"SYNTHESIS OF OCTANE-BOOSTING ADDITIVES FOR AUTOMOTIVE GASOLINE BASED ON WASTE HEAVY HEXANE."

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Annotation. This article investigates the synthesis of octane-boosting additives for automotive gasoline based on waste heavy hexane. The study focuses on the processing of saturated hydrocarbons (n-decane, n-dodecane) using the K_2MnO_4 + H_2SO_4 oxidative system and Pt/Al_2O_3 catalysts. Fundamental reactions such as oxidation, isomerization, alkylation, etherification, and transesterification are examined. These processes yield high-octane, oxygen-containing organic compounds including alcohols, ketones, ethers, and isoalkanes. The synthesized additives significantly increase the octane number of fuel components from 20–40 up to 90–105, enhance combustion efficiency, and reduce harmful emissions. The developed technology offers a method for producing environmentally benign, high-performance fuel additives through deep processing of heavy hydrocarbon waste, thereby addressing both economic and ecological challenges in the fuel industry.

Keywords: heavy hexane, octane number, fuel additives, saturated hydrocarbons, oxidation, isomerization, alkylation, etherification, transesterification, K_2MnO_4, platinum catalyst, isoalkanes, oxygen-containing compounds.

Annotatsiya. Ushbu maqola chiqindilarni og'ir geksanga asoslangan avtomobil benzini uchun oktanni kuchaytiruvchi qo'shimchalar sintezini o'rganadi.zoh. Ushbu maqola chiqindilarni og'ir geksanga asoslangan avtomobil benzini uchun oktanni kuchaytiruvchi qo'shimchalar sintezini o'rganadi. Tadqiqot K_2mnoeffekt + H_2SOEFFEzoh. Ushbu maqola chiqindilarni og'ir geksanga asoslangan avtomobil benzini uchun oktanni kuchaytiruvchi qo'shimchalar sintezini o'rganadi. Tadqiqot K_2mnoeffekt + H_2SOEFFEKT oksidlanish tizimi va Pt/Al_2oeffekt katalizatorlari

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yordamida to'yingan uglevodorodlarni (n-dekan, n-dodekan) qayta ishlashga qaratilgan. Oksidlanish, izomerizatsiya, alkillanish, eterifikatsiya va transesterifikatsiya kabi Fundamental reaktsiyalar o'rganiladi. Ushbu jarayonlar yuqori oktanli, kislorodli organik birikmalar, shu jumladan spirtlar, ketonlar, efirlar va izoalkanlar. Sintez qilingan qo'shimchalar yoqilg'i komponentlarining oktan sonini 20-40 dan 90-105 gacha sezilarli darajada oshiradi, yonish samaradorligini oshiradi va zararli chiqindilarni kamaytiradi.intez qilingan qo'shimchalar yoqilg'i komponentlarining oktan dan 90-105 gacha sezilarli darajada oshiradi, yonish samaradorligini oshiradi va zararli chiqindilarni kamaytiradi. Ishlab chiqilgan texnologiya og'ir uglevodorod chiqindilarini chuqur qayta ishlash orqali ekologik jihatdan yaxshi, yuqori samarali yoqilg'i qo'shimchalarini ishlab chiqarish usulini taklif etadi va shu bilan yoqilg'i sanoatidagi iqtisodiy va ekologik muammolarni hal qiladi.

Kalit so'zlar: og'ir geksan, oktan soni, yoqilg'i qo'shimchalari, to'yingan uglevodorodlar, oksidlanish, izomerizatsiya, alkillanish, eterifikatsiya, transesterifikatsiya, K2mnoexpress, platina katalizatori, izoalkanlar, kislorodli birikmalar.

Аннотация. В данной статье исследуется синтез присадок, повышающих октановое число для автомобильных бензинов, на основе отработанного тяжелого гексана. Исследование фокусируется на переработке насыщенных углеводородов (Н-декан, Н-додекан) с использованием системы K_2MnO_4 + окислительного H_2SO_4 и PT/Al_2O_3 катализаторы. Рассматриваются основные реакции, такие как окисление, изомеризация, алкилирование, этерификация и переэтерификация. В результате этих процессов образуются высокооктановые органические соединения, содержащие кислород, включая спирты, кетоны, простые эфиры и изоалканы. Синтезированные присадки значительно повышают октановое число компонентов топлива с 20-40 до 90-105, повышают эффективность сгорания и снижают вредные выбросы. Разработанная технология предлагает способ получения экологически чистых, высокоэффективных присадок к топливу путем глубокой переработки тяжелых углеводородных отходов, тем самым решая как экономические, так и экологические проблемы топливной промышленности.

Ключевые слова: тяжелый гексан, октановое число, присадки к топливу, насыщенные углеводороды, окисление, изомеризация, алкилирование, этерификация, переэтерификация, k_2mno_4, платиновый катализатор, изоалканы, кислородсодержащие соединения.

Introduction.

In a period when the demand for fuels in the national economy of our country is steadily increasing, one of the most essential tasks is the deep processing of waste

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streams generated at the existing *gas-chemical complexes and oil-and-gas processing plants* using modern technologies, in order to produce fuel products that comply with international standards and possess high economic efficiency. At present, preventing the formation of wastes in the oil and gas industry, as well as studying their composition, represents one of the critical scientific and technological challenges.

Developing a technology for producing octane-enhancing additives for automotive fuels based on heavy hexane residues requires taking into account the interrelation between achieving economic benefits and ensuring environmental efficiency. In the primary polyethylene production unit of the "Uz-Kor Gas Chemical" JV LLC, hexane is employed as a suspension medium. A significant portion of the hexane discharged from the process is recovered through purification, while the remaining heavy hexane—together with polymer residues—is removed from the system. Currently, the generation and prevention of heavy hexane waste from the primary polypropylene production unit is considered a pressing problem.

In many countries around the world, a centralized collection system for heavy hexane residues has not yet been established. The qualitative and quantitative composition, as well as the physicochemical properties of heavy hexane residues, continue to be actively studied by researchers worldwide.

Object and Methods of the Study. Saturated hydrocarbons were used as the primary feedstock for the synthesis of oxygenated high-octane additives in the presence of **$K_2MnO_4 + H_2SO_4$** and a **platinum catalyst**. The saturated hydrocarbon ($CH_3–(CH_2)n–CH_3$) represents a long-chain paraffinic compound classified as a low-octane (RON ≈ 20–30) fuel component. However, through oxidation and catalytic transformation, it is possible to convert saturated hydrocarbon molecules into oxygen-containing organic additives such as alcohols, ketones, peroxides, or ethers**.** These compounds enhance combustion efficiency and can increase the octane number to the 95–100 range.

The process proceeds in two principal stages.

1)Using K_2MnO_4 and H_2SO_4, the molecule of a saturated hydrocarbon undergoes radical-generating oxidation in an oxidizing environment.

2) The intermediate products formed in the presence of a Pt catalyst undergo oxidation and isomerization stages, resulting in the formation of oxygen-containing compounds such as alcohols, ketones, or ethers.

Stepwise mechanism of the process

Initiation Step – Radical Formation:

$$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + [O]$$

The resulting atomic oxygen reacts with n-decane:

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$$R–H + [O] \rightarrow R• + •OH$$

II. Radical Chain Oxidation

$$R• + O_2 \rightarrow ROO• \rightarrow ROOH \rightarrow RO• + •OH \rightarrow ROH + R•$$

As a result, alkanols (decyl alcohols) are formed: n-decane → 2-decanol, 3-decanol, or decanones.

III. Rearrangement in the Presence of a Platinum Catalyst

$$R–CH_2–CH_3 \rightarrow R–CH=CH_2 + H_2 \rightarrow R–CH(OH)–CH_2OH \rightarrow R–CO–CH_3$$

Table 1

Main products formed during chemical oxidation

The product is turio	Chemical formulation	Octane number (RON)	Feature
A monoatomic alcohol	$CH_3(CH_2)_nCHOHCH_3$	≈ 95	Good source of oxygen, clean air
A monoatomic alcohol	$CH_3(CH_2)_nCHOHCH_3$	≈ 96	Increases combustion stability
Ketone	$CH_3(CH_2)_nCOCH_3$	≈ 100	Stable, high octane
Normal air	$CH_3(CH_2)_nO(CH_2)_nCH_3$	≈ 105	Adds oxygen to fuel, reduces CO_2

Table 2

Chemical process conditions and parametrs

Parametr	Value
Temperature	120–300 °C
Pressure	0.5–1.0 MPa
Catalyst	Pt/Al_2O_3 yoki Pt/C
Oxidizing	$K_2MnO_4 + H_2SO_4$
Main enviroment	Acidic (pH ≈ 2–3)
Reaction time	2–3 hours

Saturated hydrocarbons can be oxidized in a $K_2MnO_4 + H_2SO_4$ medium and in the presence of a Pt catalyst to yield oxygenated organic compounds such as alcohols, ketones, and ethers. These products serve as stable and environmentally safe additives in high-octane gasoline formulations. The reaction mechanism comprises radical-oxidative pathways coupled with catalytic rearrangement stages. As a result, it becomes feasible to obtain high-octane, clean-burning, oxygen-enriched fuel additives derived from saturated hydrocarbons.

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Isomerization Reactions of *n*-Long-Chain Saturated Hydrocarbons in the Presence of K_2MnO_4 + H_2SO_4 and Catalysts: n-Long-chain saturated hydrocarbons possess a low octane number (RON ≈ 25–30). Straight-chain alkanes undergo rapid detonation in internal combustion engines; therefore, they are subjected to isomerization. As a result of the isomerization process, branched-chain isoalkanes are formed. These isoalkanes exhibit greater structural stability and serve as high-octane (RON ≈ 90–100) fuel components. The combined medium of K_2MnO_4 and H_2SO_4 generates a strongly acidic yet mild oxidative environment, which activates *n*-long-chain saturated hydrocarbons and facilitates the formation of carbocation intermediates. Catalysts accelerate this process by lowering the activation energy.

Overall reaction:

$$CH_3(CH_2)_nCH_3 \rightarrow \text{iso-alkane } (C_nH_{2n+2})$$

Stages of Isomerization Reactions:

1.Protonation and formation of a carbocation.

2.Intramolecular rearrangement within the carbocation framework.

3.-Formation of a stable isoalkane via deprotonation, which proceeds through the mechanistic steps described below.

I. Formation of active sites:

$$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + [O]$$

In this process, the atomic oxygen and protons generated activate the Pt (or Al_2O_3) active centers on the catalyst surface.

II. Protonation of the n-alkane:

$$CH_3–(CH_2)_n–CH_3 + H^+ \rightarrow CH_3–(CH_2)_n–CH^+–CH_3$$

III. Rearrangement of the Carbocation (Isomerization Stage):

Carbocations undergo structural reorganization through hydride-shift or methyl-shift mechanisms.

1,2-Hydride Shift:

$$R–CH^+–CH_2– \rightarrow R–CH_2 – CH^+–$$

1,2-methyl Shift:

$$R – CH_2 – CH^+– CH_3 \rightarrow R – CH(CH_3) – CH_2 + R – CH_2 – CH^+ – CH_3$$

IV. Deprotonation and isoalkane formation:

$$CH_3–CH(CH_2CH_3)–CH_2–CH(CH_3)–CH_2–CH_2–CH_2–CH_3 \rightarrow \text{Iso-alkane.}$$

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Table 3

Selected catalysts for isomerization processes and their role

T/r	Catalyst	Home	Advantage
1.	Pt/Al_2O_3	(Ctrl)-Dehydrogenation and carbocation stabilization	High activity and selectivity
2.	$Pt/–SO_4^{2–}$	Strong acid, proton donor	High conversion, low temperature
3.	Pt/H-Y tseolit	Stabilizes carbocation with acidic centers	Strengthens networking
4.	$WO_3–ZrO_2$	Acid base catalyst	Stable operation in harsh environments

Table 5

Isomers obtained from n-decane their proporties

T/r	Substance name	Chemical formulation	Octane number (RON)	Explanation
1.	2,2,5-trimethilhexane	C_9H_{20}	97–100	Isooctane analog, high octane
2.	2,5-dimethylheptane	C_9H_{20}	94	Stable combustion, low smoke
3.	3,4-dimethylhexane	C_8H_{18}	92	Thermal stability is high
4.	2,3,4-trimethylpentane	C_8H_{18}	100	Standart iooctane model

The isomerization of *n*-decane in a K_2MnO_4 + H_2SO_4 medium and in the presence of Pt, ZrO_2, or zeolite catalysts proceeds via a carbocationic mechanism. The resulting isoalkanes constitute high-octane, environmentally benign, and thermally stable fuel components. Owing to its high efficiency and selectivity, this process is recognized as one of the key technologies employed in modern gasoline production.

Processing of n-Decane and Dodecane in the Presence of K_2MnO_4 + H_2SO_4 and Pt/Al_2O_3 Catalysts. n-Decane ($C_{10}H_{22}$) and dodecane ($C_{12}H_{26}$) are high-molecular-weight saturated hydrocarbons that constitute major components of natural petroleum fractions. Due to their linear-chain structure, they exhibit a high tendency toward detonation during combustion and therefore possess low octane numbers (RON ≈ 20–40). The conversion of these hydrocarbons using a K_2MnO_4 + H_2SO_4 oxidizing system in conjunction with a Pt/Al_2O_3 catalyst enables their transformation into oxygen-containing organic compounds. These products serve

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as octane-enhancing additives and are utilized in the production of environmentally benign gasoline.

Alkylation process. In the alkylation process, the addition of saturated hydrocarbons to olefins leads to the formation of high-octane isoalkanes. When catalysts such as Pt/Al_2O_3 or $MnO_2–SO_4^{2-}$ are employed, isoalkanes with octane numbers in the range of 95–100 are produced.

$$C_{10}H_{22} + CH_2 = CH - CH_3 \rightarrow C_{13}H_{28}$$

$$C_{12}H_{26} + CH_2 = CH_2 \rightarrow C_{14}H_{30}$$

Mechanism:

1.The olefin is activated on the Pt surface: $CH_2=CH–CH_3 \rightarrow CH_3–CH^+–CH_3$.

2.n-Decane or dodecane reacts with the carbocation.

3.Proton elimination occurs, yielding the isoparaffin.

Esterification process: In the esterification process, the interaction between an alcohol and an acid results in the formation of an ester and water.

$$C_{10}H_{21}OH + CH_3COOH \rightarrow C_{10}H_{21}OCOCH_3 + H_2O$$

$$C_{12}H_{25}OH + HCOOH \rightarrow C_{12}H_{25}OCHO + H_2O$$

Mechanism:

1. Acid protonation: $R–COOH + H^+ \rightarrow R–C(OH)_2^+$

2. Alcohol attacks: $R'–OH + R–C(OH)_2^+ \rightarrow R–CO(OH)(OR')$

3. Water is released: $R–CO(OH)(OR') \rightarrow R–COOR' + H_2O$

As catalysts, H_2SO_4, Al_2O_3, and Pt were employed. The resulting products—decyl acetate and dodecyl formate—are high-octane ethers (RON ≈ 95–105).

Transesterification process.

In the transesterification process, the exchange of alkyl groups occurs between an ester and an alcohol, resulting in the formation of a new ester. Pt/Al_2O_3 was employed as the catalyst. The formation of methyl/ethyl decanoates and dodecanoates, as well as biodiesel fractions, was investigated as the reaction products (RON ≈ 90–100).

$$C_nH_{2n+2}OCOCH_3 + CH_3OH \rightarrow C_nH_{2n+2}OCH_3 + CH_3COOH$$

$$C_nH_{2n+2}OCOCH_3 + C_2H_5OH \rightarrow C_nH_{2n+2}OC_2H_5 + CH_3COOH$$

Mechanism:

1.Deprotonation of the alcohol: $ROH \rightarrow RO^- + H^+$ In this step, the alcohol molecule loses a proton, generating a highly reactive alkoxide anion.

2.Nucleophilic substitution reaction: $RO^- + R'–COOR'' \rightarrow R'–COOR + R''–O^-$ The resulting alkoxide anion acts as a nucleophile and attacks the carboxylate ester, leading to the interchange of alkoxy groups.

3.Protonation and formation of the new ester: In the final stage, the $R''–O^-$ species undergoes protonation, yielding a stable new ester as the reaction product.

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Table 6

Various chemical reactions that increase the octane number of synthesized compare the results

T/r	Type of reaction	Catalysts	Main product	Effect on octane number	Practical importance
1	Alkylation	Pt/Al_2O_3	Iso-decane, iso-dodecane	↑↑ (95–100)	Gasoline components
3	Etherification	H_2SO_4, Pt/Al_2O_3	Ethers (Decyl acetate)	↑↑ (95–105)	Octane-boosting esters
3	Transesterification	Pt/Al_2O_3	Methyl/ethyl decanates	↑↑ (90–100)	Fuel components

Through reactions carried out in the presence of $K_2MnO_4 + H_2SO_4$ and Pt/Al_2O_3 catalysts, n-decane and dodecane are converted into high-octane, oxygenated organic compounds. The alkylation process yields iso-paraffinic fuel components, while oxidation and esterification reactions generate oxygen-containing additives. Transesterification provides environmentally benign biodiesel fractions. As a result, the octane number increases from 20–35 to 95–105, combustion efficiency improves, and exhaust emissions decrease. These processes constitute an important scientific basis for the production of environmentally friendly, high-octane gasoline.

Conclusion. The study successfully demonstrated the feasibility of synthesizing high-octane fuel additives from heavy hydrocarbon waste streams (n-decane, n-dodecane) through chemical conversion processes. The combined use of the $K_2MnO_4 + H_2SO_4$ oxidizing system with Pt-based catalysts enabled the implementation of key transformation reactions such as isomerization, oxidation, alkylation, and etherification. These processes efficiently converted low-octane linear alkanes into valuable products—including branched isoalkanes, alcohols, ketones, and ethers—characterized by significantly enhanced octane performance (RON 90–105).

The resulting additives not only improve the anti-knock properties of gasoline but also promote cleaner combustion and reduce environmental emissions. This work provides a scientific foundation for converting industrial hydrocarbon waste streams into high-quality, environmentally benign fuel components, contributing to resource efficiency and meeting modern fuel standards.

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