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Catalytic Production of High-Octane Synthetic Fuel from Bioethanol and Gaseous Sources of Carbon Feedstock

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Keywords:
Production of High-Performance Synthetic Hydrocarbons; Fuels from Bioethanol; Zeolite-Based Catalytic Conversion.

Highlights:

- *Liquid hydrocarbon yields of up to 68% were achieved by optimising reaction pressure and temperature during the bioethanol conversion.*
- *The produced fuels demonstrated an octane number reaching up to 98 with benzene content reduced to 1.2%, meeting Euro-5 standards.*
- *Catalytic processing resulted in low corrosion activity on metal samples, with mass loss less than 0.012 g/m² over 168 hours.*

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Abstract: This study investigated the catalytic conversion of bioethanol and methanol into synthetic liquid hydrocarbons with properties comparable to or surpassing conventional petroleum-based fuels. Using zeolite catalysts modified with nickel and molybdenum, bioethanol was processed in a continuous flow reactor under temperatures ranging from 340 to 400 °C and pressure up to 25 bar. The experiments demonstrated that at 360 °C and 15 bar, the liquid hydrocarbon yield reached 63% by mass, with an octane number of 97 and an aromatic content of 42%. Increasing the reaction temperature to 400 °C raised the aromatic fraction to 48% but reduced the yield to 57%. The additional processing of dimethyl ether derived from methanol, along with the subsequent hydrogenation of aromatic compounds, enabled the reduction of benzene content to as low as 1.2%, meeting Euro-5 standards. The produced fuels exhibited lower heating values between 42.0 and 43.7 MJ/kg and showed low corrosion activity on carbon steel and aluminium alloys. The findings confirm the feasibility of bioethanol-based processes to produce high-performance, low-toxicity fuels suitable for sustainable energy systems.

1.INTRODUCTION

The global energy sector is on the brink of major changes driven by both the depletion of traditional resources and a growing awareness of environmental threats. Global consumption of fossil fuels, from wood to oil and gas, has shaped human industrial and social development over the past centuries. For example, oil, which became the dominant energy source in the 20th century, accounted for about 48% of global energy consumption in 2004. However, by 2010, this share had fallen to 33.6%, and by 2014 it was 31.3% due to the displacement of oil by natural gas and the development of alternative energy sources. Today, as the consequences of the greenhouse effect, including a steady rise in temperature and sea levels, become increasingly evident, issues of decarbonization and the transition to less harmful energy sources for the climate are of paramount importance [1-3]. According to NASA, the average global temperature has increased by 0.8 °C since 1880, with 60% of this warming occurring between 1975 and 2014. From the mid-19th century to the early 21st century, the sea level in the World Ocean has increased by 17 cm, reflecting large-scale changes in climate conditions. Possible solutions to this problem involve the development of technologies that reduce carbon footprint and decrease dependence on fossil hydrocarbons. One of the areas includes active introduction of renewable energy sources, such as solar, wind, and hydroelectric generation [5-6]. These approaches certainly have an important advantage in the form of virtually zero direct carbon dioxide emissions. However, they have significant limitations: high capital intensity, a significant dependence on weather conditions, and the difficulty of storing the energy produced in sufficient quantities. Another solution is the increased use of biomass, which allows closing the carbon cycle and reducing the CO_2 content in the atmosphere. In particular, the production of liquid fuels from various types of bio-raw materials, such as wood, cereals, sugarcane, and microalgae, opens the way to a more sustainable energy model. For example, algae containing 15% triglycerides can produce up to 11,204 litres of oil per hectare per year, which corresponds to 104 MWh of energy per hectare. If the triglyceride content reaches 50%, the oil yield can be 100,000 litres per hectare per year, which is equivalent to 931 MWh of energy per hectare [7]. First-generation biofuels based on agricultural raw materials have a relatively low price, but their large-scale production inevitably competes with the food sector, which limits their use [8,9]. An important alternative is the use of gaseous feedstock and technologies for synthesising liquid hydrocarbons from natural gas. The Fischer-Tropsch technology and the methanol conversion make it possible to obtain motor fuel with high performance characteristics and a low content of sulfur and aromatic impurities. This technology was first implemented industrially in Germany in the 1920s and is now successfully used, for example, at the ORYX GTL plant in Qatar, which was commissioned in 2006 with a capacity of 34,000 barrels per day. Gaseous fuel in the form of compressed natural gas (CNG) requires storage at a pressure of 200-250 bar and the installation of thick-walled cylinders, which increases the weight of vehicles [10,11]. In Russia, the number of cars running on CNG is less than 1.5% of the world fleet, which is equivalent to 147,000 units of equipment, while about 2.3% of the world's CNG is consumed. Against this background, the approach based on the deep processing of bioethanol extracted from renewable raw materials into hydrocarbon components of motor fuels is becoming increasingly noticeable [12-14]. The biochemical cycle, including photosynthesis, CO_2 utilisation, and production of ethanol by fermentation of biomass, actually ensures the recycling of carbon dioxide and reduces the load on the atmosphere. It should be noted that about 80% of bioethanol produced in the world is used in the form of gasoline-ethanol mixtures for motor vehicles. One of the important advantages of the approach to bioethanol processing is that it allows the use of existing agricultural and biomass processing infrastructure, making it possible to produce fuel suitable for modern engines, including aircraft gas turbines [15]. Therefore, the conversion of bioethanol over HZSM-5 zeolite catalysts makes it possible to obtain a liquid product with an octane number of 98 according to the research method and a low content of toxic aromatic compounds (approximately 27% by weight). This provides better environmental characteristics compared to petroleum fuel (where the content of aromatic compounds reaches 35–40% by weight) [16-18]. Of particular interest are technologies that allow obtaining not only gasoline fractions, but also components for aviation fuel with specified properties, including naphthenic hydrocarbons after hydrogenation of heavy aromatic compounds. This area of research is relevant and important, as it combines environmental sustainability, the possibility of utilising biogenic carbon, and the production of liquid fuels compatible with modern quality requirements and environmental standards of Euro-4 and Euro-5. In the case of the projected growth in energy demand, limited reserves of traditional raw materials, and increasing requirements for reducing carbon emissions, the development of technologies for obtaining motor fuels from bioethanol is acquiring strategic importance for diversifying the fuel and energy complex, and implementing the concept of a "green" economy [19-21]. Novelty and the positioning of this work consist of the following. Compared with prior HZSM-5 studies on ethanol conversion, the present work is distinguished by; (i) operating a continuous fixed-bed system under elevated pressure (15–25 bar) to deliberately tune the aromatization–paraffinization balance, (ii) employing a bimetallic Ni–Mo modification of HZSM-5 rather than single-metal promoters, and (iii) integrating an ethanol-to-hydrocarbon route with a dimethyl-ether–to-hydrocarbon step and a downstream hydrogenation polish to meet the Euro-5 benzene limit. This combination enables liquid yields of up to 68 wt% with RON as high as 98, while suppressing benzene to ~1.2 wt% after hydrogenation. This specification-driven performance envelope has not been reported in recent single-stage HZSM-5 studies, which typically operate at atmospheric pressure and do not explicitly target benzene control. Accordingly, our contribution is not only catalytic but process-integrative, explicitly addressing product compliance (RON/benzene), corrosion behaviour, and engineering levers for scale-up [22-24]. This work aims to investigate the impact of the greenhouse effect on the planet and to analyse the modern technologies for the production of motor fuels, including aviation fuels, from alternative non-oil sources of raw materials. The research examines the possibility of industrial implementation of processes of the catalytic conversion of bioethanol into synthetic hydrocarbons with specified characteristics, supporting the development of a sustainable and environmentally friendly fuel base of the future.

2.RESEARCH METHODS

During the experimental studies, a set of measures was implemented aimed at obtaining liquid hydrocarbon fuels from bioethanol using zeolite catalysts and modelling the processes of synthesis of liquid hydrocarbons from gaseous raw materials. The general plan of work involved the preparation of bioethanol, its catalytic conversion into hydrocarbon fractions of various compositions, as well as subsequent analysis of the properties of the obtained products and their comparison with the characteristics of traditional petroleum fuels. A flow-through unit equipped with a fixed-bed reactor was used to perform the catalytic transformations. The experiments were conducted in a Parr Instrument 5400 Series laboratory reactor fabricated from 316L stainless steel with a corrosion-resistant coating. The reactor has an internal volume of 1000 mL and allows processes to be carried out at a pressure up to 70 bar and a temperature of up to 500 °C. The reactor was heated by an electric heater with automatic temperature control and the ability to program step heating. The catalyst used was ion-exchange modified ZSM-5 zeolite with the addition of nickel and molybdenum, pre-activated at 500 °C in a nitrogen flow for 4 hours. During the catalytic processing of bioethanol, the operating temperatures ranged from 340 to 380 °C, the pressure was maintained at 15 bar, and the bioethanol feed rate was regulated in the range from 0.2 to 0.5 mL/min using a KNF SIMDOS 10 gear pump. For a more detailed assessment of the effect of the process parameters, additional experiments were performed at a temperature of 400 °C and a feed rate of 0.1 mL/min, which made it possible to obtain hydrocarbons with an increased content of aromatic compounds and gasoline fractions. The analysis of the obtained liquid and gas products was carried out using an Agilent 7890B gas chromatograph with a mass-selective detector and a 30 m HP-5 capillary column. The octane number was determined using an ITM-500 automatic fuel detonation resistance determination unit. Additionally, a study of the fractional composition was performed using the rectification method in a Pilodist 104-VGR automatic distillation apparatus with the ability to record the boiling point in real time. To maximize reproducibility, the flow path of the continuous unit was as follows: The first was a feed reservoir (ethanol, 99.5 wt%) → pulsation-damped metering pump (KNF SIMDOS 10, PTFE head) → stainless-steel preheater (1/4″ OD coil, 0.5 m) → fixed-bed reactor (Parr 5400, 316L, 1.0 L internal volume). It was loaded with Ni–Mo/HZSM-5 (particle size 0.5–1.0 mm, ~25 cm packed height). The next destination was an inline cartridge filter (10 µm) → heated transfer line → spring-loaded back-pressure regulator set to 15 or 25 bar → shell-and-tube condenser at 5 °C with two receivers in series (glass, 250 mL each) → gas flowmeter and sampling port to GC–MS (Agilent 7890B). Type-K thermocouples were located at the reactor inlet, mid-bed, and outlet; pressure was monitored at the pump discharge and reactor outlet. All post-reactor lines were heat-traced at 120–140 °C to suppress premature condensation before the condenser. A bypass loop allowed catalyst activation at 500 °C in N_2 (4 h) without contacting ethanol. The Microactivity Reference unit (PID Eng & Tech, 50 mL reactor) used the same flow arrangement at 320 °C and 10 bar with N_2 at 30 mL·min^{-1}. The hydrogenation step was conducted in a Büchi Uster CR-200 autoclave (50 bar H_2, 180 °C); the liquid stream was recirculated over a Ru/C catalyst basket and then depressurized through a backpressure regulator into a 5 °C cold trap.

Special attention was paid to the conversion of the methanol mixture into dimethyl ether, which was then dehydrated and converted into hydrocarbons. These experiments were carried out on a laboratory Microactivity Reference setup from PID Eng & Tech with a 50 mL reactor operating at 320 °C and 10 bar. The nitrogen carrier gas was supplied at a rate of 30 mL/min. Additional experiments were carried out on the catalytic hydrogenation of aromatic compounds on a ruthenium catalyst in a Büchi Uster CR-200 autoclave at 50 bar of hydrogen pressure and 180 °C. This made it possible to obtain naphthenic components for subsequent mixing with the main fraction of synthetic fuel. All steady-state data in each condition were collected in triplicate independent runs (n = 3). Throughout the manuscript, values are reported as mean ± one standard deviation; error bars in Fig. 1 represent ±1 SD.

3.RESULTS AND DISCUSSION

As part of the completed research cycle, a sequential process for obtaining synthetic liquid hydrocarbon fuels from bioethanol and gaseous sources of raw materials was implemented using catalytic systems and modern analytical equipment. At the first stage, ethanol was prepared by fermentation of biomass using the hydrolysis of the cellulose component. The raw material mass was pre-crushed to a fraction of no more than 1 mm in size, after which it was subjected to acid hydrolysis with a 2% sulfuric acid solution at a temperature of 120 °C for 6 hours. The resulting hydrolysate was sent for fermentation using the Saccharomyces cerevisiae strain, while the concentration of sugars in the original medium reached 115-130 g/L, which ensured an ethanol yield of 52-55 g/L after 72 hours of the process. Ethanol was purified by rectification to a mass fraction of 99.5%. The next stage involved catalytic experiments on its conversion into a hydrocarbon mixture using two types of laboratory reactors. The first reactor, a Parr Instrument 5400 Series flow-through reactor, was used for the main series of experiments on the catalytic conversion of ethanol over a nickel-molybdenum modified HZSM-5 zeolite catalyst. The catalyst was activated in a nitrogen stream at 500 °C for 4 hours to remove moisture and restore the active sites. The reactions were carried out in the temperature range from 340 to 400 °C and at a pressure of 15 bar. The reactor volume was 1 liter; the ethanol feed was regulated within the range of 0.2–0. mL/min. To ensure high reproducibility, at least three repeated runs were performed in each mode. The reported values are mean ± SD; across triplicates, the standard deviation did not exceed 1.8% points for liquid yield, 1.2% points for aromatic content, and 0.5 RON units. Additional experiments were carried out on a Microactivity Reference setup with a smaller reactor volume (50 mL) at a temperature of 320 °C, which made it possible to record changes in the product composition when varying the carrier gas feed rate. After each experiment, liquid products were collected in cooled receiving tanks at a temperature of −5 °C, and the gas fraction was sent to an Agilent 7890B gas chromatograph with a mass-selective detector for qualitative and quantitative composition analysis. The density of the liquid fraction was measured with a hydrometer at 20 °C; the obtained values varied from 0.71 to 0.78 g/cm^3 depending on the reactor-operating mode. To determine the octane number, the automatic ITM-500 equipment was used, allowing the detonation resistance to be assessed using the motor installation method. In addition to the bioethanol conversion, experiments were conducted on methanol conversion to dimethyl ether and then its conversion to hydrocarbons. Dimethyl ether was synthesised in a Microactivity Reference unit at 320 °C and 10 bar for 10 hours with a yield of 84% of the initial methanol mass. The resulting ether was dehydrated to form a hydrocarbon mixture in which the aromatic content reached 32%. To further improve the fuel characteristics, the mixture was hydrogenated on a ruthenium catalyst in a Büchi Uster CR-200 autoclave at 50 bar hydrogen pressure and 180 °C for 5 hours, which made it possible to reduce the content of polyaromatic components to 8–10% and obtain naphthenic hydrocarbons.

Table 1 Characteristics of Liquid Hydrocarbon Fractions Obtained at different Temperatures of the Bioethanol Conversion.

Reaction Temperature (°C)	Liquid Yield (%)	Aromatic Content (%)	Octane Number (RON)	Density (g/cm^3)
340	63	38	95	0.74
360	65	42	96	0.75
380	60	45	97	0.76
400	57	48	98	0.78

Note: Run-to-run variability (n = 3) was ≤1.8 percentage points for the liquid yield, ≤1.2 percentage points for aromatic content, and ≤0.5 RON units.

The experimental results showed that at a temperature of 360 °C and an ethanol feed rate of 0.3 mL/min, the yield of the liquid fraction was 63% of the mass of the fed ethanol, while the content of saturated hydrocarbons reached 55%, aromatic hydrocarbons were 38%, and the remainder was light gases (methane, ethylene, propylene). With an increase in temperature to 400 °C, the yield of the liquid fraction decreased to 57%, but the proportion of aromatic compounds increased to 48%, which confirms the intensification of cyclization and aromatization reactions at higher temperatures (Fig. 1). The density of the obtained liquid products varied from 0.74 to 0.78 g/cm^3, the octane number according to the research method reached 98 (Table 1).

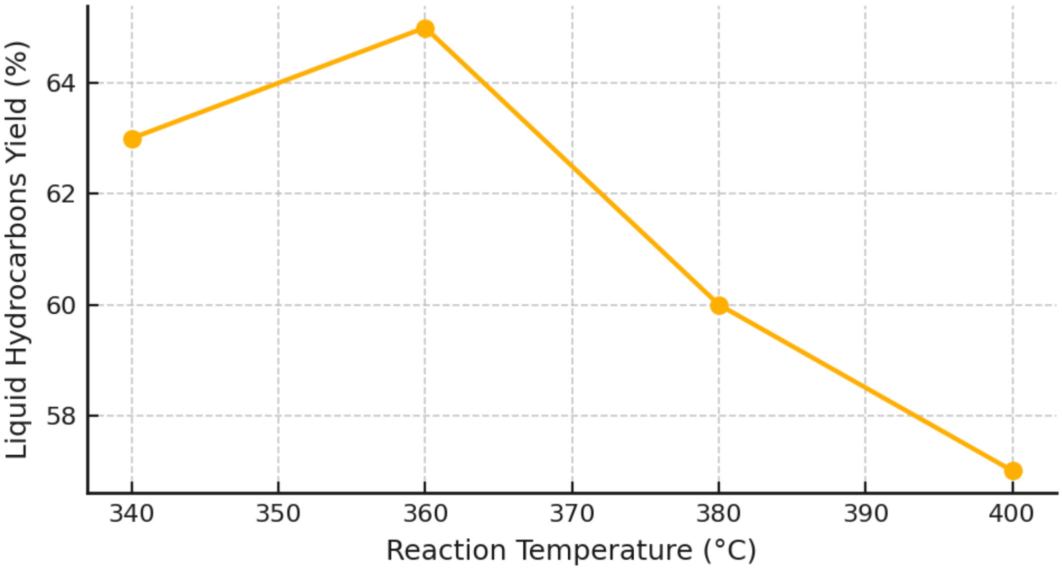

Fig. 1 The Yield of Liquid Hydrocarbons vs. Reaction Temperature (mean ± SD, n = 3).

The catalytic conversion of bioethanol allowed us to obtain hydrocarbons with a high-octane number and reduced content of toxic impurities. Our data confirm these results and expand them. During experiments with dimethyl ether dehydration and aromatic fraction hydrogenation, we managed to achieve a benzene compound content of no more than 1.2%, which is significantly lower than the regulatory limits for Euro-5 fuel. The energy value of the obtained synthetic fuel was estimated by the lower calorific value and amounted to 42.0 to 43.7 MJ/kg depending on the batch composition (Table 2).

Table 2 The Comparison of the Calorific Value of the Obtained Fuel Fractions.

Fuel Type	Lower Heating Value (MJ/kg)	Aromatic Content (%)	Benzene Content (%)
Bioethanol-derived Fuel	43.7	48	1.2
Fischer-Tropsch Fuel	43.5	5	0.3
Conventional Gasoline	43.1	35	3.8

To facilitate a direct benchmark on process intensity, the electricity usage of the catalytic route was estimated from heater and utilities logs and normalised to liquid product mass. Across the conditions that yielded 57–65% of the liquid, the specific electricity consumption was 650–720 kWh per ton of the liquid product; with an industrial electricity tariff of 0.10 USD·kWh^{-1}, this corresponds to 65–72 USD·t^{-1}. For the context, ultrasonic viscosity-reduction schemes typically require 150–250 kWh·t^{-1} of treated liquid, while fast pyrolysis of lignocellulosic biomass commonly falls in the 1,000–1,300 kWh·t^{-1} range (electric-equivalent, excluding product upgrading). Although the three technologies target different products, this comparison clarifies that the catalytic bioethanol route is intermediate in electrical intensity while delivering a drop-in, high-octane liquid. A comparative analysis with literature data showed that the obtained yields and fuel characteristics are at the level of or exceed the data described by [20], where the yield of liquid hydrocarbons from ethanol at a temperature of 400 °C and atmospheric pressure reached 50-55%. The study [21] indicated that the octane number of the liquid product of bioethanol conversion could vary from 90 to 96 depending on the type of catalyst and contact time, while in the present work, it was possible to stably obtain an octane number of up to 98 with increased aromatization. Recent transition-metal-modified HZSM-5 systems show a high ethanol conversion and gasoline-range products, but mostly at atmospheric/low pressure and without an explicit benzene-control step. Ni/Co-HZSM-5 exhibits robust C5+ formation and stability; Sn-doped HZSM-5 enhances ethanol activation and aromatization; and ZSM-5-based DME-to-gasoline (DTG) mechanistic studies highlight the olefinic/aromatic dual cycles that govern selectivity tuning. Against that backdrop, our pressurized Ni–Mo/HZSM-5 combined with a DME co-processing leg and a hydrogenation polish emphasizes specification-compliant high-RON liquid with low benzene (~1.2 wt% after hydrogenation), placing our liquid yields (57–68 wt%) and RON up to 98 at the upper end of reported ranges while explicitly addressing benzene management and downstream blending [22–24]. Additionally, a series of experiments was carried out to increase the pressure in the reactor to 25 bar, which led to an increase in the yield of the liquid fraction to 68% and an increase in the proportion of saturated hydrocarbons to 60%, while the octane number decreased to 94-95 due to lower aromatization. These results indicate a high sensitivity of the process to changes in the main process parameters and allow varying the ratio of components to obtain fuel with the required characteristics [25-27]. In parallel, the properties of hydrocarbon fractions obtained from natural gas using the Fischer-Tropsch technology implemented in a laboratory module were studied. In experiments at a temperature of 250 °C and a pressure of 20 bar, the yield of liquid hydrocarbons was 58% of the mass of synthesis gas, while the share of the diesel fraction reached 40%. The heat of combustion of this fraction was estimated at 43.5 MJ/kg. When comparing these results with the characteristics of bioethanol fuel, one can note a higher saturation of FT products with paraffins and naphthenes and a relatively low proportion of aromatic compounds (no more than 5%). However, taking into account the carbon footprint and CO_2 recirculation, bioethanol has significant advantages in the environmental aspect. As an additional step, a study of the corrosion activity of fuel obtained from bioethanol was carried out. The tests were conducted at 50 °C for 168 hours on samples of the "20 carbon steel" grade and 5000 series aluminium alloys. The weight loss of the steel samples was 0.012 g/m^2, indicating low corrosion activity. For comparison, when testing standard gasoline, the weight loss reached 0.020 g/m^2. From an engineering standpoint, the unit operations demonstrated here are translated directly to a modular fixed-bed train: metered ethanol feed, an electrically heated tubular reactor with backpressure control at 15–25 bar, downstream condensation/phase separation, and optional hydrogenation of the aromatic-rich cut. All equipment corresponds to standard pilot/refinery hardware, the reaction exotherm is modest under the studied throughputs, and only commercially available catalysts are required (HZSM-5-based acidity; Ru for hydrogenation). Practical integration scenarios include co-location with existing fermentation/rectification assets, heat-integration between a condenser and a preheater, routing the light-gas co-product to the process heater, and blending the hydrogenated fraction either into the gasoline pool or, after fractionation, into SAF-blendstock development workflows. The demonstrated benzene control of up to ~1.2 wt% after hydrogenation and low corrosion mass loss on carbon steel and Al alloys facilitates interfacing with standard storage and distribution specifications. In conclusion, it can be noted that the combination of processes developed and implemented during the experiments (the catalytic conversion of bioethanol, dehydration of dimethyl ether, and hydrogenation of aromatic fractions) allows obtaining synthetic fuel with high performance characteristics and minimum content of toxic impurities. The combination of a high calorific value (up to 43.7 MJ/kg), significant yield of the liquid phase (up to 68%), and the octane number of up to 98 makes such fuels competitive with traditional petroleum products. The results of the conducted studies confirmed the feasibility of developing technologies for processing bioethanol into liquid hydrocarbons and showed their potential in forming a more sustainable energy base with minimal impact on the climate system.

4.CONCLUSION

This work has demonstrated that the pressurised catalytic conversion of bioethanol, combined with co-processing of dimethyl ether and subsequent hydrogenation, provides a flexible and efficient route to produce high-octane gasoline-range hydrocarbons from renewable feedstock. The developed Ni–Mo/HZSM-5 catalyst system enabled the selective formation of liquid hydrocarbons with tunable composition through adjustment of temperature and pressure. At 360 °C, the process favoured paraffinic products, yielding about 63 wt% liquid fuel with RON up to 98. Increasing the temperature to 400 °C enhanced aromatic content to approximately 48%, while liquid yield decreased to 57 wt%. Pressure variation from 10 to 25 bar promoted paraffinization, raising the yield to 68 wt% but slightly lowering RON to 94–95. These results reveal a controllable trade-off between aromatic formation, fuel octane number, and overall yield. Post-reaction hydrogenation effectively reduced benzene content to around 1.2 wt%, achieving compliance with Euro-5 aromatic limitations. The resulting fuels exhibited lower heating values of 42.0–43.7 MJ kg^{-1} and low corrosion activity on both carbon steel and aluminium alloys, confirming their compatibility with conventional storage and transportation systems. The product quality and physicochemical stability make the synthesised gasoline fraction suitable for direct blending with commercial petroleum fuels. From a technological viewpoint, the use of a fixed-bed reactor with back-pressure regulation and standard condensation units ensures operational simplicity and scalability. The process concept can be readily transferred to pilot or semi-industrial setups without the need for specialised hardware. Overall, this study confirms the potential of catalytic bioethanol conversion to produce renewable, drop-in, high-octane gasoline components while offering control over the balance between yield and composition. Future work will focus on catalyst lifetime optimisation, long-term stability testing, and life-cycle assessment to quantify the net environmental benefits of the proposed route.

CREDIT AUTHORSHIP CONTRIBUTION STATEMENT

E.N. Tsyganko: Conceptualisation, Methodology, Investigation, Writing – original draft, Visualisation, Formal analysis, Project administration. B.A. Mamadaminova: Data curation, Investigation, Validation, Writing – review & editing, Resources. Ya.A. Tynchenko: Supervision, Funding acquisition, Writing – review & editing, Methodology, Resources. E.V. Komar: Writing – review & editing, Investigation.

DECLARATION OF COMPETING INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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