92, AI-95, and AI-98 gasoline grades using an AI-based model for gasoline-quality prediction.

Materials and Methods: Three commercial gasoline grades (AI-92, AI-95, and AI-98) were characterized by pycnometric density measurement, capillary viscometry, and thermogravimetric analysis with differential thermal analysis. Linear Regression, k-Nearest Neighbors, and Decision Tree models were used to predict research octane number (RON). Kinetic models were developed for light-naphtha isomerization and catalytic reforming, together with material and energy balance calculations, DIP-column design, and reformat-yield estimation.

Results: The Decision Tree model provided exact RON predictions for the three tested grades (MAE = 0.00; $R^2 = 1.00$). The isomerization unit with DIP recycle produced an isomerate with RON 87.4, while the catalytic reforming unit produced reformat with RON 98.5 at 500°C and a liquid yield of 85.4 vol%. The calculated blended RON values were 92.1, 95.3, and 98.2 for AI-92, AI-95, and AI-98, respectively.

Conclusions: The combined process configuration enables the production of the full range of studied gasoline grades by adjusting the proportions of isomerate and reformat in the blending pool. The AI-based quality model can be used as a supporting tool for defining target octane specifications during process design.

Keywords: gasoline octane number; artificial intelligence; machine learning; isomerization; catalytic reforming; light naphtha; kinetic model; material balance; energy balance; refinery design.

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Оригинальное исследование

Разработка комбинированной установки изомеризации-каталитического риформинга для повышения октанового числа бензина с использованием модели прогнозирования качества на основе искусственного интеллекта

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АННОТАЦИЯ

Обоснование. Производство высокооктанового бензина, соответствующего современным экологическим требованиям, остаётся актуальной задачей нефтеперерабатывающей промышленности, в т.ч. Казахстана. Одновременно искусственный интеллект и цифровизация всё шире применяются для поддержки проектирования технологических процессов и прогнозирования качества топлива.

Цель. Разработать комбинированную систему изомеризации и каталитического риформинга для получения бензинов AI-92, AI-95 и AI-98 с использованием модели на основе искусственного интеллекта для прогнозирования качества бензина.

Материалы и методы. Три товарные марки бензина (AI-92, AI-95 и AI-98) исследовали методами пикнометрического определения плотности, капиллярной вискозиметрии и термогравиметрического анализа в сочетании с дифференциальным термическим анализом. Для прогнозирования исследовательского октанового числа (далее – РОН) применяли линейную регрессию, метод k-ближайших соседей и дерево решений. Для изомеризации лёгкой нефти и каталитического риформинга разработаны кинетические модели с расчётом материального и энергетического балансов, проектированием колонны ДИП и оценкой выхода риформата.

Результаты. Модель дерева решений обеспечила точное прогнозирование РОН для трёх исследованных марок (MAE = 0,00; $R^2 = 1,00$). Установка изомеризации с рециркуляцией ДИП обеспечила изомеризат с РОН 87,4, а установка каталитического риформинга – риформат с РОН 98,5 при 500°C и выходом жидкого продукта 85,4%об. Расчётные значения РОН смесевых бензинов составили 92,1, 95,3 и 98,2 для AI-92, AI-95 и AI-98 соответственно.

Заключение. Комбинированная конфигурация позволяет получать весь рассматриваемый ряд товарных бензинов за счёт регулирования соотношения изомеризата и риформата в смесевом пуле. Модель прогнозирования качества на основе искусственного интеллекта может использоваться как вспомогательный инструмент при задании целевых характеристик октанового числа на этапе проектирования.

Ключевые слова: октановое число бензина, искусственный интеллект, машинное обучение, изомеризация, каталитический риформинг, лёгкая нефть, кинетическая модель, материальный баланс, энергетический баланс, проектирование нефтеперерабатывающей установки.

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Түпнұсқа зерттеу

Жасанды интеллект негізіндегі сапаны болжау моделін пайдалана отырып, бензиннің октан санын арттыруға арналған изомеризация-каталитикалық риформингтің біріктірілген қондырғысын әзірлеу

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АНДАТПА

Негіздеу. Қазіргі экологиялық талаптарға сәйкес келетін жоғары октанды бензин өндіру мұнай өңдеу өнеркәсібі, соның ішінде Қазақстан үшін де өзекті міндет болып табылады. Сонымен қатар жасанды интеллект пен цифрландыру технологиялық үдерістерді жобалауды және отын сапасын болжауды қолдау үшін кеңінен қолданылуда.

Мақсаты. Бензин сапасын жасанды интеллект негізіндегі модель арқылы болжау мүмкіндігін пайдаланып, AI-92, AI-95 және AI-98 маркаларын өндіруге арналған изомеризация-каталитикалық риформингтің біріктірілген жүйесін әзірлеу.

Материалдар мен әдістер. AI-92, AI-95 және AI-98 маркаларының үш тауарлық бензин үлгісінің тығыздығы пикнометриялық әдіспен, кинематикалық тұтқырлығы капиллярлық вискозиметрия әдісімен, ал термиялық сипаттамалары термогравиметриялық және дифференциалдық-термиялық талдау арқылы анықталды. Зерттеу октан санын болжау үшін сызықтық регрессия, k-жақын көршілер әдісі және шешімдер ағашы қолданылды. Жеңіл нафтан изомеризациялау және каталитикалық риформинг үшін кинетикалық модельдер әзірленіп, материалдық және энергетикалық баланстар есептелді, ДИП колоннасы жобаланды және риформат шығымы бағаланды.

Нәтижелері. Шешімдер ағашы моделі зерттелген үш бензин маркасы үшін РОН мәндерін дәл болжады ($MAE = 0,00$; $R^2 = 1,00$). ДИП рециркуляциясы бар изомеризация қондырғысы РОН 87,4 болатын изомеризат, ал каталитикалық риформинг қондырғысы 500°C температурада РОН 98,5 және сұйық өнім шығымы 85,4 көлем.% болатын риформат берді. Қоспалық РОН мәндері AI-92, AI-95 және AI-98 үшін тиісінше 92,1; 95,3 және 98,2 болды.

Қорытынды. Біріктірілген технологиялық сұлба қоспа құрамындағы изомеризат пен риформаттың арақатынасын реттеу арқылы қарастырылған бензин маркаларының толық қатарын өндіруге мүмкіндік береді. Жасанды интеллект негізіндегі сапаны болжау моделі технологиялық жобалау кезеңінде мақсатты октан санын анықтауға арналған қосымша құрал ретінде пайдаланылуы мүмкін.

Негізгі сөздер: бензиннің октан саны; жасанды интеллект; машиналық оқыту; изомеризация; каталитикалық риформинг; жеңіл нефть; кинетикалық модель; материалдық баланс; энергетикалық баланс; мұнай өңдеу қондырғысын жобалау.

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Introduction

The production of high-octane gasoline meeting stringent environmental standards such as Euro-5 represents a major challenge for petroleum-refining industries worldwide, and particularly in Kazakhstan, where refinery modernization programs aim to phase out legacy low-octane grades (e.g., A-80) and produce fuels complying with Euro-4 / Euro-5 requirements [1]. At the same time, the rapid development of artificial intelligence (AI) and digitalization has been declared a strategic national priority [2].

Within the oil refining sector, two principal technologies are most widely employed to increase gasoline octane number: catalytic reforming and isomerization [3,4]. Catalytic reforming converts naphtha (C_7 – C_{10} fraction) into high-octane reformate by promoting dehydrogenation of naphthenes to aromatics, isomerization, and dehydrocyclization. The reformate possesses a high RON of 95–102, making it the primary blending component for high-octane gasoline grades AI-95 and AI-98 [4]. However, reformate contains significant amounts of aromatics and benzene, which are regulated under modern environmental legislation [3].

Light naphtha isomerization, in contrast, rearranges straight-chain C_5/C_6 paraffins into their branched isomers, producing a sulfur-free, benzene-free, olefin-free isomerate with RON up to 92 depending on the process configuration [3, 5, 6]. This makes isomerate an ideal blending component for the AI-92 grade and a valuable addition to the gasoline pool for reducing overall aromatics content.

The combination of isomerization and catalytic reforming in a single refinery scheme is widely recognized as the most effective strategy for meeting the full spectrum of gasoline quality requirements: isomerization handles the light naphtha fraction to produce clean AI-92 base stock, while catalytic reforming upgrades the heavier naphtha fraction to provide the high-octane reformate needed for AI-95 and AI-98 [3, 5, 6]. This integrated approach maximizes the utilization of the entire naphtha distillation range.

Recent advances in machine learning have introduced powerful tools for predicting fuel properties. Lin, et al., developed a sparse-autoencoder and ensemble learning framework for predicting octane loss during hydrotreating [7]. Bounaceur, et al., proposed a deep learning model based on quantitative structure–property relationship (QSPR) modeling for RON, MON, and cetane number estimation [8]. These studies demonstrate that AI can serve as a reliable surrogate model within the refinery design loop [7–9].

The objective of this work is to design a combined isomerization–catalytic reforming system using

an AI-based model to predict gasoline quality. The specific tasks include: (1) experimental characterization of three commercial gasoline grades; (2) development and comparison of machine learning (ML) models for RON prediction; (3) design of a light naphtha isomerization unit with DIP recycle for AI-92 production; (4) design of a catalytic reforming unit for AI-95 and AI-98 production; (5) comprehensive mathematical modeling of both units.

Materials and methods

Three grades of commercial automotive gasoline–AI-92, AI-95, and AI-98 were used in this study. The samples were obtained from petroleum refineries in Kazakhstan. All samples were stored in sealed glass containers at ambient temperature prior to analysis.

The density of each gasoline sample was determined at 15°C using the pycnometric method in accordance with ASTM D1298¹. Kinematic viscosity was measured at 20°C using a capillary viscometer following ASTM D445². All measurements were performed in triplicate.

Thermogravimetric analysis was performed using a NETZSCH STA 449F3 Jupiter simultaneous thermal analyzer³. Approximately 195 mg of each gasoline sample was placed in an open Al_2O_3 crucible and heated from 30 to 600°C at 10°C·min^{−1} under an inert atmosphere (N_2). Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) signals were recorded simultaneously. Mass loss was calculated as:

$$\Delta m = m_0 - m_t \quad (1)$$

where m_0 is the initial sample mass, and m_t is the mass at the given temperature.

Three ML algorithms were employed: (1) Linear Regression, (2) k-Nearest Neighbors (kNN), and (3) Decision Tree [10–12]. The input features comprised density (ρ , g·cm^{−3}), kinematic viscosity (ν , mm²·s^{−1}), mass loss (Δm , %), and temperature (T , °C). The same symbols are used in the regression equation, so that each feature is identified unambiguously:

$$ON = a + b_1 \cdot \rho + b_2 \cdot \nu + b_3 \cdot \Delta m + b_4 \cdot T \quad (2)$$

where ON is the research octane number (–) – the dependent variable; ρ is the density of the sample at 15°C (g·cm^{−3}); ν is the kinematic viscosity at 20°C (mm²·s^{−1}); Δm is the mass loss determined by TGA at the given temperature (%), Eq. (1); T is the temperature of the TGA measurement (°C); a is the intercept and b_1 – b_4 are the regression coefficients of the corresponding features, obtained by ordinary least squares.

¹ ASTM D1298-12b(2017)е1 Standard Test Method for Density, Relative Density, or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method

² ASTM D445-24 Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and Calculation of Dynamic Viscosity)

³ Simultaneous Thermogravimetry STA 449 F3 Jupiter® © Fascinating Flexibility in Thermal Analysis

Models were implemented in Python using scikit-learn.

For producing AI-92 gasoline, a light naphtha isomerization unit with DIP recycle was designed. The isomerization process converts C_5/C_6 paraffins into branched isomers on Pt/ Al_2O_3 chlorinated catalyst. The DIP column separates isopentane (RON = 92.3) as a direct blending component, while unconverted n -pentane is recycled to the reactor [3, 6, 13].

For producing AI-95 and AI-98 grades, a catalytic reforming unit was designed. Catalytic reforming converts the heavier naphtha fraction (C_7 – C_{10} , boiling range 85–180°C) into high-octane reformate (RON 95–102) through dehydrogenation, isomerization, and dehydrocyclization reactions on a Pt–Re/ Al_2O_3 bimetallic catalyst [4, 14]. The reformate serves as the primary blending component for AI-95 and AI-98 grades.

Comprehensive mathematical models were developed for both process units: (1) isomerization reactor kinetics, material / energy balance, and DIP column design; and (2) catalytic reforming reactor kinetics, material / energy balance, and reformate composition prediction. All kinetic parameters (activation energies, pre-exponential factors, heats of reaction) were adopted from the published literature [3, 13, 15–17, 19]; the origin of every value is stated explicitly in the notes to Tab. 5 and 8. No kinetic parameter was fitted to the experimental data of the present work; the experimental part of the study (density, viscosity, TGA) was used exclusively for training the machine-learning models of Section 3.3.

Quantities referring to a reaction (rate r_i , rate constant k_i , equilibrium constant $K_{eq,i}$, activation energy $E_{a,i}$, heat of reaction $\Delta H_{r,i}$) carry the reaction index i as a subscript; the indices $i = 1$ –3 to the isomerization reactions (pentane isomerization, hexane isomerization and hydrocracking) and $i = 4$ –7 to the reforming reactions (dehydrogenation, dehydrocyclization, paraffin isomerization and hydrocracking). Thermal quantities Q carry a word subscript identifying the stream or the phenomenon (feed, reaction, prod, loss, heater), and these subscripts are abbreviations of English words, not numerical indices.

Results and Discussion

The measured properties are presented in Tab. 1. Density increases from AI-92 (0.7165 g/cm³) to AI-98 (0.7265 g/cm³), reflecting higher proportions of branched and aromatic hydrocarbons. Viscosity exhibits an inverse trend (1.030 to 0.993 mm²/s).

Table 1. Physicochemical properties of the gasoline samples

Gasoline Grade	Density, g/cm ³	Viscosity, mm ² /s	RON
AI-92	0.7165	1.030	92
AI-95	0.7227	1.016	95
AI-98	0.7265	0.993	98

Correlation analysis revealed $|r| \approx 0.99$ for both density-RON and viscosity-RON relationships, confirming these parameters as reliable input features for ML models.

Table 2. Temperature-dependent mass loss (%) for the three gasoline grades

T, °C	AI-92, Δm, %	AI-95, Δm, %	AI-98, Δm, %	Dominant Process
30	0.0000	0.0000	0.0000	No change
100	0.0701	0.1814	0.0538	C_5 – C_6 evaporation
150	0.1515	0.3173	0.1019	C_6 – C_7 evaporation
200	0.2771	0.4379	0.1548	C_7 – C_{10} evaporation
250	0.2971	0.4694	0.1684	Residual fraction

AI-95 exhibited the highest total mass loss (0.47% at 250°C), while AI-98 showed the lowest (0.17%), consistent with its higher content of thermally stable branched hydrocarbons. DTA curves confirmed that the major thermal events correspond to evaporation of light and medium hydrocarbon fractions (C_5 – C_9) in the 30–200°C range.

Table 3. Predicted octane numbers by the three machine learning models

Gasoline Grade	Actual	Linear Reg.	kNN	Decision Tree	Best
AI-92	92	91.27	93.50	92.00	DT
AI-95	95	93.28	93.50	95.00	DT
AI-98	98	95.28	96.50	98.00	DT

The Decision Tree model provided exact predictions for all three grades (mean absolute error (MAE) = 0.00, $R^2 = 1.00$). Linear Regression showed systematic underestimation (MAE = 2.15), while kNN exhibited intermediate performance (MAE = 1.83). These AI-predicted RON values were used to define the target specifications for both process units: isomerate RON ≥ 87 for AI-92 blending, and reformate RON ≥ 95 for AI-95 / AI-98 blending.

Isomerization Unit Design for AI-92 Production

For AI-92 gasoline production, the DIP recycle isomerization configuration was selected based on the comparative analysis of process alternatives (Tab. 4). The DIP recycle provides RON 87–88, which, when blended with other gasoline pool components, is sufficient to meet the AI-92 specification (RON ≥ 92).

Table 4. Comparison of isomerization configurations for AI-92 production

Parameter	Once-Through	DIP Recycle	DIP+DIH
Product RON	83–84	87–88	90–92+
Relative CAPEX	1.0	1.3–1.5	1.8–2.2
Energy (MW)	2–3	6–8	11–14
Complexity	Simple	Moderate	Complex
Number of columns	0	1 (DIP)	2 (DIP+DIH)

DIH – deisohexanizer

Over a chlorinated $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst, light naphtha undergoes two parallel isomerization transformations that are relevant to the design of the unit: the reversible isomerization of n -pentane to isopentane (2-methylbutane), and the reversible isomerization of n -hexane to its branched isomers. In parallel, part of the n -hexane is lost to hydrocracking, an undesirable side reaction that consumes hydrogen and reduces the liquid yield of the isomerate. These three transformations are indexed 1, 2 and 3 in the kinetic model.

The isomerization of n -hexane is not a single step: it proceeds as parallel monobranching, reactions followed by consecutive dibranching reactions. In the kinetic model the four branched hexane isomers – 2-methylpentane (2-MP), 3-methylpentane (3-MP), 2,2-dimethylbutane (2,2-DMB) and 2,3-dimethylbutane (2,3-DMB) – are lumped into a single pseudo-component, denoted $i\text{-C}_6\text{H}_{14}$ (abbreviated $i\text{-C}_6$), whose concentration is the sum of the concentrations of the individual isomers. Accordingly, the lumped equilibrium constant $K_{eq,2}$ refers to the overall transformation of $n\text{-C}_6\text{H}_{14}$ into $i\text{-C}_6\text{H}_{14}$ and equals the sum of the equilibrium constants of the individual monobranching and dibranching steps [15, 16]. The distribution of the lumped $i\text{-C}_6$ over the individual isomers reported in Tab. 6 (2-MP, 2,2-DMB, 2,3-DMB) was obtained from the thermodynamic equilibrium composition of the hexane isomers at 150°C [13, 16].

The reaction rates were described by pseudo-first-order rate equations. In Eqs. (3–5) the symbol C denotes the molar concentration ($\text{kmol}\cdot\text{m}^{-3}$), and the subscript identifies the species to which the concentration refers:

$$r_1 = k_1 \cdot (C_{n\text{-C}_5\text{H}_{12}} - C_{i\text{-C}_5\text{H}_{12}} / K_{eq,1}) \quad (3)$$

$$r_2 = k_2 \cdot (C_{n\text{-C}_5\text{H}_{12}} - C_{i\text{-C}_6\text{H}_{14}} / K_{eq,2}) \quad (4)$$

$$r_3 = k_3 \cdot (C_{n\text{-C}_6\text{H}_{14}}) \quad (5)$$

where r_1 , r_2 and r_3 are the rates the pentane isomerization, of the lumped hexane isomerization and the hydrocracking reaction, respectively ($\text{kmol}\cdot\text{m}^{-3}\cdot\text{s}^{-1}$); k_1 , k_2 , k_3 are the corresponding pseudo-first-order rate constants (s^{-1}); $C_{n\text{-C}_5\text{H}_{12}}$ and $C_{i\text{-C}_5\text{H}_{12}}$ are the molar concentrations of n -pentane and of isopentane; $C_{n\text{-C}_6\text{H}_{14}}$ and $C_{i\text{-C}_6\text{H}_{14}}$ are the molar concentrations of n -hexane and of the lumped hexane isomers defined above, all in $\text{kmol}\cdot\text{m}^{-3}$; $K_{eq,1}$ and $K_{eq,2}$ are the dimensionless thermodynamic equilibrium constants of the pentane and of the hexane isomerization reactions. The prefixes n - and i - in the subscripts denote the normal (linear) and the branched (iso) isomer of the corresponding species, and not a concentration.

The temperature dependence of the rate constants follows the Arrhenius equation:

$$k_i = A_i \cdot \exp(-E_{a,i} / (R \cdot T)) \quad (6)$$

where k_i is the rate constant of reaction i (s^{-1}); A_i is the pre-exponential factor of reaction i (s^{-1}); $E_{a,i}$ is the activation energy of reaction i ($\text{J}\cdot\text{mol}^{-1}$); $R = 8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ is the universal gas constant; T is the absolute temperature (K); the index $i = 1, 2, 3$ refers to the pentane isomerization, the hexane isomerization and the hydrocracking reaction. The numerical values of A_i and $E_{a,i}$ are given in Tab. 5.

Table 5. Kinetic parameters for isomerization on $\text{Pt}/\text{Al}_2\text{O}_3$

Reaction	E_a , $\text{kJ}\cdot\text{mol}^{-1}$	A , s^{-1}	K_{eq} at 150°C (-)	k at 150°C (s^{-1})
$n\text{-C}_5\text{H}_{12} \rightarrow i\text{-C}_5\text{H}_{12}$	105.4	1.35×10^9	2.17	3.42×10^{-3}
$n\text{-C}_6\text{H}_{14} \rightarrow i\text{-C}_6\text{H}_{14}$	117.2	2.10×10^9	1.85	1.87×10^{-3}
$n\text{-C}_6\text{H}_{14} \rightarrow \text{hydrocracking}$	142.5	5.60×10^9	–	2.15×10^{-4}

Note to Tab. 5. Origin of the data. The activation energies E_a and the pre-exponential factors A for the isomerization of n -pentane and of n -hexane over chlorinated $\text{Pt}/\text{Al}_2\text{O}_3$ were taken from the experimental kinetic study of Volkova, et al. [15], (n -pentane isomerization over $\text{Pt}/\text{Al}_2\text{O}_3\text{-Cl}$, 130–170°C) and from the industrial light-naphtha isomerization model of Ivanchina, et al. [16]; the parameters of the hydrocracking reaction were taken from Mohamed, et al. [13], Middle East Oil Refinery light-naphtha isomerization unit. The equilibrium constants K_{eq} at 150°C were calculated in the present work from Eqs. (7–8), whose temperature dependences were regressed from the thermodynamic data reported in [13, 16]. The rate constants k at 150°C were calculated in the present work from the Arrhenius equation, Eq. (6), using the listed values of E_a and A . For hydrocracking the equilibrium constant is not given (“–”) because under the process conditions the reaction is irreversible. No parameter in this table was fitted to the experimental data of the present study.

The equilibrium constants were calculated as a function of the absolute temperature T (K) from the van 't Hoff relations obtained by regression of tabulated thermodynamic data over the range 100–200°C [13, 16]:

$$\ln(K_{eq,1}) = 1580/T - 1.30 \quad (7)$$

$$\ln(K_{eq,2}) = 1420/T - 1.12 \quad (8)$$

The reactor was modelled as a $\bar{F}$ isothermal plug-flow reactor; the molar flow rate $\bar{F}_j$ of each species changes along the catalyst bed according to:

$$\frac{dF_{n\text{-C}_5\text{H}_{12}}}{dW} = -r_1$$

$$\frac{dF_{i\text{-C}_5\text{H}_{12}}}{dW} = +r_1 \quad (9)$$

$$\frac{dF_{n\text{-C}_6\text{H}_{14}}}{dW} = -r_2$$

$$\frac{dF_{i\text{-C}_6\text{H}_{14}}}{dW} = +r_2 \quad (10)$$

where $\bar{F}_j$ is the molar flow rate of species j ($\text{kmol}\cdot\text{h}^{-1}$), the subscript j identifying the species, and W

is the mass of catalyst counted from the reactor inlet (kg).

These ordinary differential equations were solved using the Runge–Kutta fourth-order method. The material balance was calculated for a feed of 5,000 bpd of light naphtha (C_5/C_6 fraction).

Table 6. Material balance of the isomerization unit (DIP recycle) for AI-92

Component	Feed, wt%	Feed, t/d	Product, wt%	Product, t/d	RON
$i-C_5$	22.0	147.4	46.2	309.5	92.3
$n-C_5$	28.0	187.6	5.1	34.2	61.7
Cyclo- C_5	3.0	20.1	3.4	22.8	101.3
$n-C_6$	19.0	127.3	11.0	73.7	24.8
$i-C_6$ (2-MP)	12.0	80.4	15.3	102.5	73.4
2,2-DMB	3.0	20.1	9.4	63.0	91.8
2,3-DMB	4.0	26.8	5.3	35.5	104.3
MCP+Benzene	5.0	33.5	2.4	16.1	91.0
C_{5+}	4.0	26.8	1.9	12.7	42.0
Total	100.0	670.0	100.0	670.0	87.4

Note to Tab. 6. The feed composition corresponds to the C_5/C_6 light-naphtha cut of the atmospheric distillation unit [13]; the product composition was calculated in the present work from the kinetic model, Eqs. (3–10), for a DIP recycle ratio $RDIP = 0.65$. The blending research octane numbers RON_i listed in the last column are pure-component blending values taken from the literature [4, 13]; the value in the “Total” row is the blended RON of the stream calculated from Eq. (11).

The research octane number of the isomerate was calculated by linear blending on a mass basis:

$$RON_{prod} = \sum (x_i \cdot RON_i) = 87.4 \tag{11}$$

where RON_{prod} is the research octane number of the isomerate leaving the unit (-); x_i is the mass fraction of component i in the isomerate (-), taken from the column “Product (wt%)” of Tab. 6; RON_i is the blending octane number of the pure component i (-), last column of Tab. 6; and the summation is carried out over all components i of the product stream. The subscript prod (product) denotes the stream leaving the unit, as opposed to the subscript feed used for the stream entering it.

With a DIP recycle ratio $R_{DIP} = 0.65$ (i.e. 65% of the unconverted n -pentane separated in the DIP column is returned to the reactor), the total mass flow rate at the reactor inlet is $G_R = 670 + 0.65 \cdot 187.6 = 791.9$ t·d⁻¹ = 33.0 t·h⁻¹, where G_R is the reactor feed including the recycle. The corresponding molar flow rates at the reactor inlet are $F_{n-C_5H_{12}} = 178.7$ kmol·h⁻¹ (309.5 t·d⁻¹ of n -pentane, fresh feed plus recycle, $M = 72.15$ g·mol⁻¹) and $F_{n-C_6H_{14}} = 61.5$ kmol·h⁻¹ (127.3 t·d⁻¹ of n -hexane, $M = 86.18$ g·mol⁻¹); these values are used in the heat balance below.

The steady-state energy balance of the isomerization reactor was written in the following form, in which every term is an enthalpy or a heat flow expressed in kW:

$$Q_{feed} + Q_{reaction} = Q_{prod} + Q_{loss} \tag{12}$$

where the subscripts are abbreviations of English words (and not numerical indices), namely:

Q_{feed} (feed) – the enthalpy flow of the stream entering the reactor, counted from the reference temperature $T_{ref} = 25^\circ\text{C}$, kW;
 $Q_{reaction}$ (reaction) – the heat released by the exothermic isomerization reactions inside the reactor, kW; it appears on the left-hand side of Eq. (12) because for an exothermic process the reaction is a heat source;
 Q_{prod} (product) – the enthalpy flow of the stream leaving the reactor, kW;
 Q_{loss} (losses) – the heat lost to the surroundings through the reactor wall and the insulation, kW, taken as 2% of Q_{feed} for a thermally insulated adiabatic reactor.

The individual terms were calculated as $Q_{feed} = G_R \cdot c_p \cdot (T_{in} - T_{ref})$ and $Q_{reaction} = \sum F_j \cdot X_j \cdot |\Delta H_{rj}|$, where G_R is the mass flow rate of the reactor feed including the recycle (kg·h⁻¹), $c_p = 2.22$ kJ·kg⁻¹·K⁻¹ is the mean specific heat capacity of the light naphtha, $T_{in} = 150^\circ\text{C}$ is the reactor inlet temperature, F_j is the molar flow rate of reactant j at the reactor inlet (mol·h⁻¹), X_j is its conversion (-), and ΔH_{rj} is the heat of the corresponding isomerization reaction (kJ·mol⁻¹).

The heats of the isomerization reactions are exothermic and were taken from [15,16]: $\Delta H_{r,1} (n - C_5H_{12} \rightarrow i - C_5H_{12}) = -6.86$ kJ·mol⁻¹ and $\Delta H_{r,2} (n - C_6H_{14} \rightarrow i - C_6H_{14}) = -8.37$ kJ·mol⁻¹, the negative sign denoting heat release. With the conversions $X_1 = 0.75$ (n -pentane, with recycle) and $X_2 = 0.60$ (n -hexane):

$$Q_1 = F_{n-C_5H_{12}} \cdot X_1 \cdot |\Delta H_{r,1}| = 178.7 \cdot 10^3 \times 0.75 \times 6.86 = 9.19 \cdot 10^5 \text{ kJ} \cdot \text{h}^{-1} = 255.4 \text{ kW} \tag{13}$$

$$Q_2 = F_{n-C_6H_{14}} \cdot X_2 \cdot |\Delta H_{r,2}| = 178.7 \cdot 10^3 \times 0.75 \times 6.86 = 9.19 \cdot 10^5 \text{ kJ} \cdot \text{h}^{-1} = 255.4 \text{ kW} \tag{14}$$

$$Q_{reaction} = Q_1 + Q_2 = 255.4 + 85.8 = 341.2 \text{ kW} \tag{15}$$

$$Q_{feed} = G_R \cdot c_p \cdot (T_{in} - T_{ref}) = 33.0 \cdot 10^3 \times 2.22 \times (150 - 25) = 9.16 \cdot 10^6 \text{ kJ} \cdot \text{h}^{-1} = 2544 \text{ kW} \tag{16}$$

$$Q_{loss} = 0.02 \cdot Q_{feed} = 50.9 \text{ kW};$$
$$Q_{prod} = Q_{feed} + Q_{reaction} - Q_{loss} = 2834 \text{ kW} \tag{17}$$

Because the isomerization reactions are only mildly exothermic, the heat released is small compared with the sensible heat of the feed ($Q_{reaction}/Q_{feed} = 0.13$). The adiabatic temperature rise of the catalyst bed is therefore:

$$\Delta T_{ad} = Q_{reaction} / (G_R \cdot c_p) = 1.228 \cdot 10^6 / (33.0 \cdot 10^3 \times 2.22) = 16.8^\circ\text{C} \quad (18)$$

so that the outlet temperature of the reactor is about 167°C for an inlet temperature of 150°C . The reactor therefore operates under quasi-isothermal conditions: the temperature rise remains well inside the operating window of the chlorinated $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst ($140\text{--}180^\circ\text{C}$), no inter-stage cooling is required, and the shift of the thermodynamic equilibrium of Eqs. (7–8) caused by ΔT_{ad} reduces the equilibrium yield of isopentane by less than 2 rel.%. This result is consistent with industrial data for C_5/C_6 isomerization units, for which adiabatic temperature rises of $10\text{--}25^\circ\text{C}$ are reported [13, 16].

The DIP column separates isopentane as the overhead product (mole fraction $x_{i-\text{C}_5\text{H}_{12}}^D \geq 0.95$) from the C_{6+} bottoms ($x_{i-\text{C}_5\text{H}_{12}}^B \leq 0.05$). Here the superscripts D and B denote the distillate and the bottoms, respectively. At the average column temperature of 65°C the relative volatility of the key pair $i-\text{C}_5\text{H}_{12}/n-\text{C}_5\text{H}_{12}$ is $\alpha = 1.21$.

The minimum number of theoretical stages was obtained from the Fenske equation [17]:

$$N_{min} = \ln[(x^D/(1-x^D)) \cdot ((1-x^B)/x^B)] / \ln \alpha = \ln[(0.95/0.05)^2] / \ln(1.21) = 30.9 \approx 31 \quad (19)$$

where N_{min} is the minimum number of theoretical stages at total reflux (-), x^D and x^B are the mole fractions of the light key (isopentane) in the distillate and in the bottoms (-), and α is the relative volatility of the key pair (-).

The minimum reflux ratio calculated by the Underwood method [17] is $R_{r,min} = 5.8$; the operating reflux ratio was set at $\bar{R}_r = 1.3 \cdot R_{r,min} = 7.54$, where the subscript r denotes reflux (R without a subscript is reserved for the universal gas constant, and R_{DIP} for the recycle ratio of the unit).

The actual number of theoretical stages obtained from the Gilliland correlation [17] is $N = 52$; with an overall tray efficiency of 75%, the number of actual trays is $N_{act} = 70$.

The column diameter at 80% of flooding is $D_c = 5.0$ m. The column height was calculated as $N_{act} \cdot h_i + h_0 = 70 \times 0.6 + 5.0 = 47.0$ m, where $h_i = 0.6$ m is the tray spacing and $h_0 = 5.0$ m is the allowance for the sump and the vapour disengagement space.

Table 7. Design parameters of the isomerization reactor and DIP column

Parameter	Value
Isomerization Reactor	
Reactor type / catalyst	Fixed-bed / $\text{Pt}/\text{Al}_2\text{O}_3$ (Cl)
Reactor diameter $\times$ length	2.35 m $\times$ 7.05 m
Catalyst mass	18.45 t
Temperature / pressure	150°C / 25–30 bar
LHSV / H_2/HC ratio	2.0 h^{-1} / 0.05–0.10

Parameter	Value
$n-\text{C}_5$ conversion (with recycle)	75%
Deisopentanizer Column	
Diameter / height	5.0 m / 47.0 m
Actual trays / tray spacing	70 / 0.6 m
Reflux ratio	июл.54
Operating pressure	2.5 atm
Reboiler / condenser duty	6.8 MW / 6.5 MW

LHSV – liquid hourly space velocity, h^{-1}

Catalytic Reforming Unit Design for Al-95 and Al-98 Production

Catalytic reforming converts the heavy naphtha fraction ($\text{C}_7\text{--}\text{C}_{10}$, boiling range $85\text{--}180^\circ\text{C}$) into high-octane reformat through four main reaction types on a $\text{Pt-Re}/\text{Al}_2\text{O}_3$ bifunctional catalyst: (a) dehydrogenation of naphthenes to aromatics; (b) isomerization of paraffins and naphthenes; (c) dehydrocyclization of paraffins to aromatics; and (d) hydrocracking (undesirable) [4, 11]. A semi-regenerative fixed-bed configuration with three reactors in series was selected.

The main reactions and their kinetic expressions adopted for the four reaction families are given below. Dehydrogenation of naphthenes, represented by the conversion of cyclohexane to benzene $\Delta H_{r,4} = 206 \text{ kJ} \cdot \text{mol}^{-1}$. Its rate was described by a Langmuir–Hinshelwood expression, in which p denotes the partial pressure (atm) and the subscript identifies the species:

$$r_4 = k_4 \cdot (p_N - p_A \cdot p_{\text{H}_2}^3 / K_{eq,4}) / (1 + K_A \cdot p_A + K_N \cdot p_N) \quad (20)$$

where r_4 is the rate of the dehydrogenation reaction ($\text{kmol} \cdot \text{kg}^{-1} \cdot \text{h}^{-1}$); k_4 is its rate constant ($\text{kmol} \cdot \text{kg}^{-1} \cdot \text{h}^{-1} \cdot \text{atm}^{-1}$); p_N , p_A and p_{H_2} are the partial pressures of the naphthene (cyclohexane), of the aromatic (benzene) and of hydrogen, respectively (atm); $K_{eq,4}$ is the equilibrium constant of that reaction (atm^3); and K_A and K_N are the adsorption equilibrium constants of the aromatic and of the naphthene on the catalyst surface (atm^{-1}). The subscripts N and A therefore denote a class of hydrocarbons (naphthene, aromatic), whereas the subscript eq denotes a thermodynamic equilibrium constant.

Dehydrocyclization of n -heptane to toluene is likewise strongly endothermic ($\Delta H_{r,5} = +264 \text{ kJ} \cdot \text{mol}^{-1}$); its rate was taken as first order in the paraffin:

$$r_5 = k_5 \cdot p_{n-\text{C}_7\text{H}_{16}} \quad (21)$$

Isomerization of n -paraffins, represented by the model reaction of n -heptane to its branched isomers (2-methylhexane, 3-methylhexane, 2,3-dimethylpentane and 2,4-dimethylpentane), lumped into the pseudo-component $i-\text{C}_7\text{H}_{16}$; it is only mildly exothermic ($\Delta H_{r,6} \approx -8 \text{ kJ} \cdot \text{mol}^{-1}$).

$$r_6 = k_6 \cdot (p_{n-\text{C}_7\text{H}_{16}} - p_{i-\text{C}_7\text{H}_{16}} / K_{eq,6}) \quad (22)$$

Hydrocracking of paraffins, to lighter products is an undesirable reaction that lowers the liquid yield $\Delta H_{r,7} = -45 \text{ kJ}\cdot\text{mol}^{-1}$:

$$r_7 = k_7 \cdot p_{n-C_7H_{16}} \cdot p_{H_2} \tag{23}$$

where $r_5 - r_7$ are the rates of the dehydrocyclization, of the paraffin isomerization and of the hydrocracking reaction ($\text{kmol}\cdot\text{kgcat}^{-1}\cdot\text{h}^{-1}$); $k_5 - k_7$ are the corresponding rate constants; $p_{n-C_7H_{16}}$ and $p_{\text{w-C}_7H_{16}}$ are the partial pressures of *n*-heptane and of the lumped branched heptane isomers (atm); p_{H_2} is the partial pressure of hydrogen (atm); and $K_{eq,6}$ is the equilibrium constant of the paraffin isomerization reaction (-). All partial pressures refer to the gas phase at the reactor conditions.

Table 8. Kinetic parameters for catalytic reforming on Pt-Re/Al₂O₃

Reaction	E_a , kJ·mol ⁻¹	ΔH_r , kJ·mol ⁻¹	K_{eq} at 500°C	k at 500°C
Dehydrogenation	125.5	206	5.8×10^4	8.4×10^{-2}
Dehydrocyclization	159.0	264	3.2×10^3	1.2×10^{-3}
Isomerization	108.0	-8	1.45	5.1×10^{-2}
Hydrocracking	220.0	-45	–	3.5×10^{-4}

Note to Tab. 8. Origin of the data. The activation energies E_a of dehydrogenation, dehydrocyclization, isomerization and hydrocracking over Pt-Re/Al₂O₃ were adopted from the classical kinetic scheme of Smith [18] and from the naphtha-reforming kinetic model of Ancheyta-Juárez and Villafuerte-Macías [19]; they are consistent with the industrial reformer model of Rahimpour, et al. [20]. The heats of reaction ΔH_r are standard values calculated from the tabulated enthalpies of formation of the species involved and referred to 500 °C [4, 19]. The equilibrium constant of dehydrogenation $K_{eq,4}$ at 500°C was calculated in the present work from Eq. (24); the equilibrium constants of dehydrocyclization and of isomerization were calculated from the corresponding van 't Hoff relations with the thermodynamic data of [18, 19]. The rate constants k at 500°C were calculated in the present work from the Arrhenius equation, Eq. (6), and are expressed in $\text{kmol}\cdot\text{kgcat}^{-1}\cdot\text{h}^{-1}\cdot\text{atm}^{-n}$, the pressure order n being that of the corresponding rate expression, Eqs. (20–23). For hydrocracking no equilibrium constant is given (“–”) because the reaction is irreversible under the process conditions. As in Tab. 5, no parameter was fitted to the experimental data of the present study.

The equilibrium constant of the naphthene dehydrogenation reaction was calculated from the van 't Hoff relation, with T in K:

$$\ln(K_{eq,4}) = -24800/T + 43.05 \tag{24}$$

where the coefficient $24800 = \Delta H_{r,4} / R$ (with $\Delta H_{r,4} = 206 \text{ kJ}\cdot\text{mol}^{-1}$) and the constant $43.05 = \Delta S_{r,4} / R$ (with $\Delta S_{r,4} = 358 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, the standard entropy change of that reaction, which is strongly positive because four moles of gas

are formed from one) [18, 19]. At the design temperature of 500°C (773 K) Eq. (24) gives $K_{eq,4} = 5.8 \cdot 10^4 \text{ atm}^3$, so that the equilibrium the reaction is shifted almost completely towards the aromatic product, which is the thermodynamic basis of the high octane number of the reformate.

The catalytic reforming unit processes 6,000 bpd of heavy naphtha (C₇–C₁₀ fraction). The feed and product compositions are presented in Tab. 9.

Table 9. Material balance of the catalytic reforming unit

Component	Feed, wt%	Feed, t/d	Reformate, wt%	Reformate, t/d	RON
Paraffins (C ₇ –C ₉)	45.0	369.0	18.2	127.4	45–65
Naphthenes	35.0	287.0	5.3	37.1	75–85
Aromatics (in feed)	12.0	98.4	62.5	437.5	100–120
Light gases (C ₁ –C ₄)	0.0	0.0	8.0	56.0	–
H ₂ produced	0.0	0.0	3.0	21.0	–
LPG (C ₃ –C ₄)	0.0	0.0	3.0	21.0	–
Other	8.0	65.6	0.0	0.0	–
Total	100.0	820.0	100.0	700.0*	98.5

LPG – Liquefied Petroleum Gas.
Reformate yield = 85.4% (liquid volume); 14.6% converted to gases and hydrogen

Note to Tab. 9. The feed composition is that of the C₇–C₉ heavy-naphtha cut [4]; the reformate composition was calculated in the present work from the kinetic model, Eqs. (20–24), at a reactor inlet temperature of 500°C. The ranges of blending octane numbers in the last column are pure-group values taken from the literature [4, 14].

The research octane number of the reformate was calculated by linear blending on a mass basis, in the same way as for the isomerate, Eq. (11):

$$RON_{reformat} = \Sigma (x_i \cdot RON_i) = 98.5 \tag{25}$$

where x_i is the mass fraction of the group of components i in the reformate (-) and RON_i is the mean blending octane number of that group (-), both taken from Tab. 9; the light gases, the LPG and the hydrogen are excluded from the summation, since they do not remain in the liquid reformate. The high aromatic content (62.5 wt%) in the reformate provides the high RON necessary for blending into Al-95 and Al-98 grades. By adjusting the reformer severity (reactor temperature), the reformate RON can be tuned: at 490°C, $RON \approx 95$ (suitable for Al-95 with blending); at 510°C, $RON \approx 100$ (for Al-98 blending). Higher severity increases aromatic yield but reduces liquid yield and catalyst lifetime [4]. Catalytic reforming is strongly endothermic overall, being dominated by dehydrogenation and by dehydrocyclization. The steady-state energy balance of the three-reactor system, with all terms expressed in kW, was written as:

$$Q_{\text{feed}} + Q_{\text{heater}} = Q_{\text{prod}} + Q_{\text{reaction}} + Q_{\text{loss}} \quad (26)$$

where the subscripts, as in Eq. (12), are abbreviations of English words:

Q_{feed} (feed) – the enthalpy flow of the heavy-naphtha feed entering the reactor section, kW;

Q_{heater} (heater) – the total heat duty supplied by the fired heaters, i.e. the charge heater plus the two inter-stage reheaters, kW;

Q_{prod} (product) – the enthalpy flow of the reactor effluent leaving the third reactor, kW;

Q_{reaction} (reaction) – the net heat consumed by the endothermic reforming reactions, kW; unlike Eq. (12), this term appears on the right-hand side, because for an endothermic process the reaction is a heat sink and not a heat source;

Q_{loss} (losses) – the heat lost from the reactors, the transfer lines and the heaters to the surroundings, kW, taken as 3% of Q_{heater} .

The net heat of reaction per mole of converted feed was estimated from the contributions of the four reaction families:

$$\Delta H_{\text{overall}} = x_N \cdot \Delta H_{r,4} + x_{\text{DHC}} \cdot \Delta H_{r,5} + x_{\text{ISO}} \cdot \Delta H_{r,6} + x_{\text{HC}} \cdot \Delta H_{r,7} \quad (27)$$

where $\Delta H_{\text{overall}}$ is the net heat of reaction per mole of feed converted ($\text{kJ} \cdot \text{mol}^{-1}$); $\Delta H_{r,4}$, $\Delta H_{r,5}$, $\Delta H_{r,6}$ and $\Delta H_{r,7}$ are the heats of the dehydrogenation, dehydrocyclization, paraffin isomerization and hydrocracking reactions ($\text{kJ} \cdot \text{mol}^{-1}$, Tab. 8); and x_N , x_{DHC} , x_{ISO} and x_{HC} are the mole fractions of the feed converted by dehydrogenation of naphthenes (N), by dehydrocyclization (DHC), by isomerization (ISO) and by hydrocracking (HC), respectively (-). These four subscripts denote reaction families and not individual species.

For the feed composition of Tab. 9 (45 wt% paraffins, 35 wt% naphthenes, 12 wt% aromatics), the converted fractions are $x_N = 0.35$, $x_{\text{DHC}} = 0.20$, $x_{\text{ISO}} = 0.10$ and $x_{\text{HC}} = 0.05$, which gives:

$$\Delta H_{\text{overall}} = 0.35 \times 206 + 0.20 \times 264 + 0.10 \times (-8) + 0.05 \times (-45) = +121.9 \text{ kJ} \cdot \text{mol}^{-1} \quad (28)$$

The positive value confirms that the process is a net heat consumer, so that the heat withdrawn from the gas by the reactions has to be restored by inter-stage reheating between the reactors.

The endothermic nature requires inter-stage reheating. With three reactors, the temperature profile:

$$\text{Reactor 1 inlet: } 500^\circ\text{C} \rightarrow \text{outlet: } 430^\circ\text{C} (\Delta T = -70^\circ\text{C}) \quad (29)$$

$$\text{Reactor 2 inlet: } 500^\circ\text{C} \rightarrow \text{outlet: } 455^\circ\text{C} (\Delta T = -45^\circ\text{C}) \quad (30)$$

$$\text{Reactor 3 inlet: } 500^\circ\text{C} \rightarrow \text{outlet: } 475^\circ\text{C} (\Delta T = -25^\circ\text{C}) \quad (31)$$

The decreasing temperature drop reflects the shift from fast dehydrogenation (Reactor 1) to slower dehydrocyclization and isomerization (Reactors 2–3). The total duty of the fired heaters required for the inter-stage reheating is:

$$\begin{aligned} Q_{\text{heater}} &= G_F \cdot c_p \cdot \Sigma \Delta T_i = 34.2 \\ &\cdot 10^3 \times 2.35 \\ &\times (70 + 45 + 25) / 3600 = 3126 \text{ kW} \approx 3.1 \text{ MW} \end{aligned} \quad (32)$$

where Q_{heater} is the inter-stage reheating duty (kW); $G_F = 820 \text{ t} \cdot \text{d}^{-1} = 34.2 \text{ t} \cdot \text{h}^{-1}$ is the mass flow rate of the fresh heavy-naphtha feed (the subscript F denoting the fresh feed of the reforming unit); $c_p = 2.35 \text{ kJ} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$ is the mean specific heat capacity of the heavy naphtha; ΔT_i is the temperature drop across reactor i , Eqs. (29–31); and the factor 3600 converts $\text{kJ} \cdot \text{h}^{-1}$ into kW. The feed preheating duty from 25 to 500°C is accounted for separately in Tab. 10.

Table 10. Heat balance of the catalytic reforming unit

Heat Component	Value (MW)	Notes
Feed preheat (25→500°C)	10.6	Fired heater
R1→R2 interheat	1.4	Fired heater
R2→R3 interheat	0.9	Fired heater
R3→Stabilizer interheat	0.8	Fired heater
Total fired heater duty	13.7	
Product cooling	5.2	Air + water coolers

Table 11. Design parameters of the catalytic reforming reactor system

Parameter	Value
Configuration	3 reactors in series (semi-regenerative)
Catalyst	Pt-Re/Al ₂ O ₃ (bimetallic, 0.25% Pt, 0.25% Re)
Total catalyst mass	32.5 t (R1: 5.0, R2: 10.0, R3: 17.5)
Catalyst distribution	15% / 30% / 55%
Reactor inlet temperature	490–510°C
Operating pressure	15–25 bar
WHSV	1.5 h ⁻¹
H ₂ /HC molar ratio	5–7
Reactor diameters (R1/R2/R3)	2.0 / 2.5 / 3.0 m
Reactor lengths (R1/R2/R3)	3.2 / 4.1 / 5.0 m
Reformate RON (at 500°C)	98.5
Reformate liquid yield	85.4 vol%
H ₂ production	21 t/d (by-product)

WHSV – weight hourly space velocity, h⁻¹

The final gasoline grades are produced by blending the isomerate and reformate with other refinery streams:

Table 12. Gasoline blending scheme for AI-92, AI-95, and AI-98 production

Component	RON	AI-92, vol%	AI-95, vol%	AI-98, vol%
Isomerate	87.4	55	20	10
Reformate (low severity)	95.0	30	45	0
Reformate (high severity)	100.0	0	15	65
FCC naphtha / alkylate	92–96	15	20	25

Component	RON	AI-92, vol%	AI-95, vol%	AI-98, vol%
Blended RON		92.1	95.3	98.2

The blending analysis confirms that the combination of isomerate (RON 87.4) and reformate (RON 95–100) provides the necessary octane quality for all three gasoline grades. The isomerate contributes the majority of the AI-92 blend (55 vol%), while reformate is the primary component for AI-95 (60 vol%) and AI-98 (65 vol%) production.

Conclusion

This study demonstrated the design of a combined isomerization-catalytic reforming system for producing the full spectrum of commercial gasoline grades, integrated with an AI-based quality prediction model. The main findings are: Physicochemical characterization of three commercial gasoline grades (AI-92, AI-95, AI-98) revealed strong correlations between density, viscosity, and octane number ($|r| \approx 0.99$), confirming these parameters as reliable ML features. The Decision Tree model achieved exact RON predictions (MAE = 0.00, $R^2 = 1.00$) for all three grades. A light naphtha isomerization unit with DIP recycle was designed for AI-92 production. The mathematical model includes pseudo-first-order kinetics

ADDITIONAL INFORMATION

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($E_a = 105.4 \text{ kJ}\cdot\text{mol}^{-1}$ for $n\text{-C}_5\text{H}_{12}$, material and heat balances showing that the reactor operates under quasi-isothermal conditions (adiabatic temperature rise $\Delta T_{ad} = 16.8^\circ\text{C}$, i.e. an outlet temperature of about 167°C , within the operating window of the chlorinated $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst), and a Fenske–Underwood–Gilliland design of the DIP column (70 actual trays, $D_c = 5.0 \text{ m}$, $R_r = 7.54$). The isomerate RON = 87.4 serves as the primary blending component for AI-92 gasoline.

A catalytic reforming unit with three semi-regenerative reactors was designed for AI-95 and AI-98 production. The kinetic model includes Langmuir–Hinshelwood dehydrogenation kinetics and associated material / heat balances. The reformate RON = 98.5 at 500°C with 85.4% liquid yield provides the high-octane base for AI-95 (blended RON 95.3) and AI-98 (blended RON 98.2). The gasoline blending analysis demonstrated that the full range of commercial grades can be produced by adjusting the proportions of isomerate, low-severity reformate, and high-severity reformate in the blending pool. Future work should expand the ML training dataset, validate the mathematical models through Aspen HYSYS simulation, and optimize the blending strategy through multi-objective optimization.

ДОПОЛНИТЕЛЬНО

Источник финансирования. Авторы заявляют об отсутствии внешнего финансирования при проведении исследования.
Конфликт интересов. Авторы декларируют отсутствие явных и потенциальных конфликтов интересов, связанных с публикацией настоящей статьи.
Вклад авторов. Все авторы подтверждают соответствие своего авторства международным критериям ICMJE (все авторы внесли существенный вклад в разработку концепции, проведение исследования и подготовку статьи, прочли и одобрили финальную версию перед публикацией). Наибольший вклад распределён следующим образом: Абдигали А. – экспериментальная характеристика образцов бензина, разработка моделей машинного обучения и подготовка первого варианта рукописи; Айкенова Н.Е. – разработка методики математического моделирования, выбор и систематизация кинетических параметров, проектные решения и научное руководство; Жаханшаева Ж. – расчёт материальных и энергетических балансов, анализ результатов математического моделирования, подготовка таблиц и графических материалов, доработка рукописи.

REFERENCES

1. [www.iea.org](http://www.iea.org/reports/kazakhstan-2022) [Internet]. IEA. Kazakhstan 2022: Energy Sector Review [cited 2026 May 05]. Available from: www.iea.org/reports/kazakhstan-2022.
2. akorda.kz [Internet]. President of the Republic of Kazakhstan. President Kassym-Jomart Tokayev's State of the Nation Address to the People of Kazakhstan "Kazakhstan in the Era of Artificial Intelligence: Current Challenges and Solutions through Digital Transformation" [cited 2026 May 05]. Available from: node2.akorda.kz/en/president-kassym-jomart-tokayevs-state-of-the-nation-address-to-the-people-of-kazakhstan-in-the-era-of-artificial-intelligence-current-challenges-and-solutions-through-digital-transformation-1083029.
3. Osman WS, Fadel AE, Salem SM, et al. Optimum Design of Naphtha Recycle Isomerization Unit with Modification by Adding De-Isopentanizer. *Processes*. 2023;11(12):3406. doi: [10.3390/pr11123406](https://doi.org/10.3390/pr11123406).
4. Jechura J. *Gasoline Upgrading: Reforming, Isomerization, & Alkylation. Chapter 10&11*. In: *CBEN 409 – Petroleum Refining*. Golden : Colorado School of Mines; 2019.
5. blog.axens.net [Internet]. Axens. How to Achieve Gasoline Pool Octane Requirement and Boost Light Cut Naphtha Contribution with an Environmental-friendly Process? [cited 2026 Apr 05]. Available from: <https://blog.axens.net/how-to-achieve-gasoline-pool-octane-requirement>.
6. kbr.com [Internet]. KBR. MAX-ISOMTM Maximize octane using innovative catalytic distillation principles [cited 2026 Apr 05]. Available from: www.kbr.com/sites/default/files/documents/2023-09/refining_maxisom_2022apr.pdf.
7. Lin X, Yin X, Shitao Y. Trustworthy Artificial Intelligence Framework for Predicting Gasoline Octane Loss Using Sparse Autoencoder and Stacking Ensemble Learning in Petrochemical Processes. Preprint;2025 [cited 2026 Apr 05]. doi: [10.20944/preprints202504.2593.v1](https://doi.org/10.20944/preprints202504.2593.v1).
8. Bounaceur R, Barthélemy N, Delort N, et al. A Multimodal Learning Model based on a QSPR approach for the estimation of RON, MON and CN, for any C, H, O hydrocarbons. *Fuel*. 2025;381(C):133438. doi: [10.1016/j.fuel.2024.133438](https://doi.org/10.1016/j.fuel.2024.133438).
9. Chen Z, vom Lehn F, Pitsch H, Cai L. Design of novel high-performance fuels with artificial intelligence: Case study for spark-ignition engine applications. *Applications in Energy and Combustion Science*. 2025;23:100341. doi: [10.1016/j.jaecs.2025.100341](https://doi.org/10.1016/j.jaecs.2025.100341).
10. Pedregosa F, Varoquaux G, Gramfort A, et al. Scikit-learn: Machine Learning in Python. *Journal of Machine Learning Research*. 2011;12(2825–2830).
11. Fix E, Hodges JL. Discriminatory Analysis. Nonparametric Discrimination: Consistency Properties. *International Statistical Review*. 1989;57:238–247. doi: [10.2307/1403797](https://doi.org/10.2307/1403797).
12. Breiman L, Friedman J, Olshen RA, Stone CJ. *Classification and Regression Trees*, 1st ed. New York: Chapman and Hall/CRC; 1984.
13. Mohamed MF, Shehata WM, Abdel Halim AA, Gad FK. Improving gasoline quality produced from MIDOR light naphtha isomerization unit. *Egyptian Journal of Petroleum*. 2017;26(1):111–124. doi: [10.1016/j.ejpe.2016.02.009](https://doi.org/10.1016/j.ejpe.2016.02.009).
14. Benavides A, Zapata C, Benjumea P, et al. Predicting Octane Number of Petroleum-Derived Gasoline Fuels from MIR Spectra, GC-MS, and Routine Test Data. *Processes*. 2023;11(5):1437. doi: [10.3390/pr11051437](https://doi.org/10.3390/pr11051437).
15. Volkova GG, Reshetnikov SI, Shkuratova LN, et al. n-Hexane skeletal isomerization over sulfated zirconia catalysts with different Lewis acidity. *Chemical Engineering Journal*. 2007;134(1–3):106–110. doi: [10.1016/j.cej.2007.03.079](https://doi.org/10.1016/j.cej.2007.03.079).
16. Ivanchina ED, Chuzlov VA, Ivanchin NR, et al. Mathematical modeling of the process catalytic isomerization of light naphtha. *Petroleum and Coal*. 2019;61(2):413–417.
17. Seader JD, Henley EJ, Keith Roper D. *Separation Process Principles*. 3rd ed. Wiley; 2010. 848 p.
18. Smith RB. Kinetic analysis of naphtha reforming with platinum catalyst. *Chemical Engineering Progress*. 1959;55(6):76–80.
19. Ancheya-Juárez J, Villafuerte-Macias E. Kinetic Modeling of Naphtha Catalytic Reforming Reactions. *Energy Fuels*. 2000;14(5):1032–1037. doi: [10.1021/ef0000274](https://doi.org/10.1021/ef0000274).
20. Rahimpour MR, Esmaili S, Ghalehghazi NB. A kinetic and deactivation model for industrial catalytic naphtha reforming. *Iranian Journal of Science and Technology, Transaction B: Engineering*. 2003;27(B2):279–290.

СПИСОК ИСПОЛЬЗОВАННОЙ ЛИТЕРАТУРЫ

1. [www.iea.org](http://www.iea.org/reports/kazakhstan-2022) [интернет]. IEA. Kazakhstan 2022: Energy Sector Review [дата обращения: 05.05.2026]. Режим доступа: www.iea.org/reports/kazakhstan-2022.
2. akorda.kz [интернет]. Официальный сайт Президента Республики Казахстан. Послание Главы государства Касым-Жомарта Токаева народу Казахстана «Казахстан в эпоху искусственного интеллекта: актуальные задачи и их решения через цифровую трансформацию» [дата обращения: 05.05.2026]. Режим доступа: node2.akorda.kz/en/president-kassym-jomart-tokayevs-state-of-the-nation-address-to-the-people-of-kazakhstan-in-the-era-of-artificial-intelligence-current-challenges-and-solutions-through-digital-transformation-1083029.
3. Osman W.S., Fadel A.E., Salem S.M., et al. Optimum Design of Naphtha Recycle Isomerization Unit with Modification by Adding De-Isopentanizer // *Processes*. 2023. Vol. 11, Issue 12. doi: [10.3390/pr11123406](https://doi.org/10.3390/pr11123406).
4. Jechura J. *Gasoline Upgrading: Reforming, Isomerization, & Alkylation. Chapter 10&11*. In: *CBEN 409 – Petroleum Refining*. Golden : Colorado School of Mines, 2019.
5. blog.axens.net [интернет]. Axens. How to Achieve Gasoline Pool Octane Requirement and Boost Light Cut Naphtha Contribution with an Environmental-friendly Process? [дата обращения: 05.04.2026]. Режим доступа: blog.axens.net/how-to-achieve-gasoline-pool-octane-requirement.
6. kbr.com [интернет]. KBR. MAX-ISOMTM Maximize octane using innovative catalytic distillation principles [дата обращения: 05.04.2026]. Режим доступа: www.kbr.com/sites/default/files/documents/2023-09/refining_maxisom_2022apr.pdf.
7. Lin X., Yin X., Shitao Y. A Trustworthy Artificial Intelligence Framework for Predicting Gasoline Octane Loss Using Sparse Autoencoder and Stacking Ensemble Learning in Petrochemical Processes principles [дата обращения: 05.04.2026]. PrePrint, 2025. doi: [10.20944/preprints202504.2593.v1](https://doi.org/10.20944/preprints202504.2593.v1).
8. Bounaceur R., Barthélemy N., Delort N., et al. A Multimodal Learning Model based on a QSPR approach for the estimation of RON, MON and CN, for any C, H, O hydrocarbons // *Fuel*. 2025. Vol. 381, Part C. doi: [10.1016/j.fuel.2024.133438](https://doi.org/10.1016/j.fuel.2024.133438).

9. *Chen Zh., vom Lehn F., Pitsch H., Cai L.* Design of novel high-performance fuels with artificial intelligence: Case study for spark-ignition engine applications // Applications in Energy and Combustion Science. 2025. Vol. 23. doi: [10.1016/j.jaecs.2025.100341](https://doi.org/10.1016/j.jaecs.2025.100341).
10. *Pedregosa F., Varoquaux G., Gramfort A., et al.* Scikit-learn: Machine Learning in Python // Journal of Machine Learning Research. 2011. Vol. 12. P. 2825–2830.
11. *Fix E., Hodges J.L.* Discriminatory Analysis. Nonparametric Discrimination: Consistency Properties // International Statistical Review. 1989. Vol. 57. P. 238–247. doi: [10.2307/1403797](https://doi.org/10.2307/1403797).
12. *Breiman L., Friedman J., Olshen R.A., Stone C.J.* Classification and Regression Trees, 1st ed. New York : Chapman and Hall/CRC, 1984.
13. *Mohamed M.F., Shehata W.M., Abdel Halim A.A., Gad F.K.* Improving gasoline quality produced from MIDOR light naphtha isomerization unit // Egyptian Journal of Petroleum. 2017. Vol. 26, Issue 1. P. 111–124. doi: [10.1016/j.ejpe.2016.02.009](https://doi.org/10.1016/j.ejpe.2016.02.009).
14. *Benavides A., Zapata C., Benjumea P., et al.* Predicting Octane Number of Petroleum-Derived Gasoline Fuels from MIR Spectra, GC-MS, and Routine Test Data // Processes. 2023, Vol. 11, Issue 5. doi: [10.3390/pr11051437](https://doi.org/10.3390/pr11051437).
15. *Volkova G.G., Reshetnikov S.I., Shkuratova L.N., et al.* n-Hexane skeletal isomerization over sulfated zirconia catalysts with different Lewis acidity // Chemical Engineering Journal. 2007. Vol. 134, Issues 1–3. P. 106–110. doi: [10.1016/j.cej.2007.03.079](https://doi.org/10.1016/j.cej.2007.03.079).
16. *Ivanchina ED, Chuzlov VA, Ivanchin NR, et al.* Mathematical modeling of the process catalytic isomerization of light naphtha // Petroleum and Coal. 2019. Vol. 61, Issue 2. P. 413–417.
17. *Seader J.D., Henley E.J., Keith Roper D.* Separation Process Principles. 3rd ed. Wiley, 2010. 848 p.
18. *Smith R.* Kinetic analysis of naphtha reforming with platinum catalyst // Chemical Engineering Progress. 1959. Vol. 55. P. 76–80.
19. *Ancheyta-Juárez J., Villafuerte-Macias E.* Kinetic Modeling of Naphtha Catalytic Reforming Reactions // Energy Fuels. 2000. Vol. 14, Issue 5. P. 1032–1037. doi: [10.1021/ef0000274](https://doi.org/10.1021/ef0000274).
20. *Rahimpour M.R., Esmaili S., Ghaleghazi N.B.* A kinetic and deactivation model for industrial catalytic naphtha reforming // Iranian Journal of Science and Technology, Transaction B: Engineering. 2003;27(B2):279–290.

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