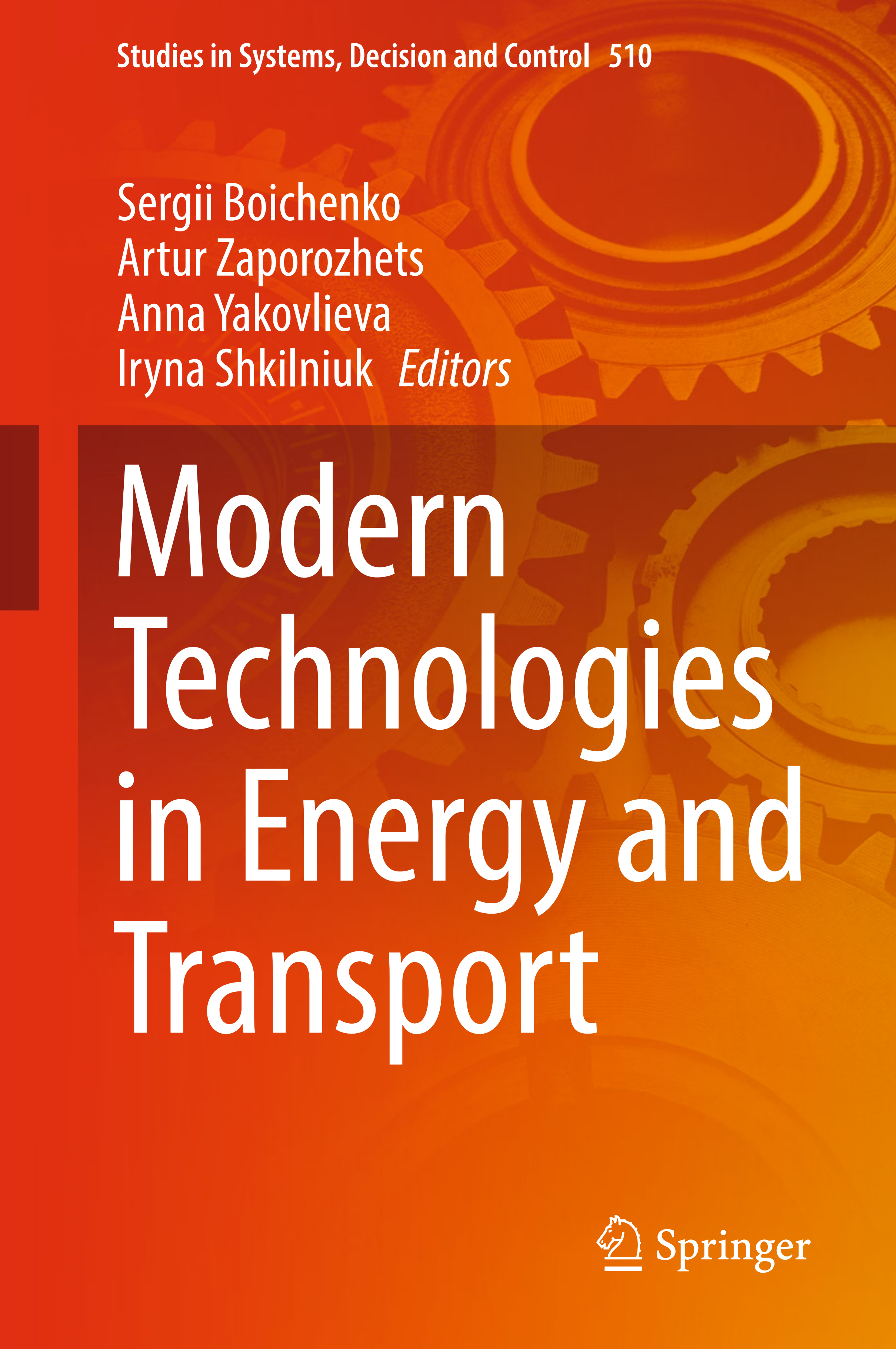


Studies in Systems, Decision and Control 510

Sergii Boichenko
Artur Zaporozhets
Anna Yakovlieva
Iryna Shkilniuk *Editors*

Modern Technologies in Energy and Transport

Springer

Studies in Systems, Decision and Control

Volume 510

Series Editor

Janusz Kacprzyk, Systems Research Institute, Polish Academy of Sciences, Warsaw, Poland

The series “Studies in Systems, Decision and Control” (SSDC) covers both new developments and advances, as well as the state of the art, in the various areas of broadly perceived systems, decision making and control–quickly, up to date and with a high quality. The intent is to cover the theory, applications, and perspectives on the state of the art and future developments relevant to systems, decision making, control, complex processes and related areas, as embedded in the fields of engineering, computer science, physics, economics, social and life sciences, as well as the paradigms and methodologies behind them. The series contains monographs, textbooks, lecture notes and edited volumes in systems, decision making and control spanning the areas of Cyber-Physical Systems, Autonomous Systems, Sensor Networks, Control Systems, Energy Systems, Automotive Systems, Biological Systems, Vehicular Networking and Connected Vehicles, Aerospace Systems, Automation, Manufacturing, Smart Grids, Nonlinear Systems, Power Systems, Robotics, Social Systems, Economic Systems and other. Of particular value to both the contributors and the readership are the short publication timeframe and the world-wide distribution and exposure which enable both a wide and rapid dissemination of research output.

Indexed by SCOPUS, DBLP, WTI Frankfurt eG, zbMATH, SCImago.

All books published in the series are submitted for consideration in Web of Science.

Sergii Boichenko · Artur Zaporozhets ·
Anna Yakovlieva · Iryna Shkilniuk
Editors

Modern Technologies in Energy and Transport

Springer

Editors
Sergii Boichenko
National Technical University of Ukraine
“Igor Sikorsky Kyiv Polytechnic Institute”
Kyiv, Ukraine

Anna Yakovlieva
Technical University of Košice
Košice, Slovakia

Artur Zaporozhets
General Energy Institute of NAS of Ukraine
Kyiv, Ukraine

Iryna Shkilniuk
National Technical University of Ukraine
“Igor Sikorsky Kyiv Polytechnic Institute”
Kyiv, Ukraine

ISSN 2198-4182 ISSN 2198-4190 (electronic)
Studies in Systems, Decision and Control
ISBN 978-3-031-44350-3 ISBN 978-3-031-44351-0 (eBook)
https://doi.org/10.1007/978-3-031-44351-0

© The Editor(s) (if applicable) and The Author(s), under exclusive license to Springer Nature Switzerland AG 2024

This work is subject to copyright. All rights are solely and exclusively licensed by the Publisher, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilms or in any other physical way, and transmission or information storage and retrieval, electronic adaptation, computer software, or by similar or dissimilar methodology now known or hereafter developed.
The use of general descriptive names, registered names, trademarks, service marks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.
The publisher, the authors, and the editors are safe to assume that the advice and information in this book are believed to be true and accurate at the date of publication. Neither the publisher nor the authors or the editors give a warranty, expressed or implied, with respect to the material contained herein or for any errors or omissions that may have been made. The publisher remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

This Springer imprint is published by the registered company Springer Nature Switzerland AG
The registered company address is: Gewerbestrasse 11, 6330 Cham, Switzerland

Paper in this product is recyclable.

Preface

The world today is facing an urgent need to transform its energy system. Global energy consumption continues to grow—around 1–2% per year. Global energy consumption will grow by just 1,3% in 2023, amid a slowing economy and high energy prices. Global climate changes will determine implementation of newer, stricter regulations, which will force companies to mitigate their impact on environment. They will need to cut energy waste and even shift to alternative electricity sources.

Energy sector development is also driven by changing customer demands. Consumers have started asking for sustainable alternatives. In the energy sector, alternative energy carriers are gaining great importance, in transport—Alternative Motor Fuels (AMF), in aviation, in particular—Sustainable Aviation Fuels (SAF).

Modern technologies in the energy sector are necessary for a variety of reasons, including climate change, increasing the availability of safe and affordable energy, and the growing use of renewable energy sources. Transport is a unique sector of the economy, not only contributing to socio-economic development but also generating external costs. The increasing number of vehicles used in road transport in the world, depletion of fossil fuel resources, and environmental concerns have all contributed to the search for alternative solutions to be implemented as innovative energy technologies in road transport.

Many industries are implementing changes and focusing on creating more sustainable environments, from solar power, energy storage, electric vehicles to innovative heat pumps, hydrogen technologies, smart electricity grids, and more alternatives for coal, oil, and gas.

Providing a balance between three key aspects of energy trillem—energy safety, acceccability, and environmental stability is the most important task during the development of energy strategies. One of the effective methods of solving the trillem's tasks on the world's scale is international collaboration and integration. They are the key to revealing unused potential of energy resources, natural routes of energy transfer, and possibilities for its storage, in particular in the transport sector.

Chemmotology became responsible for providing integrity in solving numerous tasks of energy trillem. From the philosophical point of view, we can state that exactly this science plays consolidating function of systematic integrative communication of scientists and practicians of energy, machine building, chemical engineering, oil processing, and petrochemical industries along with exploitants of equipment for solving evolution tasks of scientific-technical progress.

The book "Modern Technologies in Energy and Transport" selectively represents the chemmotological aspects of the energy and transport sector development and operation. It is devoted to the advances in the development of the transport and energy sector, the relevant problems of rational use of conventional and alternative fuels and lubricants, their quality control, and environmental aspects of the modern transport and energy sector operation. Authors have systemated unique works by scientists and practicians worldwide on questions of the rational use of AMF, SAF, alternative energy in the energy sector and transport of economy.

This book comprises selected outstanding papers presented at the IX International Scientific-Technical Conference, "Theory and Practice of Rational Use of Traditional and Alternative Fuels and Lubricants." This event was held in Kyiv, Ukraine, during July 3–7, 2023. The Conference is a traditional event, which gathers researchers, scientists, practicians, and academics in the fields of chemmotology, aviation, transport engineering, environmental safety, recycling and utilization, chemical engineering, energy saving and energy efficiency, and sustainable development from all over the world. Traditionally, the main aim of the conference is meeting of qualified specialists capable of solving tasks of any level of complexity in the field of chemmotology, exchange of experience and information, discussion of issues and options for their solution, development of intellectual potential for knowledge management with the aim of turning it into intellectual capital, ensuring the most effective results through a holistic and adequate approach to solving modern problems in the key Conference's fields, integration of the experience of the older generation and young scientists, as well as the support of qualitative research and development of new technologies aimed at increasing the rational use of fuels & lubricants, technical liquids, and additives.

The book is composed of 15 chapters in total. All chapters presented by the authors (co-authors) are published in the author's edition and aim to present an issue on how to achieve more sustainable and more environmentally safe development of the modern transport and energy sector. The chapters are grouped into three parts. Part I "Decisions for Alternative Energy Sources Use in Modern Transport" represents novel solutions in alternative energy sources development and implementation in different spheres of the modern transport sector. Part II "Solutions for Reducing Negative Impact of Energy and Transport on Environment" is devoted to advances in technologies aimed at reducing the impact of energy and transport sectors on environment and utilization of waste. Part III of the book "Advance in Alternative Motor Fuels Technology" represents recent developments in chemical technology of alternative fuel production and aspects of modern fuel quality control.

This book will be interesting and useful for the professional career of operators of air transport, jet fuels suppliers, professionals in the sphere of transport environmental safety, alternative fuel manufacturers at oil processing plants, experts in chemical technology, energy production and supply, producers of fuels, lubricants and fuel additives, aviation fuel handling companies, etc. The book will be also interesting for researchers at all stages of careers.

The contributions of the authors and reviewers and the assistance of conference organizers in the preparation of this book are sincerely appreciated.

Kyiv, Ukraine	Sergii Boichenko
Kyiv, Ukraine	Artur Zaporozhets
Košice, Slovakia	Anna Yakovlieva
Kyiv, Ukraine	Iryna Shkilniuk
June 2023	

Contents

Decisions for Alternative Energy Sources Use in Modern Transport

Solutions for Reducing Negative Impact of Energy and Transport on Environment

Advance in Alternative Motor Fuels Technology

Decisions for Alternative Energy Sources Use in Modern Transport

Econometrics of the Functional Connection of the Price and Reliability of Hybrid Aircraft Technology

Pavol Kurdel, Natália Gecejová, Marek Češkovič, and Mária Gamcová

1 Introduction

For many high-quality and innovative hybrid systems, the cost of implementation into the currently used aviation technology and practice is too high [1–3]. For this reason, it is crucial to streamline the quality of research into alternative flying devices and to look for research methods in dichotomous states of precise measurement of the elements of a given hybrid system. In research, this issue can be conceptually classified among intelligent transport systems in the group of polyergatic systems. The new direction and monitoring of the dependence between price and reliability must reflect the principles of targeted efficiency in the meta-principles that are the criteria for their development [4, 5]. These principles consider the individual econometric stages in implementing such an alternative element in hybrid air transport vehicles [6]. The solution is possible by exemplary development and modelling of econometric situations within the framework of intelligent technologies of hybrid air transport vehicles covering non-trivial physical platforms. In principle, the reciprocity of the distribution of artificial or natural targets is accepted, which is an information source for evaluating the quality of the given means of transport. This means that the introduction of new elements of hybrid air transport means also includes the processes of managing the process itself. Together, they create a connection linked to the limits of comprehensive flight safety [1, 3].

Alternative air transport complexes still have a limited range of applicability in operation due to the aspects of flight safety and efficiency. In analyzing the effectiveness and safety of ergative alternative elements in hybrid flying systems, significant

---

P. Kurdel · N. Gecejová (✉) · M. Češkovič
Faculty of Aeronautics, Technical University of Košice, Košice, Slovakia
e-mail: natalia.gecejova@tuke.sk

M. Gamcová
Faculty of Electrical Engineering and Informatics, Technical University of Košice, Košice, Slovakia

S. Boichenko et al. (eds.), *Modern Technologies in Energy and Transport*, Studies in Systems, Decision and Control 510, https://doi.org/10.1007/978-3-031-44351-0_1

concepts represent inputs to the operational use analysis itself. From the position of a systemic approach, it is a method characterized by complex polyergatic systems. Increasing the reliability of systems is conditioned by another monitored aspect, namely the growth of financial expenses. With a known volume of funds intended for designing reliable alternative systems, the price and reliability of individual elements can be predicted [6, 7]. It is also clear that prices and reliability are affected by the effects of random inputs. The conditions also limit price and reliability, time of use, and the progress of science and technology when the element was implemented in research.

2 Methodical Ways of Evaluating the Reliability and Price of Hybrid Aircraft Technologies

Ways of methodological procedures to the rating of alternative aircraft systems are determined by correlation with existing elements without the degree of replacement by the alternative. Econometrics has been proven to make it possible to create marginal restrictions of financial and reliability indicators with the help of analyzes and evaluations [6–9]. For example, comparative analysis and evaluation of a particular used system for economic and physical indicators may not be sufficient to draw conclusions about the quality of an alternative element on an aircraft. In the evaluation process, such an alternative aircraft system is considered, in which we will work with inputs and outputs, as shown in the following figure (Fig. 1).

In the case defined in this way, the following methods can be used:

- Economic efficiency–it is used to process economic information from observing the behaviour of an alternative element and belongs to the group of analysis methods of elimination. Elimination represents the exclusion of the influence of a whole range of factors except for one of them [8].
- The index method determines the influence of individual factors on synthetic indicators, which are made up of a combination of quantitative and qualitative indicators in air transport [8, 9].

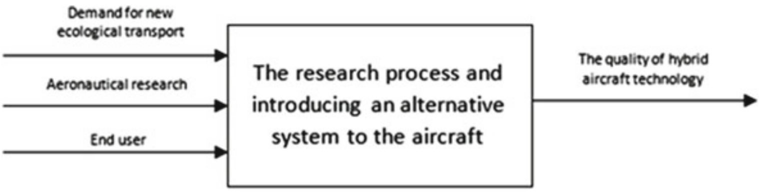


Fig. 1 Graphical representation of inputs and outputs in the process of the research of alternative aircraft system

For example, the value index (l_h) of the basic research price (1) can be expressed as the product of the price index (l_c) and the physical volume index (l_{fo}) spent on the research [7]:

$$l_h = l_{fo} l_c \tag{1}$$

The change of value index elements can be calculated as (2):

$$\Delta l_h = \Delta_{q1} \cdot p_1 - \Delta_{q0} \cdot p_o \tag{2}$$

where q_0—represents a number of alternative elements hypothetically implemented on the aircraft; q_1—represents a number of alternative elements really implemented on the aircraft; p_0—average price per element in the hypothetical case; p_1—average price per element in the real case.

The given Eqs. (1) and (2) point out that a change in two factors causes any change in the synthetic indicator, in the given case, a change in the physical amount of system elements and the average price spent on operational-research implementation.

This indicator indicates whether or not an alternative system element constitutes economic added value when the aircraft is put into service. Reliability indicators' advantage is that they do not work with the cost item for basic and ongoing research. It is used in controlling cases where it is impossible to work with the amounts spent on experimentation [7]. The calculation is based on the fact that there is a correlation between value creation and the selected quantitative variables in Eq. (3):

$$IN = \frac{-0.017A}{CZ} + \frac{4.573EBIT}{A} + \frac{0.481V}{A} + \frac{0.015A}{(KZ + KFV)}, \tag{3}$$

where A—assets; CZ—foreign sources; $EBIT$—hybrid aircraft earnings are assumed; V—revenues from the hybrid aircraft; KZ—short-term liabilities to design offices; KFV—financial assistance (projects) for research and implementation of model structures.

The resulting rating of the hybrid aircraft using the IN index is as follows:

- $IN \geq 2.070$—the hybrid aircraft create value;
- $1.420 \leq IN < 2.070$—the hybrid aircraft rather creates value;
- $1.089 \leq IN < 1.420$—cannot determine whether or not a hybrid aircraft creates value;
- $0.684 \leq IN < 1.089$—the hybrid aircraft tend not to create value;
- $IN < 0.684$—the hybrid aircraft does not create value.

From the calculated values from the established alternative systems with multidimensional statistics of the movement of their financial costs, a model will be created to classify new elements for alternative aircraft systems involved in this process. The system of influence and significance of the most important indicators of the final value of such a hybrid aircraft is checked using regression models:

- Determining patterns of change and productivity on the volume of the money invested in alternative resource deployment research;
- Identifying the area of effectiveness, considering the forecast estimation of the functioning of such aircraft in the future (time series analyse, Markov processes).

Research into the functional effectiveness of alternative options usable in aviation refers to the investigation and evaluation of dependencies between two or more quantitative statistical features, which are problematic in the context of applying new technological systems to a hybrid aircraft. The essence of this research is a deeper penetration into the problems of the monitored elements and processes of the given alternative. Causal dependence occurs when the occurrence of a certain state causes the existence of another state of effectiveness. In economic and aviation practice, the problems are much more complicated when the occurrence of a certain condition is related to the occurrence of another, or rather it is related to the existence of a group of problematic conditions, which results in the onset of another condition and the like.

There are two types of dependencies, the so-called fixed and free dependencies [8]. If the occurrence of one condition is clearly associated with the occurrence of another condition, we are talking about a fixed, i.e., functional dependence of research activities during the testing of an alternative system. From a probabilistic point of view, it is a relationship that will occur with certainty, i.e., with a probability of 1. In such a case, the value of another variable is assigned to each variable. In real practice, we often encounter the second type of dependence, the so-called free dependence, especially when researching an unknown phenomenon manifested in an alternative system introduced into a hybrid aircraft. If this dependence refers to quantitative statistical features, it is also referred to as statistical dependence. In these cases, a unit change in one variable causes a change in the other variable. The method of regression and correlation analysis or the correlation coefficient is used to recognize and mathematically describe the statistical dependence between quantitative statistical signs [6–8].

The linear regression line is thus defined as (4):

$$Y = \beta_0 + \beta_1 X. \tag{4}$$

At the same time, the point of the estimation is (5):

$$y_j = b_0 + b_1 x_j, \tag{5}$$

where: b_0—locate constant; b_1—regression coefficient; y_j—theoretical value of the dependent variable; x_j—value of the independent variable.

The locate constant can be expressed by an Eq. (6):

$$b_0 = \frac{\sum_{i=1}^{n} x_1^2 \sum_{i=1}^{n} y_1 - \sum_{i=1}^{n} x_1 \sum_{i=1}^{n} x_i y_i}{n \sum_{i=1}^{n} x_i^2 - \left(\sum_{i=1}^{n} x_i\right)^2}. \tag{6}$$

If the regression coefficient is known so (7):

$$b_0 = \frac{\sum_{i=1}^{n} y_i - b_i \sum_{i=1}^{n} x_i}{n} = \overline{y} - b_1 \overline{x}. \tag{7}$$

While the regression coefficient can be expressed by an Eq. (8):

$$b_1 = \frac{n \sum_{i=1}^{n} x_i y_i - \sum_{i=1}^{n} x_i \sum_{i=1}^{n} y_i}{\sum_{i=1}^{n} x_i^2 - \left(\sum_{i=1}^{n} x_i\right)^2}. \tag{8}$$

The correlation index is expressed by an Eq. (9):

$$i_{yx} = \sqrt{\frac{\sum_{i=1}^{n} (y_i - \overline{y})}{\sum_{i=1}^{n} (y_i - \overline{y})}}. \tag{9}$$

And the determination index is expressed by an Eq. (10):

$$i^2 = 1 - \frac{\sum_{i=1}^{n} (y_i - \overline{y})^2}{\sum_{i=1}^{n} (y_i - \overline{y})^2}. \tag{10}$$

3 Methodology of Solving the Issue of Linking the Reliability and Price of a Hybrid Aircraft Technology

The problem described above can be solved using a suitable statistical method, thanks to which the link between price and reliability can be found. The solution is possible by accepting the conditions:

- increasing the reliability of alternative systems conditions the growth of financial costs, thus increasing the price of the system and its elements;
- functional reciprocity between price and reliability has a monotonous expression;
- the mathematical connection of price and reliability accepts functional links in both its manifestations.

The stated conditions are satisfied by Eq. (11), which defines the reciprocity of price and reliability of alternative systems:

$$C = \frac{k_1}{q^{k_2}} = k_1 q^{-k_2} \tag{11}$$

where C—total price of the system; q—probability of a system failure.

The coefficients k_1 and k_2 are calculated using Eqs. (12) and (13):

$$k_1 = Cq_1{}^{k_2}; \tag{12}$$

$$k_2 = \frac{\log_{10}(C_2) - \log_{10}(C_1)}{\log_{10}(q_1) - q_2}, \tag{13}$$

where k_1—price drop coefficient in case of failure of the alternative system; k_2—coefficient of price growth in the event of a failure on one alternative system in independently separated functions or the event of a failure of two elements in an alternative system; C_1, C_2—conventional and real values of the prices of the two alternative systems; q_1, q_2—conventional or real values of the probability of failures of two alternative systems and their elements.

For more systems (elements) than two, we consider the mean values. Consider a hybrid aircraft complex that has $N = 12$ new alternative elements. Probabilities of qi disturbances are known. The price of system C is known, as well as the price of the *i*-th element. The prices of the *i*-th elements will make it possible to calculate the coefficients $\mathrm{k}_{1\mathrm{i}}$, $\mathrm{k}_{2\mathrm{i}}$, $\mathrm{i} = 1;2;\ldots;12$.

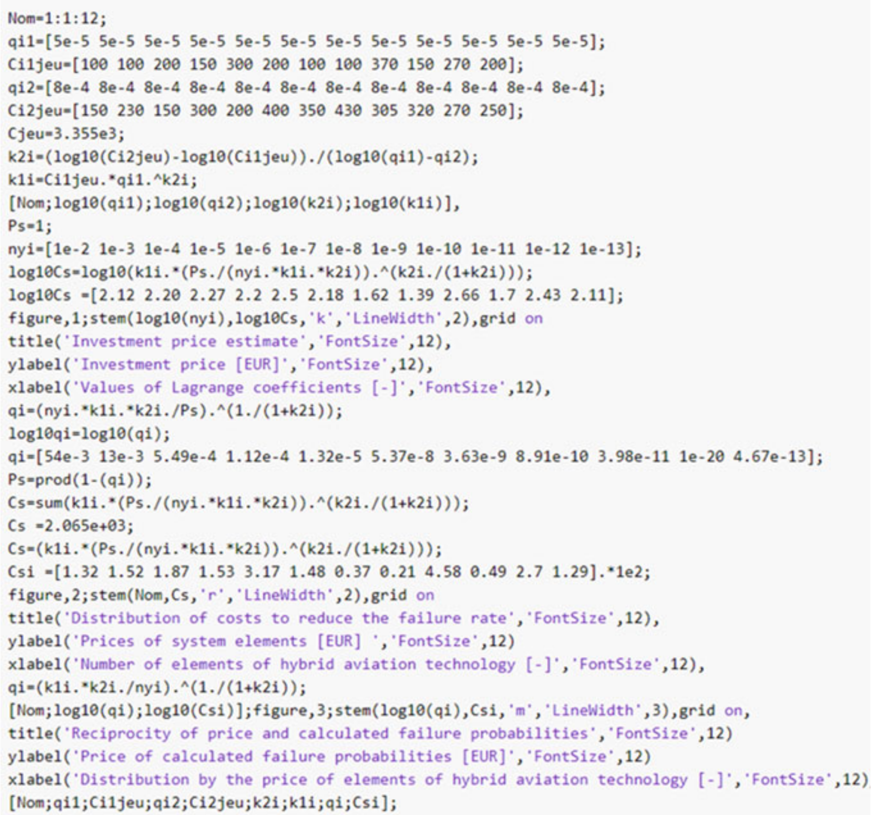
The final task is the calculation of the maximum achievable reliability probability of the hybrid aircraft complex with the given parameters and their optimal distribution among the system elements in comparison with the price of the given hybrid aircraft technology. The Matlab environment was used for calculation, and statistical evaluation (Fig. 2), and the input data represented statistically collected data from the manufacturer of alternative hybrid systems.

The manufacturer did not grant permission for the presentation of specific values but allowed the reproduction of the results in graphic form after creating a statistical evaluation complex linking the price and reliability of hybrid technology with regard to the costs incurred for research, implementation and subsequent use of aircraft technology in flight conditions (Figs. 3, 4 and 5).

The difference between the desired and existing probability of failure represents a significant reduction. Such a development trend, however, requires a reasonable increase in investments, which in the model is a decrease in the Lagrange coefficient. In such a case (Fig. 5):

4 Conclusions

The character of the presented method applies a priori because it is practically impossible to obtain absolute values of output characteristics from alternative elements. It allows the designers and technicians of hybrid aircraft or their subsequent end users to create an idea of the financial burden when switching to new technologies. Costs are often the limiting factor in optimizing the reliability and efficiency of electrical systems in aircraft. The presented method has no basis in legislation, and it is not covered by regulations. For this reason, the only criterion for its application is flight



```
Nom=1:1:12;
qi1=[5e-5 5e-5 5e-5 5e-5 5e-5 5e-5 5e-5 5e-5 5e-5 5e-5 5e-5 5e-5];
Ci1jeu=[100 100 200 150 300 200 100 100 370 150 270 200];
qi2=[8e-4 8e-4 8e-4 8e-4 8e-4 8e-4 8e-4 8e-4 8e-4 8e-4 8e-4 8e-4];
Ci2jeu=[150 230 150 300 200 400 350 430 305 320 270 250];
Cjeu=3.355e3;
k2i=(log10(Ci2jeu)-log10(Ci1jeu))./(log10(qi1)-qi2);
k1i=Ci1jeu.*qi1.^k2i;
[Nom;log10(qi1);log10(qi2);log10(k2i);log10(k1i)],
Ps=1;
nyi=[1e-2 1e-3 1e-4 1e-5 1e-6 1e-7 1e-8 1e-9 1e-10 1e-11 1e-12 1e-13];
log10Cs=log10(k1i.*(Ps./(nyi.*k1i.*k2i)).^(k2i./(1+k2i)));
log10Cs =[2.12 2.20 2.27 2.2 2.5 2.18 1.62 1.39 2.66 1.7 2.43 2.11];
figure,1;stem(log10(nyi),log10Cs,'k','LineWidth',2),grid on
title('Investment price estimate','FontSize',12),
ylabel('Investment price [EUR]','FontSize',12),
xlabel('Values of Lagrange coefficients [-]','FontSize',12),
qi=(nyi.*k1i.*k2i./Ps).^(1./(1+k2i));
log10qi=log10(qi);
qi=[54e-3 13e-3 5.49e-4 1.12e-4 1.32e-5 5.37e-8 3.63e-9 8.91e-10 3.98e-11 1e-20 4.67e-13];
Ps=prod(1-(qi));
Cs=sum(k1i.*(Ps./(nyi.*k1i.*k2i)).^(k2i./(1+k2i)));
Cs =2.065e+03;
Cs=(k1i.*(Ps./(nyi.*k1i.*k2i)).^(k2i./(1+k2i)));
Csi =[1.32 1.52 1.87 1.53 3.17 1.48 0.37 0.21 4.58 0.49 2.7 1.29].*1e2;
figure,2;stem(Nom,Cs,'r','LineWidth',2),grid on
title('Distribution of costs to reduce the failure rate','FontSize',12),
ylabel('Prices of system elements [EUR] ','FontSize',12)
xlabel('Number of elements of hybrid aviation technology [-]','FontSize',12),
qi=(k1i.*k2i./nyi).^(1./(1+k2i));
[Nom;log10(qi);log10(Csi)];figure,3;stem(log10(qi),Csi,'m','LineWidth',3),grid on,
title('Reciprocity of price and calculated failure probabilities','FontSize',12)
ylabel('Price of calculated failure probabilities [EUR]','FontSize',12)
xlabel('Distribution by the price of elements of hybrid aviation technology [-]','FontSize',12)
[Nom;qi1;Ci1jeu;qi2;Ci2jeu;k2i;k1i;qi;Csi];
```

Fig. 2 Example of a computing program for the analysis of the connection between price and reliability of hybrid aircraft technology in the Matlab environment

safety and protection, which increases with the rate of reduction in the failure rate of alternative elements of hybrid technology.

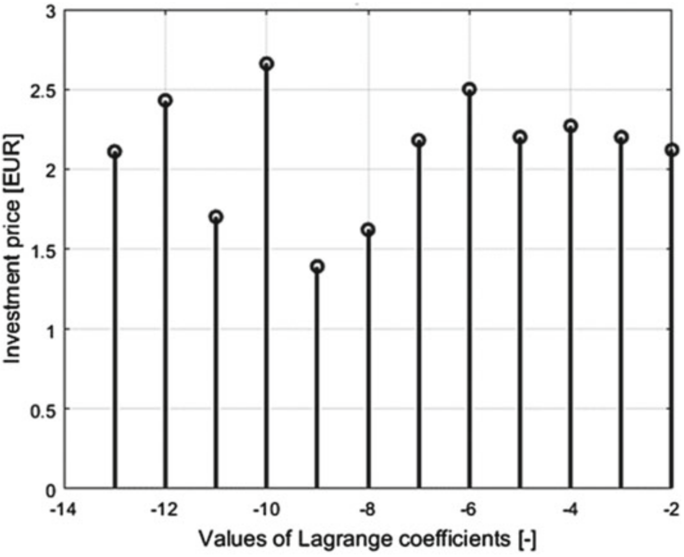


Fig. 3 The estimated cost of research into alternative elements of hybrid aircraft technology

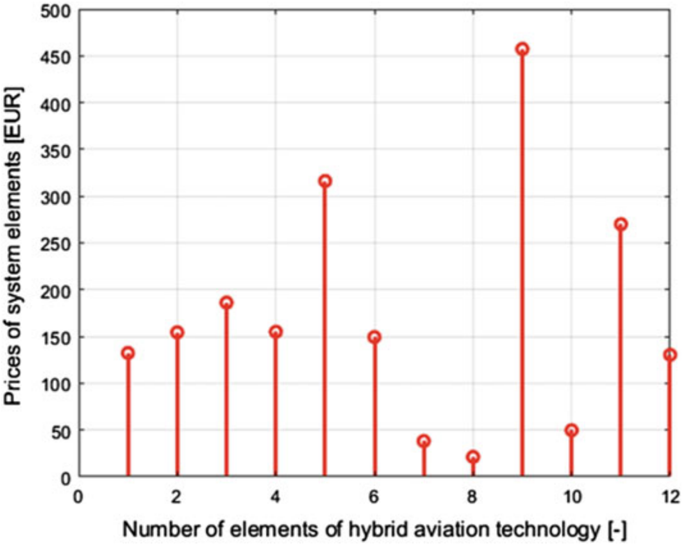


Fig. 4 Graphical representation of the price distribution of components implemented in hybrid aircraft technology with a reduced failure rate

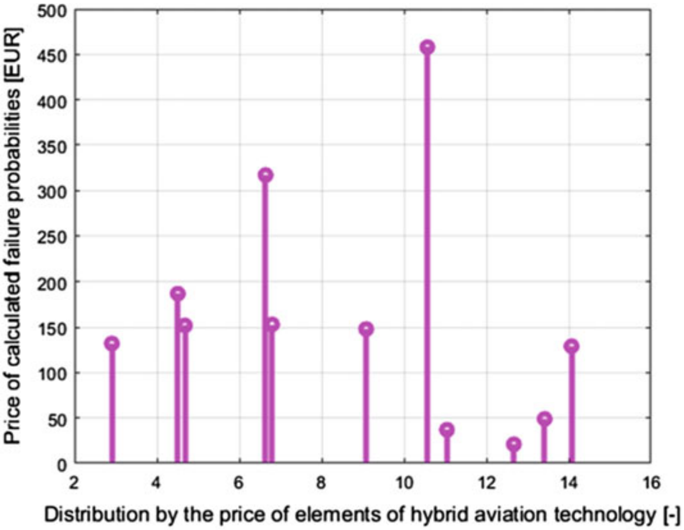


Fig. 5 Reciprocity of the price and calculated failure probabilities of the hybrid aircraft technology

Acknowledgements This work was supported by the Scientific Grant Agency (VEGA) of the Ministry of Education, Science, Research and Sport of the Slovak Republic under the contract No. 1/0584/20.

References

1. Xie, Y., Savvarisal, A., Tsourdos, A., Zhang, D., Gu, J.: Review of hybrid electric powered aircraft, its conceptual design and energy management methodologies. Chin. J. Aeronaut. **34** (2021). https://doi.org/10.1016/j.cja.2020.07.017
2. Friedrich, C., Robertson, P.A.: Hybrid-electric propulsion for automotive and aviation applications. CEAS Aeronaut. J. **6** (2014). https://doi.org/10.1007/s13272-014-0144-x
3. Pornet, C., Kaiser, S., Gologan, C.: Cost-based flight technique optimization for hybrid energy aircraft. Aircr. Eng. Aerosp. Technol. **84** (2014). https://doi.org/10.1108/AEAT-05-2014-0075
4. Boggero, L., Fioriti, M., Corpino, S.: Development of a new conceptual design methodology for parallel hybrid aircraft. J. Aerosp. Eng. **233** (2017). https://doi.org/10.1177/0954410017745569
5. Rendón, M.A., Sánchez, C.D., Gallo, J., Anzai, A.H.: Aircraft hybrid-electric propulsion: development trends, challenges and opportunities. J. Control, Autom. Electric. Syst. **32** (2021). https://doi.org/10.1007/s40313-021-00740-x
6. White, W.H.: How useful are econometric models? Finance Dev. **6** (1969). https://www.elibrary.imf.org/view/journals/022/0006/001/article-A004-en.xml?ArticleTabs=fulltext
7. Gorajek, A.: Econometric interpretations of index numbers. In: International Association for Research in Income and Wealth, vol. 12 (2021). https://iariw.org/wp-content/uploads/2021/08/gorajek_paper.pdf

8. Intriligator, M.D.: Chapter 3 Economic and econometric models. In: Handbook of Econometrics, vol. 7, (2020). https://doi.org/10.1016/S1573-4412(83)01007-7
9. Gorajek, A.: Capturing the impact of fuel price on jet aircraft operating costs with Leontief technology and econometric models. Transp. Res. **33** (2013). https://doi.org/10.1016/j.trc.2011.05.015

Implementation Research of Alternative Fuels and Technologies in Maritime Transport

Oleksiy Melnyk, Svitlana Onyshchenko, Oleg Onishchenko, Oleksandr Shumylo, Andrii Voloshyn, Valentyna Ocheretna, and Oleksandr Fedorenko

1 Introduction

Ships are considered one of the strongest sources of environmental pollution. Fuel oil which is the most popular fuel for ships contains on average 3,5% of sulfur compounds. For comparison, the content of sulfur impurities in gasoline and diesel of Euro-5 environmental class cannot exceed 0.001% of the total product weight. But IMO Sulfur 2020–the resolution adopted by the International Maritime Organization, which regulates the content of sulfur components in fuels for river and sea transport–not more than 0,5%, which fundamentally changes the situation on the market of oil products for the shipping industry.

Thus works [1, 2] devoted to the analysis of cost competitiveness of alternative maritime fuels in the new regulatory framework and impact of alternative fuels on the optimal economic ship speed. In works [3–5] carbon–neutral maritime fuels production, fueling options in the maritime sector and life cycle of greenhouse gas emission assessment reviewed. Marine fuel emissions tracking along with advances in research on alternative marine fuels and future trends reviewed in [2, 6–8]. In paper [9], energy consumption of a new re-liquefaction system integrated with the Fuel Supply System (FSS) for a liquefied natural gas carrier is analyzed in comparison with conventional systems. The concept of hydrogen as a marine fuel and the possibility of transferring LNG experience to hydrogen systems was investigated in [10]. In [11–13] application of alternative maritime power port supply, knowledge gaps about offshore hybrid power plants based on fuel cells and alternative fuels as well as recent trends in the use of environmentally friendly ammonia as an energy carrier in the maritime

---

O. Melnyk (✉) · S. Onyshchenko · O. Shumylo · A. Voloshyn · V. Ocheretna · O. Fedorenko
Odesa National Maritime University, Odesa, Ukraine
e-mail: m.onmu@ukr.net

O. Onishchenko
National University “Odesa Maritime Academy”, Odesa, Ukraine

S. Boichenko et al. (eds.), *Modern Technologies in Energy and Transport*, Studies in Systems, Decision and Control 510, https://doi.org/10.1007/978-3-031-44351-0_2

industry considered. Potential alternative fuel pathways and the use of alternative fuels for maritime decarbonization researched in [14–16]. Issues related to effective safety of ship operation process in different conditions and under the influence of different factors are considered in [17–21, 23–26, 29]. Technical and operational measures to reduce greenhouse gas emissions and improve the environmental and energy efficiency of ships studied in [22]. Modeling the dynamics of the structure of the organization's development project portfolio proposed in [27, 28]. Study of environmental efficiency of ship operation in terms of freight transportation effectiveness provision and assessment of ship information security risks proposed in [30, 31]. The model of organization of the container feeder line is focused on the nature and parameters of external container flows and the development of line shipping is studied in [32, 33]. The study of the stability of economic indicators of complex port equipment use and optimization of the structure of the seaport equipment park under unbalanced workload is proposed in [34, 35]. Additional questions about the future of marine fuels, comparison and perspective, and exploration of alternative fuels and technology for greener shipping are explored in [36–38].

Thus, due to the growing demands for the use of low-carbon energy sources, alternative fuels have become widespread. The new energy sources presented are also subject to the requirements of conventional fuels used and those on the energy market, namely quality, reliability and sustainability, and are of interest for further comprehensive study.

2 Overview of Existing Alternative Fuels for the Marine Industry

Maritime transport accounts for about 11% of the world's total fuel consumption, or about 10 million barrels per day. It is an important fact that in the current situation of competition between alternative fuels, seagoing ships largely set the trend in favor of one fuel or another. Significant volumes of fuel consumption by maritime transport justify mass production of refined products, construction of fuel bases and infrastructure in general, setting the course for a certain type of fuel and betting on it in other segments of the market. Thus, after the ban on the use of heavy fuel oil from 2024, only diesel oil will remain possible. This is an opportunity for the maritime transport industry to reconsider its position before that date and to take more active steps to adapt to the new standards, in the context of the review of alternatives, among others. Undoubtedly, for making a decision on choice of priority fuel for international shipping more accurate and thorough researches on estimation of ecological footprint from alternative fuels use, starting from raw materials extraction to emissions. A separate issue is the assessment of consequences from spills of alternative fuels, which requires laboratory and field studies of spills, especially at low temperatures, high wind speeds, etc. Of additional interest is the degree of long-term environmental

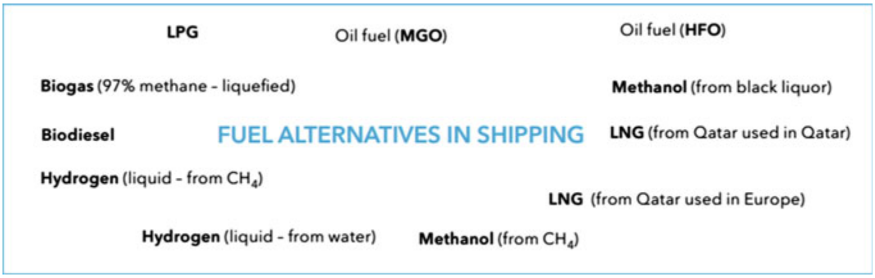


Fig. 1 Main types of alternative marine fuels

impact of blends of alternative fuels with the aquatic environment. Main types of alternative marine fuels presented in Fig. 1.

To date, LNG and sulfur fuel oil have beaten all of their competitors on price, but that does not mean that LNG will remain the leader for long. The recent gas price hike will inevitably force shipowners to think about the feasibility of gas fuel rates. It should be noted that one of the problems, which has not been solved yet, is the bunkering of ships. At present, LNG production projects are already being successfully implemented, which can serve as a source of LNG bunkering for transport ships. Nowadays, LNG bunkering can be performed by both mobile and stationary bunkers. Onshore, truck-to-ship (TTS) bunkering is used for relatively small amounts of LNG, up to 200 cubic, while port-to-ship (PTS) bunkering is used for larger volumes. Specialized LNG bunkers are used for refueling ships of various sizes and can have a capacity of up to 20,000 cubic meters, including LNG fuel for very large container ships enroute between Asia and the European Union. LNG bunkering is currently available at more than 120 ports around the world, with more than 30 LNG bunkering vessels in operation. Advantages and disadvantages of LNG fuel presented in Table 1.

3 Analysis of the Environmental Impact and Cost of Alternative Fuels

According to DNV GL, the use of LNG emits the least greenhouse gases the major ones are water vapor, carbon dioxide, methane, and ozone. However, unburned methane, which is the main component of LNG, creates emissions with 20 times more powerful greenhouse effect than carbon dioxide (carbon dioxide).

Nevertheless, according to assurances of producers of dual-fuel engines, the amount of unburned methane in modern equipment is not so large, and their use gives a reduction of greenhouse gases in shipping by 10–20%.

The carbon footprint (the amount of greenhouse gases caused by the activities of organizations, the actions of cargo transportation) from the use of methanol or hydrogen is much greater than with heavy fuel (HFO) and marine gasoil (MGO).

Table 1 Advantages and disadvantages of LNG fuel

Advantages of LNG fuel	Disadvantage of LNG fuel
The cleanest fuel is liquefied natural gas, as it produces the least amount of greenhouse gases	LNG has a higher specific energy content than fuel oil, but the energy content per unit volume is only 43% that of high sulfur fuel oil. Therefore, fuel tanks take up 3–4 times more space compared to ships operating on conventional fuel
LNG has been used as a fuel for ships since the early 2000s, so the technology is already quite mature and there are many suppliers on the market, which helps keep prices down	Bunkering problems. The general reluctance to introduce LNG-fueled engines into the shipping industry has been due in part to logistical difficulties. Liquefied natural gas for marine engines can still only be found in a limited number of ports around the world, which does not suit most players
Piston engines, gas turbines and their consumables, as well as special cryogenic fuel systems for LNG, are produced on an industrial scale and are freely available	Often ships have long itineraries in which the next point is not predetermined, which means fuel must be available at any port. Therefore, companies often take a wait-and-see approach to new technology

With renewable energy and biofuels, the carbon footprint is smaller. The most environmentally friendly fuel is hydrogen, produced from renewable energy. Liquid hydrogen can be used in the future. However, it has a rather low volumetric energy density, which leads to the need for large storage sites.

In terms of nitrogen emissions, Otto cycle internal combustion engines powered by LNG or hydrogen do not need exhaust treatment equipment to meet the Tier III standard. In most cases, dual-fuel diesel-cycle engines are not suitable to meet the standard.

The Tier III standard refers to the limitation of nitrogen oxides (NOx) emissions for LNG or hydrogen-fueled ships to reduce the environmental impact of shipping. For internal combustion engines with an Otto cycle running on LNG or hydrogen, NOx emission limits are set at 3.4 g/kWh.

To achieve the Tier III standard for Otto-cycle internal combustion engines fuelled by LNG or hydrogen, various technologies must be used to reduce NOx emissions, such as a catalytic converter, exhaust gas recirculation systems, high-temperature combustion systems, etc. In general, to achieve Tier III for Otto-cycle internal combustion engines running on LNG or hydrogen, many different technologies are required to reduce NOx emissions, which can make these engines less harmful to the environment.

For example, the Tier III standard refers to the limitation of nitrogen oxides (NOx) emissions for ships using diesel internal combustion engines. This standard was introduced to reduce the environmental impact of shipping, in particular air pollution. To meet the Tier III standard, marine engines must use various technologies to reduce NOx emissions, such as water injection systems to reduce combustion temperatures, catalytic converters, exhaust gas recirculation systems, and others. For new vessels

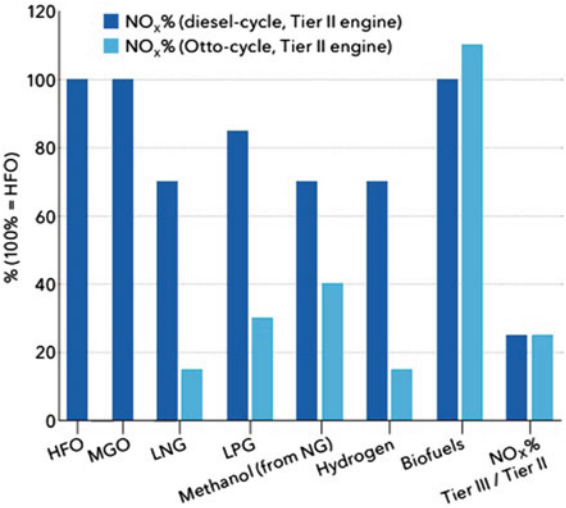


Fig. 2 Nitrogen emissions from different fuels Source: DNV GL

built after January 1, 2016 and having engines with a capacity of more than 130 kW, Tier III compliance is mandatory. For ships built before January 1, 2016, the Tier III standard is optional, but may be applied on a voluntary basis. Data of nitrogen emissions from different fuels presented in Fig. 2.

The price of implementation is not the main criterion for choosing a particular technology, but the price of fuel is. It depends on several factors, including the hard-to-predict ones. For example, according to sources, the lowest price in the previous decade is observed on HFO. Only LNG and LPG can compete with it. The price of methanol produced from natural gas is higher than that of LNG. Biofuels are produced from biomass and are traditionally more expensive than Brent oil. These fuels are likely to compete with MGO in the future. Dispersion of prices for possible marine fuels given in Fig. 3.

Hydrogen is not considered here because it is much more expensive than other fuels. It is completely uncompetitive on the market in terms of price. It will have a chance only with significant subsidies or high taxes on conventional fuel. Speaking about fuel production, it is worth noting that all fuels except LNG would require significant investments if the decision is made to use one or the other on a mass scale. LNG production is much higher than the fuel needs of the global fleet, so switching to it is possible today.

4 Conclusions

Environmental concerns and rising fuel prices lead to the need to find new solutions for shipping. There are not many alternatives. At the same time the legislation has already determined the conditions for the use of LNG, followed by methanol and

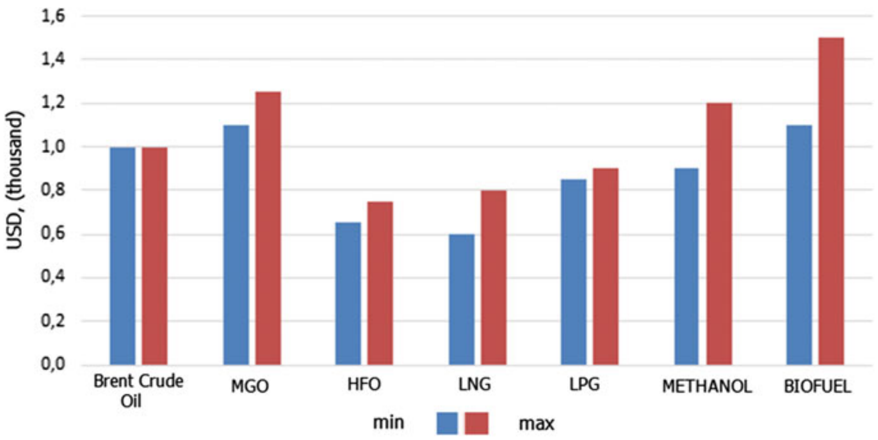


Fig. 3 Qualitative dispersion of prices for possible marine fuels (*Source* DNV GL, IEA)

biofuels. According to experts, development of IGF Code (International Code of Safety for Ships Using Gases) for LPG and hydrogen will take a little time. In order to comply with the IMO requirements by 2050 it will be necessary not only to convert the fleet to another, more environmentally friendly type of fuel, but also to develop new technologies to reduce greenhouse gas emissions from ships. One of the most promising technologies is the use of fuel cells, but it is still only in its infancy. Any ban is not only a limiting factor, but also creates a field of opportunities for qualitative development. Therefore, banning HFO can stimulate the development of the market for alternative marine fuels, such as LNG and methanol. This is especially important in light of the poorly understood environmental impact of new blends of petroleum fuels. The use of alternative fuels will allow ship owners to ensure the sustainability of operations over the long term with respect to atmospheric pollution. The consequences of spills of new types of fuels, including low-sulfur petroleum fuels, are not well understood. However, for climatic conditions, the effects of marine water pollution from spills are a key factor. The use of distillate fuels will result in an immediate increase in operating costs, and installing a scrubber may not be the right investment when residual fuels are banned, and the investment in equipment will not have time to pay off. Shipowners have even greater risks when building new vessels that require high capital investments. By aggregate properties oil and petroleum products have no competitors on the world market. But regular informational throw-ups of “oil is running out” and carbon addiction stimulate attempts to find a replacement for oil as a fuel and raw material for the chemical industry, therefore the most obvious candidates for such a replacement are ethanol and methanol.

References

1. Solakivi, T., Paimander, A., Ojala, L.: Cost competitiveness of alternative maritime fuels in the new regulatory framework. Transp. Res. Part D: Transp. Environ. **113**, 103500 (2022). https://doi.org/10.1016/j.trd.2022.103500
2. Kouzelis, K., Frouws, K., van Hassel, E.: Maritime fuels of the future: what is the impact of alternative fuels on the optimal economic speed of large container vessels. J. Shipp. Trade **7** (2022). https://doi.org/10.1186/s41072-022-00124-7
3. Carvalho, F., Miranda Müller Drumond Casseres, E., Poggio, M., Nogueira, T., Fonte, C., Ken Wei, H., Portugal Pereira, J., Rochedo, P., Szklo, Al., Schaeffer, R.: Prospects for carbon-neutral maritime fuels production in Brazil. J. Clean. Prod. **326**, 129385 (2021). https://doi.org/10.1016/j.jclepro.2021.129385
4. Yakovlieva, A., Boichenko, S.: Energy efficient renewable feedstock for alternative motor fuels production: solutions for Ukraine. Stud. Syst. Decis. Control **298**, 247–259 (2020). https://doi.org/10.1007/978-3-030-48583-2_16
5. Huang, J., Fan, H., Xu, X., Liu, Z.: Life cycle greenhouse gas emission assessment for using alternative marine fuels: a Very Large Crude Carrier (VLCC) case study. J. Marine Sci. Eng. **10**, 1969 (2022). https://doi.org/10.3390/jmse10121969
6. Heine, D., GGde, S., Dominioni, G.: Unilaterally removing indirect subsidies for maritime fuel. SSRN Electron. J. (2014). https://doi.org/10.2139/ssrn.2512747
7. Livaniou, S., Chatzistelios, G., Lyridis, D., Bellos, E.: LNG vs. MDO in Marine Fuel Emissions Tracking. Sustainability **14**, 3860 (2022). https://doi.org/10.3390/su14073860.
8. Md Moshiul, A., Mohammad, R., Hira, FA., Maarop, N.: Alternative marine fuel research advances and future trends: a bibliometric knowledge mapping approach. Sustainability **14** (2022). https://doi.org/10.3390/su14094947
9. Seo, Y., Kim, J., Park, E., Lee, J., Cho, M., Han, S.: Analysis of energy consumption of novel re-liquefaction system integrated with Fuel Supply System (FSS) for LPG-Fuelled LPG carrier to conventional systems. Energies **15**, 9384 (2022). https://doi.org/10.3390/en15249384
10. Nerheim, A.R., Æsøy, V., Holmeset, F.T.: Hydrogen as a maritime fuel-can experiences with LNG be transferred to hydrogen systems? J. Marine Sci. Eng. **9**, 743 (2021). https://doi.org/10.3390/jmse9070743
11. Pekşen, D.A., G.: Application of Alternative Maritime Power (AMP) supply to cruise port. J. ETA Marit. Sci. **6**, 307–318 (2018). https://doi.org/10.5505/jems.2018.15870
12. Mallouppas, G., Ioannou, C., Yfantis, E.: A review of the latest trends in the use of green ammonia as an energy carrier in maritime industry. Energies **15**, 1453 (2022). https://doi.org/10.3390/en15041453
13. Benet, Á., Villalba-Herreros, A., d'Amore-Domenech, R., Leo, T.J.: Knowledge gaps in fuel cell-based maritime hybrid power plants and alternative fuels. J. Power. Sources **548**, 232066 (2022). https://doi.org/10.1016/j.jpowsour.2022.232066
14. Christodoulou, A., Cullinane, K.: Potential alternative fuel pathways for compliance with the 'FuelEU Maritime Initiative.' Transp. Res. Part D: Transp. Environ. **112**, 103492 (2022). https://doi.org/10.1016/j.trd.2022.103492
15. Barberi, S., Campisi, T., Neduzha, L.: The role of cold ironing in maritime transport emissions. In: AIP Conference Proceedings, vol. 2611, pp. 060013 (2022). https://doi.org/10.1063/5.0119881
16. Wang, Q., Zhang, H., Huang, J., Zhang, P.: The use of alternative fuels for maritime decarbonization: special marine environmental risks and solutions from an international law perspective. Front. Mar. Sci. **9** (2023). https://doi.org/10.3389/fmars.2022.1082453
17. Burmaka, I., Vorokhobin I., Melnyk, O., Burmaka, O., Sagin, S.: Method of prompt evasive maneuver selection to alter ship's course or speed. Trans. Marit. Sci. **11**(1) (2022). https://doi.org/10.7225/toms.v11.n01.w01.
18. Onyshchenko S., Melnyk O.: Probabilistic assessment method of hydrometeorological conditions and their impact on the efficiency of ship operation. J. Eng. Sci. Technol. Rev. **14** (6), 132–136 (2021). https://doi.org/10.25103/jestr.146.15

19. Onyshchenko, S., Melnyk, O.: Efficiency of ship operation in transportation of oversized and heavy cargo by optimizing the speed mode considering the impact of weather conditions. Transp. Telecommun. J. **23**(1), 73–80 (2022). https://doi.org/10.2478/ttj-2022-0007
20. Melnyk, O., Bychkovsky, Y., Voloshyn, A.: Maritime situational awareness as a key measure for safe ship operation. Sci. J. Sil. Univ. Technol. **114**, 91–101 (2022). ISSN: 0209-3324. https://doi.org/10.20858/sjsutst.2022.114.8
21. Melnyk, O., Onyshchenko, S.: Ensuring safety of navigation in the aspect of reducing environmental impact. In: ISEM 2021 LNNS, vol. 463, pp. 1–9 (2022). https://doi.org/10.1007/978-3-031-03877-8_9
22. Onishchenko, O., Golikov, V., Melnyk, O., Onyshchenko, S., Obertiur, K.: Technical and operational measures to reduce greenhouse gas emissions and improve the environmental and energy efficiency of ships. Sci. J. Sil. Univ. Technol. **116**, 223–235 (2022). https://doi.org/10.20858/sjsutst.2022.116.14
23. Melnyk, O., Onishchenko, O., Onyshchenko, S., Voloshyn, A., Kalinichenko, Y., Rossomakha, O., Naleva, G., Rossomakha, O.: Autonomous ships concept and mathematical models application in their steering process control. TransNav, Int. J. Marine Navig. Saf. Sea Transp. **16**(3), 553–559 (2022). https://doi.org/10.12716/1001.16.03.18
24. Melnyk, O., Onyshchenko, S.: Navigational safety assessment based on Markov-model approach. Sci. J. Marit. Res. **36**(2), 328–337 (2022). https://doi.org/ https://doi.org/10.31217/p.36.2.16
25. Melnyk, O., Onyshchenko, S., Onishchenko O., Lohinov O., Ocheretna V.: Integral approach to vulnerability assessment of ship's critical equipment and systems. Trans. Marit. Sci. Split, Croatia **12**(1) (2023)
26. Melnyk, O., Onyshchenko, S., Koryakin, K.: Nature and origin of major security concerns and potential threats to the shipping industry. Sci. J. Sil. Univ. Technol. Ser. Transp. **113**, 145–153 (2021). ISSN: 0209-3324. https://doi.org/10.20858/sjsutst.2021.113.11
27. Bushuyev, S., Onyshchenko, S., Bushuyeva, N., Bondar, A.: Modelling projects portfolio structure dynamics of the organization development with a resistance of information entropy. In: International Scientific and Technical Conference on Computer Sciences and Information Technologies, vol. 2, pp. 293–298 (2021). https://doi.org/10.1109/CSIT52700.2021.9648713
28. Bushuyev, S., Bushuieva, V., Onyshchenko, S., Bondar, A.: Modeling the dynamics of information panic in society. COVID-19 case. In: CEUR Workshop Proceedings, vol. 2864, pp. 400–408 (2021)
29. Onishchenko, O., Shumilova, K., Volyanskyy, S., Volyanskaya, Y., Volianskyi, Y.: Ensuring cyber resilience of ship information systems. TransNav **16**(1), 43–50 (2022). https://doi.org/10.12716/1001.16.01.04
30. Melnyk, O., Onishchenko, O., Onyshchenko, S., Golikov, V., Sapiha, V., Shcherbina, O., Andrievska, V.: Study of environmental efficiency of ship operation in terms of freight transportation effectiveness provision. TransNav Int. J. Marine Navig. Saf. Sea Transp. **16**(4), 723–722 (2022). https://doi.org/10.12716/1001.16.04.14
31. Melnyk, O., Onyshchenko, S., Onishchenko, O., Shumylo, O., Voloshyn, A., Koskina, Y., Volianska, Y.: Review of ship information security risks and safety of maritime transportation issues. TransNav, Int. J. Marine Navig. Saf. Sea Transp. **16**(4), 717–722 (2022). https://doi.org/10.12716/1001.16.04.13
32. Drozhzhyn, O., Koskina, Y., Tykhonina, I.: "Liner shipping": the evolution of the concept. Pomorstvo **35**(2), 365–371 (2021)
33. Drozhzhyn, O., Koskina, Y.: The model of container feeder line organization focused on the nature and parameters of external container flows. Commun. Sci. Lett. Univ. Žilina **23**(2), A94–A102 (2021)
34. Malaksiano, N.: On the stability of economic indicators of complex port equipment usage. Actual Probl. Econ. **138**(12), 226–233 (2012)
35. Lapkina, I., Malaksiano, M., Malaksiano, M.: Optimization of the structure of sea port equipment fleet under unbalanced load. Actual Probl. Econ. **183**(9), 364–371 (2016)
36. Ship fuel of the future. Comparison and prospect. https://sudostroenie.info/novosti/23327.html

37. Alternative fuels and technologies for greener shipping (2018) DNV GL. Summary of an assessment of selected alternative fuels and technologies (2018). https://www.dnv.com
38. Maritime Safety Agency: Update on potential of biofuels in shipping, EMSA, Lisbon (2022). https://www.emsa.europa.eu/publications/reports/item/4834-update-on-potential-of-biofuels-for-shipping.html

Innovative Technologies for the Maritime Industry: Hydrogen Fuel as a Promising Direction

Oleksiy Melnyk, Oleg Onishchenko, Svitlana Onyshchenko, Nadiia Yaremenko, Eduard Maliuha, Iryna Honcharuk, and Oleksii Shamov

1 Introduction

Shipping is one of the largest sources of global greenhouse gas emissions, accounting for approximately 2.9% of total emissions. The International Maritime Organization (IMO) has set ambitious targets to reduce these emissions, including a goal of reducing greenhouse gas emissions from shipping by at least 50% by 2050. Maritime transportation accounts for about 11% of global fuel consumption, or about 10 million barrels per day. It is important to note that in the current situation of competition between alternative fuels, ships largely set the trend in favor of one or another type of fuel. Significant volumes of fuel consumption by maritime transport justify the mass production of refined products, the construction of fuel bases and infrastructure in general, setting the course for a certain type of fuel and relying on it in other market segments. For example, after the ban on the use of marine fuel oil in 2024, only diesel fuel will remain. This provides an opportunity for the maritime transport industry to reconsider its position in the short term before this date and take steps that are more active to adapt to the new standards, including in the context of considering alternative options.

Hydrogen is one of the alternative fuels being explored for use in shipping. As a fuel, hydrogen has a number of advantages over traditional fossil fuels such as diesel and fuel oil. One of the main advantages is that burning hydrogen produces only water as a by-product, making it a clean, emission-free fuel. However, the use of hydrogen as a fuel in shipping is fraught with challenges. One of the biggest challenges is the storage and transportation of hydrogen, which needs to be compressed or liquefied

---

O. Melnyk (✉) · S. Onyshchenko · N. Yaremenko · I. Honcharuk · O. Shamov
Odesa National Maritime University, Odesa, Ukraine
e-mail: m.onmu@ukr.net

O. Onishchenko · E. Maliuha
National University "Odesa Maritime Academy", Odesa, Ukraine

S. Boichenko et al. (eds.), *Modern Technologies in Energy and Transport*, Studies in Systems, Decision and Control 510, https://doi.org/10.1007/978-3-031-44351-0_3

for storage on board. This requires specialized equipment and infrastructure, which are currently limited. Another challenge is the cost of hydrogen production, which is still relatively high compared to traditional fuels. However, as hydrogen production and storage technology improves and demand for clean energy grows, the cost of hydrogen is expected to decline.

Thus, the competitiveness of alternative marine fuels in the new regulatory framework is investigated in [1]. The marine fuels of the future and how alternative fuels affect the optimal economic speed of large container ships are studied in [2]. Research paper [3] proposes an assessment of life-cycle greenhouse gas emissions when using alternative marine fuels using the example of an oil tanker (VLCC). The article [4] explains the reasons for the unilateral abolition of indirect subsidies for marine fuels. Achievements in the field of alternative marine fuel research and future trends and application of alternative marine electricity (AME) in cruise ports are proposed in [5, 6]. The gaps in knowledge about marine hybrid fuel cell power plants and alternative fuels and the role of cold ironing in maritime transport emissions are presented in [7, 8]. The use of alternative fuels for maritime decarbonization, taking into account the specifics of maritime environmental risks and solutions from the point of view of international law, is discussed in [9]. Ensuring the safety of navigation in terms of reducing environmental impact, technical and operational measures to reduce greenhouse gas emissions and increase the environmental and energy efficiency of ships [10, 11]. The principles of using hydrogen-powered engines on mixed navigation vessels and other problems of port infrastructure and navigation safety are considered in [12, 13]. In [14, 15], the use of hydrogen-powered engines on mixed navigation vessels is analyzed. Different issues concerning the safety of ship operations and safety of marine environment considered in [14, 16–18]. Review of ship information security risks and safety of maritime transportation issues in [19]. Efficiency of port operations and stability indicators examined in [20, 21]. Marine diesel engines operation performance research presented in [22, 23]. Alternative fuel and technologies and updates on potential of biofuels in shipping [24, 25].

In [26] authors investigated the effectiveness of using hydrogen fuel as an alternative to oil and gas fuels and concluded that the use of hydrogen fuel would reduce the environmental impact and improve energy efficiency. In [27] considered the advantages and disadvantages of fuel cells in comparison with traditional energy sources on ships and conclude that fuel cells are a promising option for ship transport. Paper [28] considers issues of improving the energy efficiency of container ships using hydrogen fuel. In sources [29, 30] devoted to the technical and economic analysis of the possibility of using hydrogen fuel on ferries in Indonesia and proposed review of research on hydrogen energy storage technology. Review of hydrogen fuel technology on ships and description of fuel cell systems developed for marine applications in [30]. This review [31] of articles and research examines the prospects for using hydrogen fuel cells on ships and analyzes the possibilities of introducing this technology into marine transportation. The paper [32] analyzes the possibility of using hydrogen energy in the marine industry and discusses the technological, economic, and environmental aspects of hydrogen use on ships. The prospects of using hydrogen as a fuel for ship traffic and discuss technological and economic aspects of introducing this technology into maritime transport proposed in [33–35].

Thus, despite all these challenges, there are already examples of ships using hydrogen as fuel. In general, although hydrogen is a promising alternative fuel for shipping, there are still a number of technological, logistical and economic challenges that need to be addressed before it can be widely implemented as a mainstream fuel. Therefore, the purpose of the article is to explore the potential of using hydrogen fuel as an alternative to traditional fossil fuels in the maritime industry. The article discusses the current state of the industry, challenges and opportunities associated with the use of hydrogen fuel, as well as potential benefits from the introduction of this alternative energy source.

2 Materials and Methods of the Study

Undoubtedly, more accurate and thorough research is needed to assess the environmental footprint of alternative fuels, from raw material extraction to environmental emissions, in order to make a decision on the choice of the preferred fuel for international shipping. A separate issue is the assessment of the consequences of alternative fuels spills, which requires laboratory and experimental studies of spills, especially at low temperatures, high wind speeds, etc. Of additional interest is the degree of long-term impact of alternative fuel blends on the aquatic environment. Environmental problems and rising fuel prices are leading to the need to find new solutions for shipping. There are not many alternatives. At the same time, the legislation has already determined the conditions for the use of LNG (liquefied natural gas), followed by methanol and biofuels.

According to experts, it will not take long to develop the IGF Code for LNG and hydrogen. In order to meet the requirements by 2050, it will be necessary not only to switch the fleet to another, environmentally friendly fuel, but also to develop new technologies to reduce greenhouse gas emissions from ships. Hydrogen fuel has also become a potential solution to achieve these goals, but its implementation is not without challenges. The full cycle of renewable hydrogen production is shown in Fig. 1.

One of the main advantages of hydrogen fuel is its zero emissions profile. When hydrogen is burned, the only byproduct is water vapor, making it a clean and renewable energy source. In addition, hydrogen fuel has a high energy density, which means it can provide more energy per unit weight than traditional fossil fuels. This could lead to smaller and more efficient marine engine systems. H_2 is more than just another interesting alternative marine fuel option that is being actively considered for use on ships. Hydrogen is either liquefied (a cryogenic liquid with a temperature of -240 °C) and placed in compression tanks or stored as a chemical compound. Today, H_2 is produced from natural gas and electrolysis. The latter can be carried out at solar and wind power plants simultaneously with electricity generation. Produced from renewable energy sources, hydrogen becomes one of the cleanest fuels, with

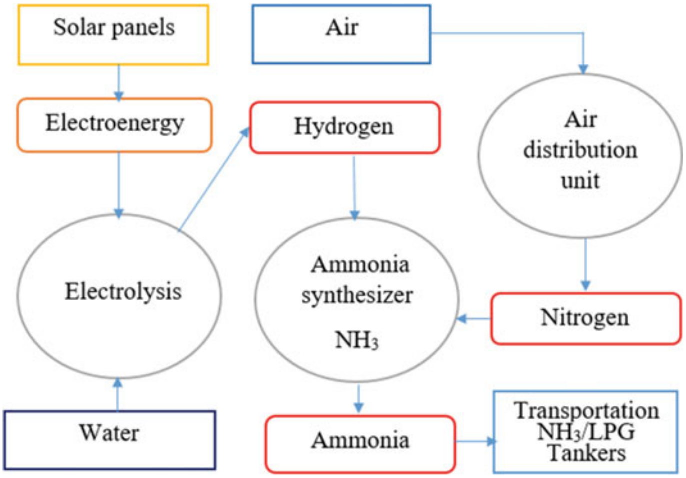


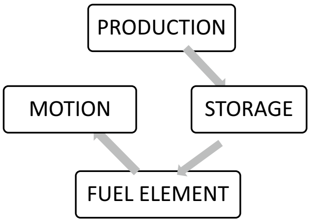
Fig. 1 Production cycle of renewable hydrogen

zero greenhouse gas emissions. The most efficient energy generator for hydrogen is fuel cells. Both hydrogen and fuel cell production is well developed, but they still remain uncompetitive in terms of price compared to conventional marine engines.

There are several ongoing projects and initiatives exploring the use of hydrogen fuel on ships. In 2020, the world's first hydrogen fuel cell vessel was launched in France, and several other countries, including Japan, Norway, and South Korea, are already investing heavily in hydrogen fuel technology for shipping. However, the widespread adoption of hydrogen fuel on ships is still in its early stages and requires further technological progress and infrastructure development.

Potentially, hydrogen can be used on a large scale as a fuel for ships. It is argued that a significant reduction in the cost of producing zero-carbon hydrogen is expected in the next 10–15 years due to the development of the global hydrogen economy. However, the direct use of hydrogen on large-tonnage vessels–in internal combustion engines or in fuel cells in combination with electric motors–poses problems due to its low volume density. For a long voyage, hydrogen storage would require too much physical volume. The use of hydrogen fuel on ships can be achieved through the following cycle consisting of production, storage, fuel cells, and actual movement (Fig. 2).

Fig. 2 Hydrogen utilization cycle on ships



Hydrogen can be produced by various methods other than electrolysis through steam reforming of natural gas or biomass gasification. The hydrogen is stored on board the ship in high-pressure tanks, cryogenic tanks or in the form of metal hydrides. The stored hydrogen is fed into a fuel cell, which converts the chemical energy of hydrogen into electrical energy through an electrochemical process. The electrical energy generated by the fuel cell is used to power the ship's electric motor, which essentially propels the ship forward. The hydrogen storage system is carried out in high-pressure cylinders (a 40-foot container with 25 MPa cylinders holds 794 kg of hydrogen, a 40-foot container with 50 MPa cylinders holds 1050 kg of hydrogen). In liquefied form at a temperature of −252 °C, a 40-foot container holds about 2.478 kg of hydrogen using LOHC (Liquid Organic Hydrogen Carrier), which are organic compounds that can absorb and release hydrogen as a result of chemical reactions. 1 m^3 of LOHC can produce 57 kg of hydrogen. A 40-foot container can hold about 3.200 kg of hydrogen, and given the need to store the "discharged" liquid, about 1.600 kg of hydrogen.

The formula for optimizing a marine engine using hydrogen will depend on various factors, such as the type and size of the vessel, the specific design of the hydrogen engine, operating conditions, and performance goals. However, a general formula that can be used as a starting point is:

$$P = (r\,Q_B)/\gamma \tag{1}$$

where P–the mass flow rate of hydrogen, the amount of hydrogen fuel consumed by the engine per unit of time (kg/s); r–higher heating value of hydrogen or the amount of thermal energy released during the complete combustion of one unit of hydrogen (MJ/kg); Q_B–engine efficiency, percentage of fuel energy converted by the engine into useful work; γ–specific gravity of hydrogen, i.e. the density of hydrogen gas relative to air.

One of the most important factors in optimizing the operation of a vessel using hydrogen as fuel is to maximize the efficiency of the main engine. This can be achieved by various methods, including optimizing the fuel injection system, adjusting the ignition timing, and modifying the combustion chamber design. An example is the formula for optimizing the performance of a hydrogen-fueled ship's engine:

$$\eta = [(P_{in} - P_{out})/P_{in}] \times Q_{in}/H_{H2}, \tag{2}$$

where η–engine efficiency, P_{in}–power consumption (kW), P_{out}–power output (kW), Q_{in}–hydrogen fuel consumption (in kg/h), H_{H2}–heating value of hydrogen (MJ/kg).

The given formula takes into account the power input and output of the engine, as well as the consumption of hydrogen fuel and the heat of combustion of hydrogen. The difference between the power input and output is divided by the power consumption to determine the engine efficiency. The hydrogen fuel consumption is multiplied by the heating value of hydrogen to determine the energy consumed by the engine.

Additional factors such as air-to-fuel ratio, compression ratio, and exhaust gas recirculation rate can be taken into account to further optimize engine performance. By carefully adjusting these factors, you can achieve the maximum possible efficiency from the engine and minimize fuel consumption, emissions, and other environmental impacts. Using the formula presented here, the output power of a hydrogen engine can be calculated, which can then be used to optimize the design and operation of the marine engine and the ship as a whole. Other factors such as propeller type and size, hull design, and operating conditions must also be considered to achieve the best performance and efficiency.

The formula for optimizing a marine engine for hydrogen fuel may include the following elements:

1. Calculation of engine efficiency that can be estimated using the engine's coefficient of performance (thermal efficiency), which determines the ratio of energy released during engine operation to energy input. Engine efficiency:

$$\eta = \dot{W} / \dot{Q}_u \times 100\% \tag{3}$$

where: $\dot{W}$–useful power output by the engine; $\dot{Q}_u$–heat input to the engine.

2. Selecting the optimal way to store hydrogen in various forms, such as liquid hydrogen, compressed hydrogen, or hydrogen absorbed on nanoparticles. The model can take into account the cost and energy efficiency of each storage method to select the best option. Mass energy density can be found as:

$$H_2 = \dot{W} / m, \tag{4}$$

where m–mass of hydrogen stored in a certain form.

3. Consideration of technical constraints. Hydrogen engines may require special technical requirements, such as a special fuel supply and storage system, as well as additional cooling systems. The model can take into account the costs of these additional systems and calculate their impact on engine efficiency. In order to take into account technical limitations: Engine power = (displacement x number of cylinders x number of revolutions per minute x mechanical efficiency factor) / (4 × stage):

$$P = (V_b \times n_c \times N_{max} \times \eta_m) / (4 \times \kappa), \tag{5}$$

where V_b–engine capacity; n_c–number of cylinders; N_{max}–maximum engine speed; η_m–mechanical efficiency; κ–compression ratio.

4. Determining the environmental impact: The model can calculate the emissions of pollutants during the combustion of hydrogen and take into account the environmental impact of the engine:

$$E = \left(V_f \times \left(CO_f / C_x\right) \times M_\times\right) / \left(V_e \times \rho_f\right), \tag{6}$$

where V_f–volume of fuel burned per cycle; CO–the amount of carbon monoxide emitted during fuel combustion; C_x–carbon content in the fuel; M_x–carbon molar mass; V_e–volume of pollutant emissions; ρ_f–fuel density.

5. Cost calculation: the model can take into account the cost of developing and producing the engine, the cost of purchasing and storing hydrogen, and the cost of maintaining and repairing the engine:

$$C = (C_r + C_m) / N, \tag{7}$$

where C_r–cost of research and development; C_m–production costs; N–number of engines manufactured. The cost of hydrogen:

$$C_{H_2} = {}^{C_f}\!/_{H_{LHV}}, \tag{8}$$

where C_f–cost of fuel; H_{LHV}–lower heating value of hydrogen.

Again, this algorithm is only a general example and may vary significantly depending on the specific engine model and its parameters, as well as operating conditions. In order to calculate most accurately the optimal parameters of an engine for hydrogen fuel, it is necessary to conduct a detailed analysis of technical and economic parameters, as well as take into account factors that affect the efficiency of the engine, such as pressure, temperature, rotational speed, and others. Therefore, specialized personnel using appropriate software and equipment should carry out the calculation of the optimal parameters. Considering these elements can help develop an optimal formula for optimizing a marine engine for hydrogen fuel.

Hydrogen is the most environmentally friendly fuel produced from renewable energy. Liquid hydrogen may be used in the future, but it has a rather low volumetric energy density, which leads to the need for large storage facilities.

The Tier III standard refers to the limitation of nitrogen oxides (NO_x) emissions for ships running on LNG or hydrogen in order to reduce the environmental impact of shipping. For internal combustion engines with the Otto cycle running on LNG or hydrogen, NO_x emission limits are set at 3.4 g/kWh. In order to achieve the Tier III standard for internal combustion engines with an Otto cycle running on LNG or hydrogen, it is necessary to use various technologies to reduce NOx emissions, such as the use of a catalytic converter, exhaust gas recirculation systems, high-temperature combustion systems, etc.

Therefore, in order to achieve the Tier III standard for Otto-cycle internal combustion engines running on LNG or hydrogen, many different NO_x reduction technologies must be used to make these engines less harmful to the environment. In terms of nitrogen emissions, Otto-cycle internal combustion engines fired with LNG or hydrogen do not require exhaust gas after treatment equipment to meet the Tier III standard. In most cases, dual-fuel engines operating on a diesel cycle are not suitable for meeting the standard. Analytical data on the level of nitrogen emissions when using different types of fuel is presented in Fig. 3.

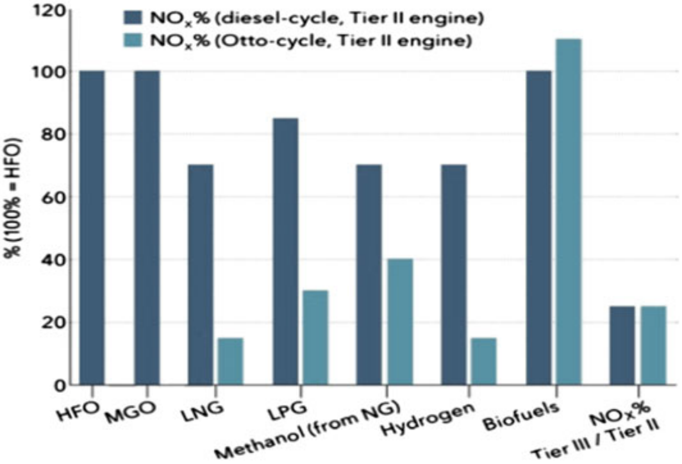


Fig. 3 Nitrogen emissions from different fuels (*Source*: *DNV GL*)

In fact, the cost of introducing alternative fuels on ships is not the main criterion for choosing a particular technology; it is the cost of fuel that determines this choice. It depends on several factors that are sometimes difficult to predict. According to sources, the lowest price is observed for HFO (marine fuel oil), and only LNG can compete with it. The price for methanol produced from natural gas is higher than for LNG. Biofuels are produced from biomass and are traditionally more expensive than Brent crude oil. These fuels are likely to compete with MGO (diesel fuel) in the future.

As for hydrogen, it is not considered here because it is much more expensive than other fuels. It is absolutely not competitive in the market in terms of price, so it will only have a chance to become widespread if there are significant subsidies or high taxes on conventional fuels.

Undoubtedly, the use of alternative fuels will help shipowners ensure the sustainability of transportation operations in the long term in terms of air pollution. The consequences of spills of new types of fuels, in particular low-sulfur oil, are not well understood, but the effects of marine pollution from spills are a key factor in climate conditions. The use of distillate fuels will lead to an immediate increase in operating costs, and the installation of a scrubber may be a bad investment if a ban on the use of residual fuels is introduced, and the investment in equipment will not pay off in time. Shipowners face even greater risks when building new vessels, which require high capital investments. Oil and oil products have no competitors on the global market in terms of their properties, but regular information about oil reserves being depleted and growing demands stimulate attempts to find a replacement for oil as a fuel and raw material.

Despite the advantages of hydrogen fuel, there are also a number of challenges that need to be addressed for its implementation on ships. One of the main challenges is the high cost of hydrogen production and storage. Although technological advances are reducing costs, it is still more expensive than traditional fossil fuels. In addition, hydrogen is flammable and requires special handling and safety measures, making it a potential safety hazard on board ships. However, hydrogen diesel engines can be developed on the basis of standard medium-speed marine diesel engines or can be modernized to run on hydrogen, so based on such data, it can be noted that the use of hydrogen as a fuel on ships is not a remote prospect from a technical point of view, but a fully realized action.

Based on the study of the use of hydrogen fuel for marine engines, the following conclusions can be drawn:

- Hydrogen fuel is one of the most promising alternative sources of energy for ship traffic, as it allows significantly reducing emissions of harmful substances and reducing dependence on petroleum products.
- Development of a mathematical model to optimize the ship engine for hydrogen fuel can help improve engine efficiency, reduce fuel costs and improve the overall environmental friendliness of marine transport.
- The introduction of hydrogen fuel in marine transport has become possible due to the development of technologies for its production and storage, as well as the creation of the appropriate infrastructure for fueling and transportation.

The prospects for further development and use of hydrogen fuel in maritime transport are very encouraging. The need to reduce emissions of harmful substances and the dependence on petroleum products is growing every year and hydrogen fuel is one of the key elements in solving these problems. In addition, modern technologies for the production and storage of hydrogen fuel continue to improve, which could lead to lower costs and greater competitiveness compared to conventional fuels.

3 Conclusions

Hydrogen fuels have the potential to play a significant role in reducing greenhouse gas emissions from shipping, but their implementation is not without its challenges. Although the technology is still in its early stages of development, ongoing initiatives and projects are paving the way for a cleaner and more sustainable future for shipping. With continued research and development, hydrogen fuel could become a major solution for reducing emissions and mitigating climate change in the shipping industry. The use of hydrogen as a fuel in ships has the potential to reduce greenhouse gas emissions and improve air quality, making it an attractive option for the shipping industry. However, there are still challenges that need to be overcome, including the cost of production and storage, as well as limited infrastructure for hydrogen bunkering of ships. Several sources [36–39] include a study on optimizing port equipment structure, an online discussion about future ship fuels, a summary on alternative fuels and technologies by DNV GL, and an update on biofuels potential in shipping from EMSA. The article discusses the environmental benefits of using hydrogen fuel, including the potential for significant reductions in greenhouse gas emissions and improved air quality. It also explores the technical challenges associated with the use of hydrogen fuel, such as the need for storage and distribution infrastructure, as well as the potential costs and economic impacts of switching to this alternative energy source.

References

1. Solakivi, T., Paimander, A., Ojala, L.: Cost competitiveness of alternative maritime fuels in the new regulatory framework. Transp. Res. Part D: Transp. Environ. **113**, 103500 (2022). https://doi.org/10.1016/j.trd.2022.103500
2. Kouzelis, K., Frouws, K., van Hassel, E.: Maritime fuels of the future: what is the impact of alternative fuels on the optimal economic speed of large container vessels. J. Shipp. Trade **7** (2022). https://doi.org/10.1186/s41072-022-00124-7
3. Huang, J., Fan, H., Xu, X., Liu, Z.: Life cycle greenhouse gas emission assessment for using alternative marine fuels: a Very Large Crude Carrier (VLCC) case study. J. Marine Sci. Eng. **10**, 1969 (2022). https://doi.org/10.3390/jmse10121969
4. Heine, D., GGde, S., Dominioni, G.: Unilaterally removing indirect subsidies for maritime fuel. SSRN Electron. J. (2014). https://doi.org/10.2139/ssrn.2512747
5. Md Moshiul, A., Mohammad, R., Hira, F., Maarop, N.: Alternative marine fuel research advances and future trends: a bibliometric knowledge mapping approach. Sustainability **14** (2022). https://doi.org/10.3390/su14094947
6. Pekşen, D., Alkan, G.: Application of Alternative Maritime Power (AMP) supply to cruise port. J. ETA Marit. Sci. **6**, 307–318 (2018). https://doi.org/10.5505/jems.2018.15870
7. Benet, Á., Villalba-Herreros, A., d'Amore-Domenech, R., Leo, T.J.: Knowledge gaps in fuel cell-based maritime hybrid power plants and alternative fuels. J. Power. Sources **548**, 232066 (2022). https://doi.org/10.1016/j.jpowsour.2022.232066
8. Barberi, S., Campisi, T., Neduzha, L.: The role of cold ironing in maritime transport emissions. In: AIP Conference Proceedings, vol. 2611, pp. 060013 (2022). https://doi.org/10.1063/5.0119881
9. Wang, Q., Zhang, H., Huang, J., Zhang, P.: The use of alternative fuels for maritime decarbonization: Special marine environmental risks and solutions from an international law perspective. Front. Marine Sci. **9** (2023). https://doi.org/10.3389/fmars.2022.1082453
10. Burmaka, I., Vorokhobin I., Melnyk, O., Burmaka, O., Sagin, S.: Method of prompt evasive maneuver selection to alter ship's course or speed. Trans. Marit. Sci. **11**(1) (2022). https://doi.org/10.7225/toms.v11.n01.w01.
11. Onyshchenko, S., Melnyk, O.: Probabilistic assessment method of hydrometeorological conditions and their impact on the efficiency of ship operation. J. Eng. Sci. Technol. Rev. **14**(6), 132–136 (2021). https://doi.org/10.25103/jestr.146.15
12. Onyshchenko, S., Melnyk, O.: Efficiency of ship operation in transportation of oversized and heavy cargo by optimizing the speed mode considering the impact of weather conditions. Transp. Telecommun. J. **23**(1), 73–80 (2022). https://doi.org/10.2478/ttj-2022-0007
13. Melnyk, O., Bychkovsky, Y., Voloshyn, A.: Maritime situational awareness as a key measure for safe ship operation. Sci. J. Silesian Univ. Technol. **114**, 91–101. ISSN: 0209-3324 (2022). https://doi.org/10.20858/sjsutst.2022.114.8
14. Melnyk, O., Onyshchenko S.: Ensuring safety of navigation in the aspect of reducing environmental impact. In: ISEM 2021, LNNS, vol. 463, pp. 1–9 (2022). https://doi.org/10.1007/978-3-031-03877-8_9
15. Melnyk, O., Onishchenko, O., Onyshchenko, S., Golikov, V., Sapiha, V., Shcherbina, O., Andrievska, V.: Study of environmental efficiency of ship operation in terms of freight transportation effectiveness provision. TransNav, Int. J. Marine Navig. Saf. Sea Transp. **16**(4), 723–729 (2022). https://doi.org/10.12716/1001.16.04.14

16. Onishchenko, O., Golikov, V., Melnyk, O., Onyshchenko, S., Obertiur, K.: Technical and operational measures to reduce greenhouse gas emissions and improve the environmental and energy efficiency of ships. Sci. J. Silesian Univ. Technol. **116**, 223–235 (2022). https://doi.org/10.20858/sjsutst.2022.116.14.
17. Melnyk, O., Onishchenko, O., Onyshchenko, S., Voloshyn, A., Kalinichenko, Y., Rossomakha, O., Naleva, G., Rossomakha, O.: Autonomous ships concept and mathematical models application in their steering process control. TransNav. **16**(3), 553–559 (2022). https://doi.org/10.12716/1001.16.03.18
18. Melnyk, O. Onyshchenko, S.: Navigational safety assessment based on Markov-model approach. Sci. J. Marit. Res. **36**(2), 328–337 (2022). https://doi.org/10.31217/p.36.2.16
19. Melnyk, O. Onyshchenko, S., Onishchenko O., Lohinov O., Ocheretna V.: Integral approach to vulnerability assessment of ship's critical equipment and systems. Trans. Marit. Sci. **12**(1) (2023)
20. Melnyk, O., Onyshchenko, S., Koryakin, K.: Nature and origin of major security concerns and potential threats to the shipping industry. Sci. J. Silesian Univ. Technol. **113**, 145–153 (2021). https://doi.org/10.20858/sjsutst.2021.113.11
21. Onishchenko, O., Shumilova, K., Volyanskyy, S., Volyanskaya, Y., Volianskyi, Y.: Ensuring cyber resilience of ship information systems. TransNav, Int. J. Marine Navig. Saf. Sea Transp. **16**(1), 43–50 (2022). https://doi.org/10.12716/1001.16.01.04
22. Melnyk, O., Onyshchenko, S., Onishchenko, O., Shumylo, O., Voloshyn, A., Koskina, Y., Volianska, Y.: Review of ship information security risks and safety of maritime transportation issues. TransNav, Int. J. Marine Navig. Saf. Sea Transp. **16**(4), 717–722 (2022). https://doi.org/10.12716/1001.16.04.13
23. Malaksiano, N.: On the stability of economic indicators of complex port equipment usage. Actual Probl. Econ. **138**(12), 226–233 (2012)
24. Lapkina, I., Malaksiano, M., Malaksiano, M.: Optimization of the structure of sea port equipment fleet under unbalanced load. Actual Probl. Econ. **183**(9), 364–371 (2016)
25. Yakovlieva, A., Boichenko, S.: Energy efficient renewable feedstock for alternative motor fuels production: solutions for Ukraine. Stud. Syst. Decis. Control **298**, 247–259 (2020). https://doi.org/10.1007/978-3-030-48583-2_16
26. Minchev, D., Varbanets, R., Aleksandrovskaya, N., Pisintsaly, L.: Marine diesel engines operating cycle simulation for diagnostics issues. Acta Polytech. **3**(61), 428–440 (2021). https://doi.org/10.14311/AP.2021.61.0435
27. Yeryganov, O., Varbanets, R.: Features of the fastest pressure growth point during compression stroke. Diagnostyka **19**(2), 71–76 (2018). https://doi.org/10.29354/diag/89729
28. Alternative Fuels and Technologies for Greener Shipping: DNV GL. Summary of an assessment of selected alternative fuels and technologies (2018). https://www.dnv.com
29. Maritime Safety Agency: Update on potential of biofuels in shipping. EMSA, Lisbon. (2022). https://www.emsa.europa.eu/publications/reports/item/4834-update-on-potential-of-biofuels-for-shipping.html
30. Li, Y., Wei, W., Li, Y., Huang, T.: Research on the optimization of ship propulsion system based on hydrogen fuel. J. Marine Sci. Eng. **9**(3), 278 (2021)
31. Kulkarni, P., Shah, P., Kulkarni, P.: Fuel cell technology for maritime applications. Int. J. Marit. Eng. **162**(1), 55–64 (2020)
32. Chen, J., Zhang, H., Liu, B.: Energy efficiency optimization of a hydrogen-powered container ship. J. Marine Sci. Eng. **7**(10), 318 (2019)
33. Ghafir, M.F.A., Harahap, I.S.H., Taufik, T.: Technical and economic feasibility analysis of hydrogen fuel cell power plant for Indonesian ferry. Int. J. Renew. Energy Res. **8**(3), 1361–1371 (2018)
34. Chen, H., Zhang, X., Wu, Y., Huang, Y.: A review of research on hydrogen energy storage technology. Int. J. Hydrog. Energy **42**(20), 14345–14363 (2017)
35. Hoang, D.L., Kim, T., Lee, K.: Hydrogen fuel cell systems for ships: a review. J. Clean. Prod. **246**, 119025 (2020). https://doi.org/10.1016/j.jclepro.2019.119025

36. Konold, W.E.: Maritime energy transition: hydrogen fuel cells as a future alternative for shipping. Transp. Policy **89**, 50–58 (2020). https://doi.org/10.1016/j.tranpol.2020.04.007
37. Li, Y., Li, P.: Feasibility analysis of hydrogen energy application in shipping industry. Energy Procedia **187**, 50–55 (2020). https://doi.org/10.1016/j.egypro.2020.07.015
38. Schmieder, P., Krieg, O.: Perspectives of hydrogen use for ship propulsion. J. Marine Sci. Eng. **8**(12), 994 (2020). https://doi.org/10.3390/jmse8120994
39. Su, H., Peng, H., Lin, Y., Wang, Z.: Investigation of hydrogen fuel cell ships considering different operation modes. Int. J. Hydrog. Energy **45**(50), 27676–27684 (2020). https://doi.org/10.1016/j.ijhydene.2020.09.192

The Improvement of Fuel Efficiency and Environmental Characteristics of Diesel Engine by Using Biodiesel Fuels

Maksym Pavlovskyi

1 Introduction

In order to generate energy with minimal fuel consumption, diesel engines are among the most efficient internal combustion engines. Due to their inherent high fuel and economic performance, diesel engines are widely used as vehicle powerplants. The maximum total capacity of diesel engines is concentrated in freight and passenger vehicles and self-propelled agricultural machinery; in addition, the share of passenger cars with diesel engines is steadily growing. A significant increase in the scale of production and the rate of dieselisation will lead to further growth in the use of diesel fuel, which is limited in terms of oil refining and does not exceed 15–20% [1]. In addition, Ukraine is facing an acute shortage of domestically produced oil resources, which makes it difficult to use diesel engines on a large scale.

At the current stage of development of energy production for internal combustion engines (ICE), there is a need to reform the energy balance, namely, to transform it into one based on polyenergy, i.e. a system that uses several types of energy production sources [1, 2]. Among the aspects of energy use is the transition from using only traditional energy sources (light oil products) to alternative energy sources, which are obtained from sources with less limited raw materials or from renewable sources to expand the fuel base of wheeled vehicles.

An analysis of studies on the use of biodiesel fuels for transport diesel engines has shown that biodiesel has a number of disadvantages, namely: low volatility, increased density and kinematic viscosity, lower calorific value, increased coking ability, high cloud point and solidification, and increased surface tension coefficient. The above parameters have a significant impact on the efficiency of biodiesel use and worsen the environmental performance of the engine (due to the increased content of nitrogen oxides in the EG). In most of the analysed studies, it is noted that these shortcomings

---

M. Pavlovskyi (✉)
National Transport University, Kyiv, Ukraine
e-mail: maks.pavlovskyi@gmail.com

S. Boichenko et al. (eds.), *Modern Technologies in Energy and Transport*, Studies in Systems, Decision and Control 510, https://doi.org/10.1007/978-3-031-44351-0_4

are caused by the mismatch of physical and chemical properties of biodiesel fuels compared to diesel fuel. At the same time, the analysed studies note that the presence of oxygen in the biodiesel molecule and high cetane number contribute to higher combustion efficiency [2, 3].

Improving the environmental performance of cars with modern diesel engines equipped with an electronic control system, adjustable gas turbine supercharging, exhaust gas recirculation (EGR) system and electronic crankshaft speed control system is possible by ensuring compliance with the requirements of regulatory documents through a systematic, phased transition from powering diesel engines with regular fuel to powering them with alternative fuels, namely by adding methyl esters of rapeseed oil (MERO) to regular petroleum diesel fuel (DF).

The use of blends of MERO and regular diesel fuel can improve the environmental performance of diesel and reduce mass emissions of harmful substances (HS) with exhaust gases. In view of this, it is important to study the impact of MERO additives to diesel fuel on the environmental, fuel and energy performance of modern vehicles.

2 Use of Alternative Fuels from Renewable Sources in Diesel Engines

Prerequisites for Using Fuels from Renewable Energy Sources

The increasing energy needs of humanity lead to an increase in energy consumption, which leads to their depletion and environmental pollution. It is known that heat engines are the main source of energy for vehicles. Recently, the need to save natural resources and preserve the environment while increasing the production of energy required to meet the needs of mankind has become an acute issue [1, 3, 4].

The largest amount of energy is produced by internal combustion engines (ICEs), which simultaneously consume the bulk of oil refining products and are the main source of chemical, mechanical, thermal, noise and other types of harmful environmental pollution. The most significant chemical pollution of the atmosphere is caused by harmful substances (HS) of exhaust gases (EG).

In terms of energy production from a minimum amount of fuel, the most suitable internal combustion engine is the diesel engine. Due to their high fuel and economic performance, diesel engines are widely used as vehicle powerplants. The maximum total capacity of diesel engines is concentrated in freight and passenger vehicles and self-propelled agricultural machinery, and the number of passenger cars with diesel engines is growing steadily.

The increased level of NO_x and particulate matter (PM) emissions into the environment is a disadvantage of diesel engines compared to spark ignition engines. The presence of the above-mentioned disadvantages of diesel engines makes it important to conduct research and implement measures aimed at reducing the concentration of

NO_x and particulate matter in exhaust gases while maintaining the existing level of fuel efficiency and, if possible, increasing it.

In the energy complex of developed countries, about 80% of the energy produced by power plants is obtained from ICEs [1]. The main share of ICE capacities is concentrated in road transport–60% and in the agricultural sector–25% [2].

Along with the increase in the production of ICEs, the demand for petroleum fuels is growing. In Ukraine, ICEs used in road transport and the agricultural sector consume about 16 million tons of petroleum-based fuels annually, 30% of which are diesel fuel [3].

In addition, it is predicted that in the near future, diesels will partially replace spark-ignition engines in trucks, city and intercity buses, and about half of passenger cars will also be equipped with diesels [4].

The implementation of research, the introduction of modern technologies and measures to improve fuel efficiency has made it possible to reduce diesel fuel consumption by 5–7% over the past twenty years [5].

However, despite significant achievements in improving fuel efficiency, the increase in production and dieselization rates will lead to further growth in the use of diesel fuel (DF), which can be produced by oil refining in limited quantities and does not exceed 15–20% [6]. In addition, Ukraine is facing an acute shortage of domestically produced oil resources, which complicates the widespread use of diesel. Domestic of oil and gas condensate production used for diesel fuel does not exceed 4 million tons per year [3, 6]. Even if the volume of oil refining is further doubled, imports of oil or oil products will still amount to about 80–90%.

The shortage of fuels derived from oil is causing increased interest in the use of new alternative fuels in ICEs, which are derived from sources with less limited resources or from renewable sources.

In recent years, a large number of foreign research centres of engine-building companies have been conducting research aimed at solving the problems of fuel economy and replacing traditional liquid hydrocarbon oil fuels with alternative fuels of non-mineral origin. Alternative fuels can be classified according to the following criteria:

- composition–alcohols, ethers, hydrogen fuels with additives;
- by aggregate state–liquid, gaseous, solid;
- in the volume of the main fuel, or as an additive to the regular fuel;
- by sources of raw materials–from coal, peat, shale, biomass, etc.

The most prospective alternative fuels are considered to be biofuels (BF) and plant-mineral mixtures (BF with mineral diesel) in different proportions.

In 2001, the European Commission identified three prospective alternatives to motor fuels: natural gas, biofuels and hydrogen. Each of these fuels could reach a level above 5% of total mineral fuel production in the motor fuel market by 2020.

The main factors that determine the need to replace petroleum motor fuels with fuels of biological (plant) origin are the following: environmental, economic and sanitary.

Passenger cars and buses equipped with diesel engines account for more than 9% of the emissions of the main HS [7]. More than 1000 different substances are present in the exhaust gases of ICEs, 200 of which have been identified [8]. On average, emissions from one diesel passenger car contain 2–4 g of toxic substances per kilometre travelled. The main feature of fuel combustion in a diesel engine is that this process occurs in a diffusion flow when liquid droplets enter it, which undoubtedly leads to the formation of a significant amount of soot (carbon) and polycyclic aromatic hydrocarbons due to the thermal decomposition of fuel molecules in a lack of oxygen.

In a diffusion flow, the most intensive combustion develops in the stoichiometric zone (at $\alpha \approx 1$) at the maximum combustion temperature, resulting in the intensive formation of nitrogen oxides NO_x. Therefore, one of the main harmful components of diesel EG is nitrogen oxides NO_x, the share of which in the total toxicity index can be more than 90% [6–8].

In addition, diesel fuel contains sulphur, which in the process of combustion in diesel, with an excess of oxygen, turns into sulphur oxides SO_2.

The modern energy transport system is a mono-energy system based on the use of one dominant energy source—oil. At the current stage of development of energy production for ICEs, there is a need to reform the energy balance, namely to transform it into one based on polyenergy, i.e. a system that uses several sources for energy production. The basis of polyenergy is the transition from using only traditional energy sources (light oil products) to using alternative energy sources, which are obtained from sources with less limited raw materials or from renewable sources.

These issues are most acute for the Ukrainian economy. Importing about 90% of oil in Ukraine not only reduces the production of motor petrol and diesel fuels, but also deteriorates their quality in the face of steadily rising fuel prices [4]. The constant increase in the cost of oil fuels leads to excessive costs for the main consumers of light oil products, and also has a negative effect on the economy of domestic agricultural producers.

Today, the issue of fuel "environmental friendliness" has acquired an independent significance due to the tightening of sanitary requirements for both fuels and their combustion products. These requirements are declared in international documents, which Ukraine also follows. Table 1 shows the environmental standards that modern fuels must meet, and Table 2 shows the emission standards for diesel vehicles [9].

One of the ways to solve the problem of expanding the energy base for diesel engines and partially resolving environmental and sanitary problems is to use fuels from renewable energy sources—first-generation fuels of plant origin, which include biodiesel (BD) and plant oil. In the future, with the improvement of biomass fuel production technology and reduction of production costs, the use of second-generation plant-based fuels may be possible.

Currently, fuels derived from renewable sources include plant oils (rapeseed, sunflower, peanut, soybean, etc.), esters, alcohols, biogas.

Table 1 Main environmental indicators of diesel fuels

Indicators	UNECE regulations, fuel standard according to EN 590–93	Euro 2, fuel standard according to EN 590–96	Euro 3, fuel standard according to EN 590–2000
Cetane number, not less than	45	49	51
Mass fraction of sulphur, %, not more than	0.3…0.5	0.050	0.035
Content of polycyclic aromatic hydrocarbons, %, not more than	Not regulated	Not regulated	11

Table 2 Maximum permissible emissions for passenger cars with diesel engines

Normative document	Year of introduction of requirements		Maximum permissible emissions, g/km			
	Europe	Ukraine	Carbon monoxide CO	Nitrogen oxides NO_x	$HC + NO_x$	Particles PM
Euro – 1	1992	–	2.72(3.16)	–	0.97(1.13)	0.14(0.18)
Euro – 2	1996	2006	1.0	–	0.7	0.08
Euro – 3	2000	2013	0.64	0.50	0.56	0.05
Euro – 4	2005	2014	0.50	0.25	0.30	0.025
Euro – 5	2009	2016	0.500	0.180	0.230	0.005
Euro – 6	2014	2018	0.500	0.080	0.170	0.005

Production, Physical and Chemical Properties and Standards for Plant Oils and Fuels Based on Them

The first attempts to use plant oils as a motor fuel for diesel engines were made by Rudolf Diesel [4]. In 1900, at the World Exhibition in Paris, he demonstrated a diesel engine running on peanut oil. But as diesel engines were further developed, more attention was paid to fuels made from oil refining products. The depletion of mineral deposits and the need to replace exhaustible energy sources with renewable ones has led to a revival of interest in raw materials of plant and animal origin. The following can be used as raw materials for motor fuels: animal fat, wood and woodworking waste, agricultural and food processing waste, algae and other marine bioresources [10, 11].

Today, more than 30 countries produce liquid biofuels from various types of plant material. Among these biofuels are plant oils, their derivatives, bioethanol, biomethanol, biodimethyl ether, biomethyl tertiary butyl ether (bioMTBE), bioethyl

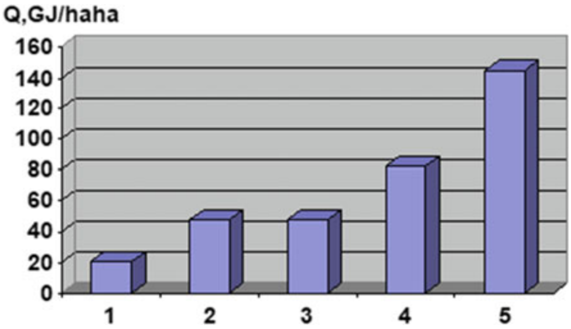


Fig. 1 Average estimated energy yield of BF per hectare of land for different crops under EU conditions [33]: 1–sunflower; 2–rapeseed; 3–wheat; 4–potato; 5–sugar beet

tertiary butyl ether (bioETBE), synthetic BF, biogas, and biohydrogen [12, 13]. It should be noted that under the same conditions of production of raw materials, alcohol fuels require less arable land than fuels based on plant oils (Fig. 1) [14].

At the same time, the physical and chemical properties of fuels derived from plant oils are closer to those of regular mineral diesel. Therefore, diesel engines are more suitable for use with plant oils and their derivatives.

The source of plant oils is oily plants that contain fats in their seeds or fruits.

There are several climatic zones where oilseeds are grown, which are the raw material for the production of oils and their esters. Rapeseed is grown in Western, Central and Eastern Europe, some parts of Asia (China, India), and Canada. The leading countries that grow soybeans are the United States, Brazil, Argentina and China. Sunflower is cultivated in Ukraine, Russia, Spain, Austria, the USA, and Canada. China, Japan, and Indonesia have significant raw material resources for producing peanut oil. Ukraine produces large volumes of sunflower and rapeseed.

The following types of oils are of the greatest industrial importance: legume (soybean), rapeseed, sunflower, palm, corn, castor, hemp, sesame, linseed, poppy, cottonseed, and almond. The global production of plant oils has reached 80 million tons per year [14]. The production of only four of them–soybean, rapeseed, sunflower and palm oils–amounted to 39.6 million tons per year [15].

A typical representative of plant oils is rapeseed oil (RO), which is obtained from rapeseed. Rapeseed is an annual plant of the cruciferous family. There are two varieties of rapeseed: spring and winter. For Ukraine, it is more expedient to produce RO from winter rapeseed. The scheme of rapeseed processing and production of fuel oil and motor fuels based on it is shown in Fig. 2 [16].

Methyl ester of rapeseed oil (MERO) is obtained as a result of direct esterification of fatty acids of RO with methyl alcohol (methanol) at a temperature of 80–90 °C in the presence of a catalyst, most often potassium hydroxide. The esterification of 1040 kg of RO and 144 kg of methanol produces 1 tonne of RO methyl ester and about 200 kg of glycerol (Table 3) [17].

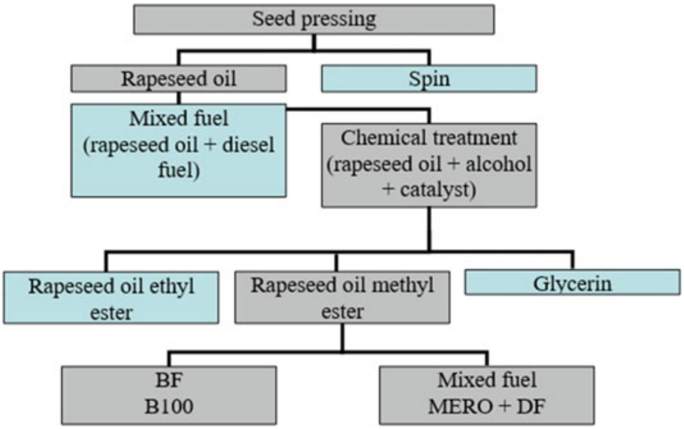


Fig. 2 Scheme of rapeseed processing and production of rapeseed oil and fuels

Table 3 Feedstock and products obtained in the production of one tonne of rapeseed oil methyl ester

Feedstock and processed products	Consumption, kg
Rapeseed seeds	3050
Rapeseed oil	1040
Methanol	144
Potassium hydroxide	19
Filter component	6
Pressed oilcake	1952
Glycerin	200

Plant oils are fats from the seeds or fruits of various plants, which are obtained by pressing or extraction using solvents. Plant oils generally consist (95–97%) of triacylglycerols, which are organic compounds, esters of glycerol, and mono- and diacylglycerols. Acylglycerols, in turn, contain molecules of various fatty acids bound to the glycerol molecule $C_3H_5(OH)_3$ [18, 19].

In terms of their chemical structure, fatty acid molecules differ from each other only in the content of hydrocarbon atoms and the level of saturation of the fatty acid, so the properties of plant oils are determined mainly by the content and composition of fatty acids that form triacylglycerols. Usually, these are saturated and unsaturated (with one to three double bonds) fatty acids with an even number of carbon atoms (mainly C16–C18). In addition, small amounts of fatty acids with an odd number of carbon atoms are present in plant oils (C15–C23).

Plant oils under normal conditions can be in a solid state, but more often they are oily liquids with increased density (usually $\rho = 900–1000$ kg/m^3) and viscosity ($\nu = 60–100$ mm^2/s at t = 20 °C, and $\nu = 30–40$ mm^2/s at t = 40 °C) and a relatively low auto-ignition temperature (Table 4) [13, 19–21]. Liquid plant oils, in turn, are divided into those that dry out (linseed, hemp, tung), those that partially dry out (poppy, cottonseed, sunflower, rapeseed) and those that do not dry out (castor).

Fatty acids, which are the main component of plant oils, are high molecular weight oxygen-containing compounds with a hydrocarbon backbone. Therefore, all plant oils can be used as motor fuels. The low volatility and high viscosity of plant oils makes it impossible to use them in petrol engines. However, they can be successfully used as motor fuels for diesel engines [21–24].

Table 4 Physical and chemical properties of plant oils [21]

Physical and chemical properties	Oils							
	Rapeseed	Peanut	Sunflower	Soybean	Palm	Olive	Cotton	Castor
Density at 20 °C, kg/m^3	916	917	923	924	918	914	919	1069
Kinematic viscosity, mm^2/s at:								
20 °C	75.0	81.5	65.2	–	–	–	–	–
40 °C	36.0	36.5	30.7	32.0	–	–	–	–
100 °C	8.1	8.3	7.4	7.7	8.6	8.4	7.7	19.9
Cetane number	36	37	33	50	49	–	–	–
Amount of air required for the combustion of 1 kg of substance, kg	12.6	11.2	11.1	–	–	–	–	–
Heat of combustion, MJ/kg	37.3	37.0	37.0	36–39	37.1	–	–	–
Auto-ignition point, °C	318	–	320	318	315	285	316	296
Freezing point, °C	–20	–	–16	–12	+ 30	–12	–18	–27
Sulphur content, %	0.002	–	–	–	–	–	–	–
Content %, by weight:								
C	78.0	78.0	–	–	–	–	–	–
H	10.0	12.3	–	–	–	–	–	–
O	12.0	9.4	–	–	–	–	–	–
Acidity, mg KOH/100 ml of fuel	4.66	–	2.14	0.03	0.17	5.90	0.23	0.19
Coking point of 10% residue, %, not more than	0.40	–	0.51	0.44	–	0.20	0.23	–

A special feature of plant oils is the presence of a fairly large amount of oxygen (8–12%) in their composition. This leads to a decrease in their calorific value. Thus, the lower calorific value of plant oils is 36–39 MJ/kg compared to 42–43 MJ/kg of diesel fuels, which contain almost no oxygen in their composition. The presence of oxygen in the molecule of plant oils reduces their combustion temperature and significantly improves diesel efficiency and environmental performance. In many studies of diesel engines running on plant oils, a decrease in the smoke content of the EG and the content of products of incomplete combustion was observed [17].

The possibility of using plant oils as the main fuel for diesel engines is limited by increased soot formation–the deposition of coke on injector nozzles and other parts of the cylinder-piston group. Significant soot formation is caused by the presence of resinous substances and their increased ability to coke. While DF, according to the current DSTU, have a coking ability of 10% residue, not exceeding 0.3%, the coking ability of plant oils is 0.4–0.5%.

In addition, the disadvantage of plant oils used as fuel for diesel engines is the relatively high temperature of their clouding and solidification, caused mainly by the presence of unsaturated fatty acids in their composition (Table 5) [25, 26]. Plant oil fuels are characterized by their ability to biodegrade relatively quickly. Once they get into natural water bodies or soil, they are almost completely decomposed within a few weeks. In addition, plant oils differ from mineral diesel fuels in their low content of sulphur and polycyclic aromatic hydrocarbons [15, 26, 27].

A typical example of plant oils is RO, an oily brown liquid that turns light yellow after refining. Rapeseed oil is a mixture of mono-, di-, and triacylglycerols. It contains both saturated fatty acids—palmitic and stearic, and unsaturated fatty acids—oleic, linolenic, linolenic, eicosenic, and erucic (Table 5).

Table 4 shows the physical and chemical properties of average RO. The density of the RO is $\rho = 900–920$ kg/m^3, the kinematic viscosity at 20 °C is $\nu = 70–90$ mm^2/s.

The above data indicate that plant oils have physical and chemical properties that differ significantly from those of DF. Therefore, it is desirable to use refined products of plant oils in diesel engines—their refined products, ethyl and methyl esters of these oils. Physical and chemical properties of some of them are given in Table 6 [25, 27–29].

Table 5 Fatty acid content of average rapeseed oil [25]

Fatty acid	Chemical formula	Content, % (by weight)
Palmitic	$C_{16}H_{32}O_2$	4.8
Stearic	$C_{18}H_{36}O_2$	1.7
Oleic	$C_{18}H_{34}O_2$	43.7
Linoleic	$C_{18}H_{32}O_2$	20.9
Linolenic	$C_{18}H_{30}O_2$	8.5
Eicosenic	$C_{20}H_{38}O_2$	4.8
Erucic	$C_{22}H_{42}O_2$	15.6

Table 6 Physical and chemical properties of fuels derived from plant oils [27]

Physical and chemical properties	Oil-based fuels					
	Sunflower oil refined	Soybean refined oil	Rapeseed methyl ester	Rapeseed ethyl ester	Soybean methyl ester	Palm oil methyl ester
Density at 20 °C, kg/m^3	920	923	877	895	884	870
Kinematic viscosity, mm^2/s at:						
20 °C	–	–	9.8	*	–	–
40 °C	34.4	31.2	5.2	*	4.1	4.5
Cetane number	40	27	51	–	46	62
The amount of air required for the combustion of 1 kg of a substance, kg	–	–	12.6	12.6	–	–
Heat of combustion, H_u, MJ/kg	–	–	37.8	36.8	–	40.1
Auto-ignition point, °C	202	220	230	–	141	174
Freezing point, °C	–20	–12	–21	–	–1	–
Sulphur content, % (by weight)	0.007	0.005–0.01	0.002	–	0.005–0.01	–
Content %, by weight:						
C	–	–	77.5	77.6	–	–
H	–	–	12.0	12.0	–	–
O	–	–	10.5	10.4	–	–
Coking ability of 10% residue, %, not more than	–	–	0.3	0.3	–	–

Notes "–" properties were not determined

The difference between the physical and chemical properties of plant oils and fuels based on them and those of mineral diesel fuels has an impact on the course of diesel engine operations. This primarily concerns the processes of fuel supply and the dynamics of mixture formation. These processes largely determine such physical properties of the fuel as density, viscosity, compressibility, surface tension.

Compared to diesel fuel, plant oils (rapeseed oil) have a higher density. Thus, while diesel fuel (DSTU 4840:2007) at a temperature of t = 20 °C has a density of $\rho = 820–840$ kg/m^3, RO has a density of $\rho = 910$ kg/m^3 [27]. RO almost does

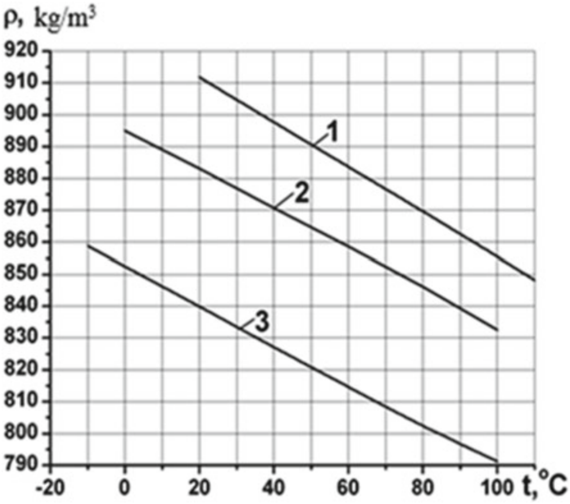


Fig. 3 Dependence of density change on temperature: 1–RO; 2–MERO; 3–DF

not differ from DF in the dependence of density change on temperature (Fig. 3) [28]. Esters produced on their basis have a lower density compared to plant oils. In particular, at a temperature of t = 20 °C, the density of RO (Fig. 3) is $\rho = 910$ kg/m^3, and that of MERO is $\rho = 886$ kg/m^3.

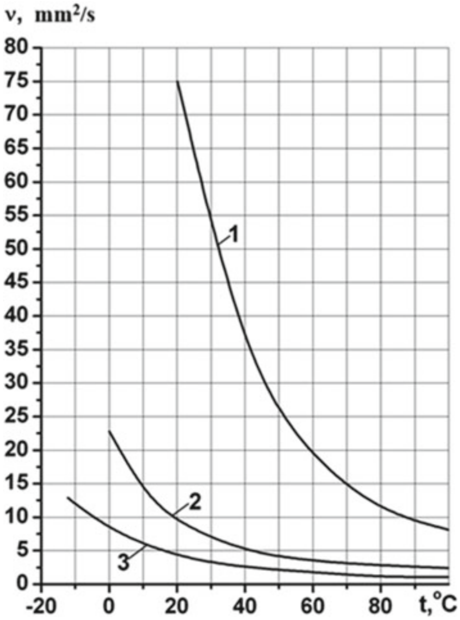
Plant oils are characterized by high kinematic viscosity, which exceeds the kinematic viscosity of standard diesel fuels by an order of magnitude. Under normal atmospheric conditions, the kinematic viscosity of DF "S" (summer) ($\nu = 3.5$–4 mm^2/s) is one level lower than the kinematic viscosity of RO. Thus, in accordance with characteristic 1 (Fig. 4) [29], at t = 20 °C, the viscosity of the RO is $\nu = 75$ mm^2/s [29]. At the same time, at higher temperatures, which are typical for fuel supply systems of transport diesel engines (at an ambient temperature of t = 20 °C, the fuel temperature in the fuel supply system is t = 40–60 °C [30]), the viscosity of the RO decreases sharply and at t = 40 °C is approximately $\nu = 37$ mm^2/s (Fig. 4).

However, such kinematic viscosity values are too high, which makes it difficult to pump them through the fuel lines of the fuel supply system, organise the process of supplying and spraying plant oil in the diesel combustion chamber.

The list of biofuels with lower viscosity compared to RO includes products of their processing, namely MERO. In the production of plant oil esters, their esterification removes glycerol residues from acylglyceride molecules, which leads to a decrease in the kinematic viscosity of the resulting fuels. In particular, at a temperature of t = 20 °C, the kinematic viscosity of MERO is approximately $\nu = 10$ mm^2/s (Fig. 4). This is significantly lower than the kinematic viscosity of plant oils, but two times higher than the kinematic viscosity of petroleum diesel fuels. An acceptable value of kinematic viscosity can be obtained by mixing MERO with a less viscous component, such as kerosene, diesel fuel.

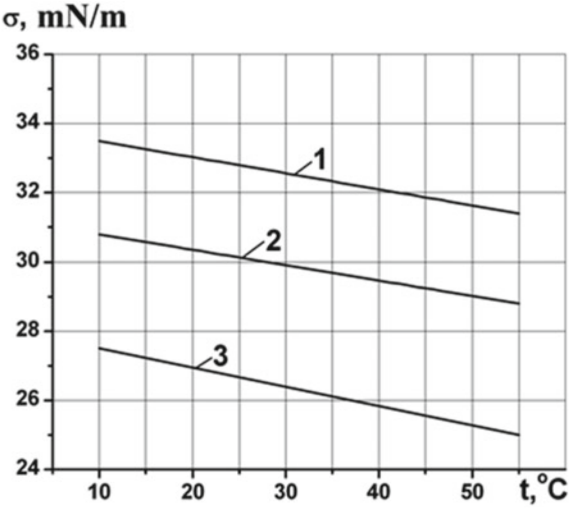
The surface tension coefficient σ has a significant impact on the dynamics of fuel blending. Plant oils have a higher surface tension than diesel fuel. Under normal

Fig. 4 Dependence of viscosity change on temperature: 1–RO; 2–MERO; 3–DF



atmospheric conditions (t = 20 °C, p = 0.1 MPa), the surface tension coefficient of DF is σ = 27.1 mN/m, RO σ = 33.2 mN/m, MERO σ = 30.7 mN/m (Fig. 5) [31]. According to the dependences shown in Fig. 5, it can be seen that the surface tension coefficient of the presented fuels insignificantly depends on the temperature.

Fig. 5 Dependence of the change in the surface tension coefficient on temperature: 1–RO; 2–MERO; 3–DF



These features of the physical properties of plant oils and fuels based on them have a significant impact on the parameters of the fuel supply process, and, as a result, change the characteristics of the injection and spraying of these fuels, and, consequently, the processes of mixture formation and combustion [28–32]. The high values of density, kinematic viscosity, and surface tension coefficient of these fuels, which are fed into the combustion chamber by the standard diesel fuel supply system, cause an increase in their cycle supply and hourly consumption compared to diesel fuels in accordance with DSTU 4840:2007 [29].

The increased density of plant oils and fuels based on them causes a long-range fuel jet [33]. An increase in the length of the fuel jet worsens self-ignition (due to an increase in the ignition delay period) [33]. As a result, during the ignition delay period, the plant oil jet reaches the walls of the combustion chamber, part of the fuel that hits the walls does not burn completely, volumetric mixing is disturbed, piston rings lose mobility and engine oil dilution occurs.

At high kinematic viscosity and surface tension coefficient, the fuel plume opening angle decreases and the spray atomisation and fineness deteriorate, with an increase in the average droplet diameter. In addition, the increased surface tension of plant oils increases the heterogeneity of their spray. Higher values of density and kinematic viscosity of these fuels lead to an increase in the maximum injection pressure. The actual moment of injection start shifts towards an increase in the fuel injection advance angle. The above factors indicate the expediency of implementing measures that will improve the quality of fuel supply, spraying and mixture formation processes when a diesel engine runs on plant oils and fuels based on them.

One of the main conditions for normal operation of the engine when running on BF is its compliance with the standard. The standard for BF abroad is EN 14,214:2008 [34], and in Ukraine, DSTU 6081:2009 [35]. A comparison of these standards is given in Table 7.

Plant-based fuels, like oil, have different characteristics [36]. Whereas the physical and chemical properties of oil depend on the place of extraction, the characteristics of fuels of plant origin depend on geographical and climatic conditions, as well as on the variety and agronomic measures used in growing.

Despite the differences between the physical and chemical properties of plant oils and fuels based on them and those of diesel fuel, they are considered to be promising non-traditional fuels. This is due to the high environmental properties of fuels from plant oils and the renewability of raw materials for the production of these fuels. Therefore, research is being conducted on the adaptation of diesel engines when powered by the above fuels [36–38].

However, this approach to solving this issue requires significant changes to the design and regulation of diesel fuel supply system elements, which is unacceptable for diesel engines in operation.

The differences between the physical and chemical properties of MERO and the physical and chemical properties of regular diesel fuel have a significant impact on the energy, environmental and fuel economy performance of engines.

Taking into account the small volumes of biodiesel production, it is more appropriate and necessary for WV with diesel engines to adapt not diesel engines to

Table 7 Standards for biodiesel in Ukraine and Europe [35, 36]

Name of the indicator	DSTU 6081:2009	EN 14214:2003	Presented sample
Mass fraction of ethers, %, not less than	96.5	96.5	96.5
Density at 15 °C, kg/m^3, within	860–900	860–900	887.5
Kinematic viscosity at 40 °C, mm^2/s, in a range	3.5–5.0	3.5–5.0	5.5
Flash point, °C	120	101	183
Sulphur contents, mg/kg, not more than	10	10	110
Coking ability of 10% of the distillation residue, %, not more than	0.30	0.30	0.1
Cetane number, not less than	51	51	51
Ash content, % (mas.) not more than	0.02	0.02	0.005
Mass fraction of water: mg/kg, not more than %, not more than	500 0.05	500	1200 0.12
Content of mechanical impurities: mg/kg, not more than	24	24	80
Test on a copper plate (3 h at 50 °C)	Class 1	Class 1	Class 1
Oxidative stability at 110 °C, h, not less than	6.0	6.0	–
Acid number, mg KOH/100g, not more than	0.50	0.50	0.6
Iodine number, g of iodine /100 g, not more than	120	120	52.5
Mass fraction of linolenic acid methyl ester, %, not more than	12.0	12.0	–
Mass fraction of polyunsaturated methyl esters, %, not more than	1	1	–
Mass fraction of methanol, %, not more than	0.20	0.20	0.14
Mass fraction of monoglycerides, %, not more than	0.80	0.80	1.4
Mass fraction of diglycerides, %, not more than	0.20	0.20	0.6
Mass fraction of triglycerides, %, not more than	0.20	0.20	0.3
Mass fraction of free glycerol, %, not more than	0.02	0.02	0.01
Mass fraction of total glycerol, %, not more than	0.25	0.25	–

(continued)

Table 7 (continued)

Name of the indicator	DSTU 6081:2009	EN 14214:2003	Presented sample
Mass fraction of alkali metals:			
(Na + K), mg/kg, not more than	5.0	5.0	4.5
(Ca + Mg), mg/kg, not more than	5.0	5.0	4.5
Mass fraction of phosphorus, mg/kg, not more than	10	4	7.0

biodiesel fuels, but to prepare blended biodiesel fuels with the following physical and chemical properties that do not differ significantly from the physical and chemical properties of regular diesel fuel.

When using MERO as an additive to regular DF (hereinafter referred to as two-component biodiesel fuels), the kinematic viscosity increases with the increase in the volume fraction of MERO in the mixture. To prevent an increase in the kinematic viscosity of two-component biodiesel fuels, a component with a lower viscosity should be added (hereinafter referred to as three-component biodiesel). In this case, it is possible to expand the fuel base for diesel engines in operation.

The environmental performance of a diesel engine significantly depends on the physical properties of the fuel, which primarily include its density and viscosity [33].

Fuel viscosity is a direct factor influencing the operation of fuel delivery equipment, determining the internal friction of the fuel flow and thus hydraulic energy losses in the fuel delivery system. The degree of fuel throttling in the filling and cut-off holes of the fuel pump plunger sleeve, as well as in the nozzle channels, partly depends on the viscosity. With increasing viscosity, throttling increases when the plunger closes the filling hole of the sleeve, which causes an earlier start of fuel supply, and when it opens, it causes a later end of fuel supply, which leads to an increase in the cycle fuel supply. Due to the throttling of fuel in the storage and cut-off holes, the actual duration of the supply usually exceeds the geometric duration calculated by the moments when the holes are closed by the plunger edges. However, the main factor affecting the viscosity of the fuel supply cycle is the leakage (loss) of fuel through the gaps of the precision pairs of fuel supply equipment. Wear and tear of precision pairs of fuel delivery equipment also depends on the fuel viscosity. The lower limit of viscosity at which the lubricating ability of the fuel is ensured depends on the design features of the fuel equipment and its operating conditions. The higher the viscosity and density, the larger the droplets formed during spraying, and the longer the range of the fuel jet. At the same time, the quality of fuel spraying and evaporation deteriorates. Spray deterioration is also observed when injecting fuel with excessively low viscosity and density. In this case, a shortened fuel plume is formed, which does not cover the entire space of the combustion chamber, and not all the air charge is involved in the process of fuel oxidation.

The data under consideration indicate that the amount of fuel injected into the diesel combustion chamber depends on the fractional and group hydrocarbon composition of the fuels. With an increase in the boiling point of a fuel fraction, its density and viscosity increase, while its compressibility decreases. High-boiling aromatic hydrocarbons are characterized by higher density and viscosity values. For example, diesel fuel of paraffinic naphthenic base (composition) obtained from West Siberian oil has a viscosity of $\nu_{20} = 3.5\text{–}4.0\ \mathrm{mm}^2/\mathrm{s}$, and the same fractional composition of naphthenic aromatic base (composition) fuel from Sakhalin oil has a viscosity of $\nu_{20} = 5.5\text{–}6.0\ \mathrm{mm}^2/\mathrm{s}$ [36]. Changes in these properties also occur as a result of changes in fuel temperature. Due to the weighting of the fuel used, these three properties, complementing each other, lead to an increase in the cycle fuel supply and corresponding changes in the toxicity of the EG.

When studying the operation of the Detroit Diesel 60 series diesel engine in transient modes, it was noted that an increase in the density of the fuel used from 820 to 845 kg/m^3 is accompanied by an increase in soot emissions from 0.40 to 0.425 g/(kWh), i.e. by 8% [31]. This is due to the fact that an increase in fuel density leads to an increase in the mass cycle fuel supply, a decrease in the excess air coefficient α, an increase in diesel power, and a significant increase in specific soot emissions.

Other physical properties of fuels include their low-temperature properties, which are characterized by their pour point and cloud point, as well as their viscosity-temperature characteristics. Lowering the fuel temperature is accompanied by an increase in the cycle fuel supply and, as mentioned above, a corresponding change in the environmental performance of the diesel engine.

In general, the following patterns of influence of the physicochemical properties of fuels on the toxicity of EG diesel engines with direct injection and split combustion chambers can be noted [33]. Low NO_x emissions are observed at low content of aromatic hydrocarbons in the fuel, which is characterised by lower density and viscosity, as well as a low boiling point of 96% of the fuel. Insignificant emissions of C_mH_n are observed when using fuels with higher values of density, viscosity, CN and 96% boiling point. CO emissions and smokiness of EG increase with increasing aromatic hydrocarbon content, fuel distillation end temperature and decreasing EG.

Optimal values of the cetane number in the range of 55–60 and above are considered to be the best in terms of the total toxicity of EG. The highest (maximum) CNs are for fractions that boil in the range of 200–350 °C, those containing a high content of alkane hydrocarbons and a low content of aromatic hydrocarbons. An increase in the boiling point above 350 °C leads to a slight decrease of the CN, which is mainly due to the increased content of polycyclic aromatic hydrocarbons in these fractions.

Thus, it should be noted that optimisation of the physical and chemical properties of the fuels used is one of the effective ways to reduce the toxicity of EG. This is achieved both by improving the fuel parameters and narrowing their limits of change. Therefore, fuel producers need, on the one hand, to ensure that fuel specifications are in line with current standards, and, on the other hand, to improve fuel parameters that determine its quality and narrow the limits of their possible change.

The analysis of the influence of fuel properties on the toxicity of EG was carried out for diesel engines operating on standard diesel fuels. However, engines for transport and motor tractors can also be operated on fuels of other, non-mineral (petroleum) origin. Therefore, when choosing a fuel and adapting it for specific engine types, environmental performance can be significantly improved.

3 Assessment of Fuel Efficiency and Environmental Performance of the Vehicle in the European Driving Cycle Modes, When Running on Regular and Mixed Biodiesel Fuels

Automobile engines are mobile sources of environmental pollution operating in a wide range of load and speed modes that determine the conditions of vehicle movement in traffic. The main operating modes are: acceleration (deceleration), steady-state movement, engine braking (forced idling) and active idling. Thus, automotive engines operate, as a rule, in unsteady-state modes during vehicle operation, with successive cyclic transitions from one mode to another.

Therefore, the most accurate results, which fully take into account transient processes and individual characteristics of the engine and the vehicle as a whole, can be obtained by testing the vehicle on a simulator roller stand according to certain driving cycles.

To determine the level of emissions of harmful substances from the EG as accurately as possible, the vehicle must be tested under conditions that are as close as possible to real-world operating conditions. In contrast to road tests, tests on a roller simulator can be carried out in precise accordance with time-sensitive speeds, without the need to take into account actual traffic conditions. In this way reproducible and comparable vehicle test results can be obtained.

The aim of the modelling roller bench test is to determine the influence of the physical–chemical properties of mixed biodiesel fuels (two- and three-component) in order to optimize them to improve the fuel-economic and environmental performance of a diesel vehicle in operation equipped with an adjustable gas turbine supercharger, an EG recirculation system and an electronic crankshaft speed regulator.

Research Programme and Methodology

The programme of the study of conditional movement of a car on a simulating roller stand according to the European driving cycle includes the determination and comparative analysis of fuel consumption and the determination of mass emissions of harmful substances (carbon monoxide CO, hydrocarbons C_mH_n, nitrogen oxides NO_x, and particulate matter) during operation on the studied fuels:

- regular diesel fuel;
- two-component biodiesel fuel with a MERO content of 20%;
- three-component biodiesel fuel with a MERO content of 20%.

The following parameters were continuously recorded during the vehicle tests on the simulator: car speed V_C, instantaneous and total fuel consumption Gf, concentrations of carbon monoxide C_{CO}, hydrocarbons C_{CmHn}, nitrogen oxides C_{NOx} in diluted EG and in diluted air. The mass of polluting particles G_{PM} was determined by gravimetric analysis.

The calculation method was used to determine the following: mass emissions per cycle of carbon monoxide G_{CO}, carbon dioxide G_{CO2}, hydrocarbons G_{CmHn}, nitrogen oxides G_{NOx} and particles G_{PM}.

The research was carried out in accordance with the methodology of the current standard DSTU UN/ECE R 83–05:2009 "Unified technical requirements for the approval of wheeled vehicles with regard to pollutant emissions depending on the fuel required for engines" [38]. The EU and EEC (European Economic Commission) test cycle—also called the European Driving Cycle—is carried out according to the programme shown in Fig. 6, which closely simulates the movement of cars in cities Urban Driving Cycle (UDC). In 1993, the cycle was supplemented by a suburban cycle with a speed of up to 120 km/h Extra Urban Driving Cycle (EUDC). Consisting of urban and suburban cycles, the new cycle is called NEDC (New Urban Driving Cycle).

In addition, the Euro 3 standard (2000) cancelled the preheating of the engine for 40 s before the start of the EG measurement (this cycle is called MNEDC—i.e. modified NEDC).

The city cycle consists of four identical parts, each lasting 195 s, which are completed without pauses. The stage is 4.052 km long, with a resulting average speed of 18.7 km/h. The maximum speed is 50 km/h.

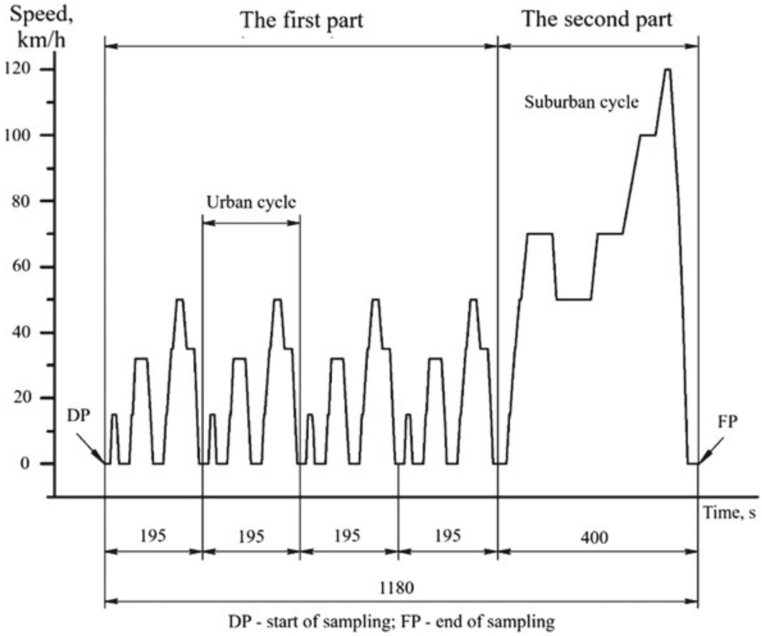


Fig. 6 Modified EU/ECC test cycle for cars and light trucks

Fig. 7 General view of the test setup

The country cycle is performed directly after the city cycle. The part of the country cycle lasts 400 s and the length of this stage is 6.955 km.

During the test, the EG is analyzed continuously or sampled into elastic containers using the Constant Volume Sampling (CVS) method. The mass emissions of C_mH_n are calculated based on the average values of concentrations of harmful substances in the EG, obtained either as a result of processing the data set of instantaneous values of concentrations of harmful substances in the EG, or on the average value of C_mH_n concentrations in diluted exhaust gases taken into an elastic container.

Tests to determine fuel and economic performance and mass emissions of harmful substances from the EG on a simulation roller stand in accordance with UNECE Regulation No. 83 were carried out on a production car Škoda Octavia 1.9Tdi (Fig. 7) (VIN TMBDG41U48B012562) equipped with a VAG ASV 1.9Tdi engine with adjustable gas turbine supercharging, an EG recirculation system, and an electronic crankshaft speed regulator. The technical characteristics of the Škoda Octavia 1.9Tdi are shown in Table 8.

Instruments and Equipment of the Research

A general view of the test setup with the Škoda Octavia 1.9Tdi is shown in Fig. 7.

The test vehicle is mounted with the drive wheels on rollers 3 (Fig. 8). In order to obtain the results of emissions of harmful substances from the EG on the simulation roller stand that correspond to road conditions, it is necessary to reproduce the forces of resistance, forces of change of inertial moment, rolling force and air resistance acting on the vehicle, which are reproduced on the rollers of the stand using an asynchronous DC motor. Braking devices provide the rollers with the necessary resistance, which depends on speed and load. Electric motors brake the rollers, and this force is overcome by the driving wheels of the vehicle. To simulate inertial mass, the test bench uses an electric flywheel mass simulator.

The change in braking load with speed and the required inertial moment reduced to the flywheel were determined with an accuracy of 0.4%.

Table 8 Brief technical characteristics of the Škoda Octavia 1.9Tdi

Option	Value
Unladen weight of the vehicle, kg	1300
Cargo weight, kg	100
The motor's moment of inertia,	0.15
The moment of inertia of the wheel	0.7
Dynamic wheel radius, m	0.317
Gear ratios of the transmission:	
–1 gear	3.778
–2 gear	2.063
–3 gear	1.348
–4 gear	0.967
–5 gear	0.769
–main gear	3.3389
Transmission efficiency	0.9

Fan 1, installed at a distance of 1 m from the car, simulated the oncoming air flow, while providing cooling of the engine radiator.

Gas sampling by the CVS method is carried out as follows: The vehicle exhaust gas in the tunnel 13 is diluted with air coming from the environment 12 through the filters 7 in a certain ratio, depending on the type of engine. The volumetric flow rate of the diluted EG must be the same, so the excess is pumped out by pump 8. This means that the addition of air is determined by the instantaneous flow rate of the EG. A constant amount of EG diluted with air was proportionally sampled throughout the test and collected in several elastic containers 5.

After completion of the driving cycle, the concentration of harmful substances in the tanks corresponds to the average concentration of the entire mixture of air and EG that was sampled. Based on the average concentrations of harmful substances in the EG and the volume of the diluted EG mixture, mass emissions of harmful substances were calculated.

It should be noted that dilution of the EG with air prevents condensation of water vapour contained in the EG, which significantly reduces the concentration of nitrogen oxides in the EG sampling tanks. In addition, dilution with air significantly minimizes the mutual reactions of EG components, primarily hydrocarbons.

The CVS method is characterized by the fact that in the course of the test:

- accounting for the actual volume of gas during testing;
- recording of all stationary and non-stationary operating modes;
- elimination of water vapour condensation.

Testing vehicles equipped with diesel engines. Since 1975, vehicles equipped with diesel engines have been tested using the CVS method. The CVS method was slightly

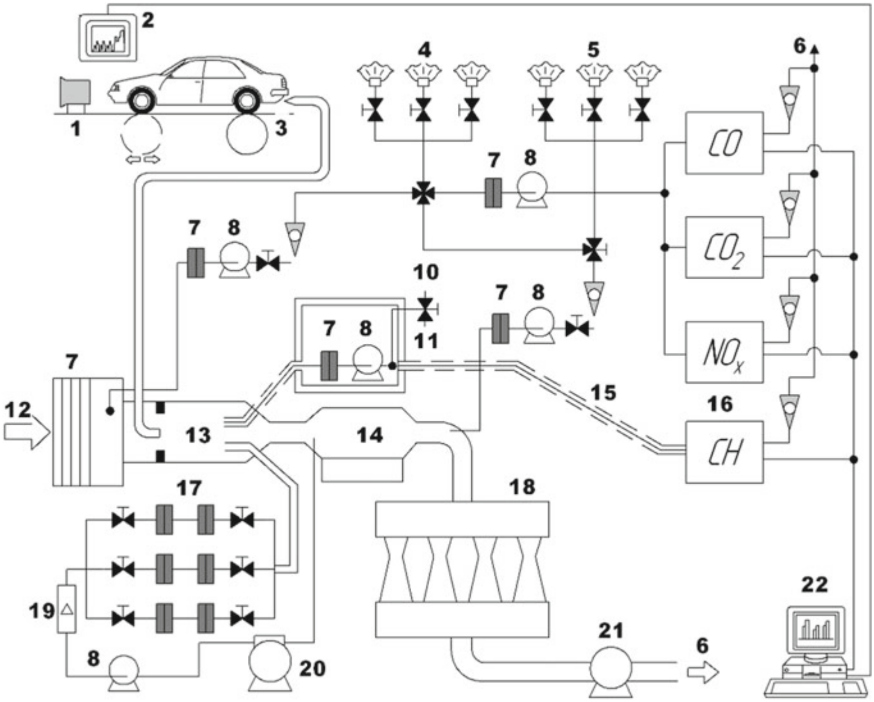


Fig. 8 Schematic of the test setup: 1–fan; 2–monitor for displaying the progress of the driving cycle; 3–rollers; 4–air sampling tanks; 5–LPG sampling tanks; 6–EG outlet; 7–filter; 8–vacuum pump; 9–heater; 10–valve for supplying the tare mixture; 11–valve for supplying "zero" (neutral) gas; 12–air supply; 13–tunnel for dilution of the gas; 14–heat exchanger/heater; 15–heated pipeline; 16–gas analysers; 17–filter; 18–venturi nozzles; 19–gas flow meter for particle detection; 20–air flow meter; 21–centrifugal vacuum pump; 22–computer for processing results

modified to test vehicles with diesel engines. Firstly, to avoid condensation of high-boiling hydrocarbons from the gas sample or to evaporate condensed hydrocarbons, the entire gas sampling system was heated to +190 °C.

In addition, the CVS method was modified to determine the particle content in the EG. For this purpose, a tunnel 13 (Fig. 7) was integrated into the measuring complex to crush the flow of gases with high internal turbulence (Reynolds number >40,000), which is equipped with appropriate filters 17 for particle selection.

The principle of measuring the concentration of harmful substances. In countries where the use of the CVS method has been incorporated into EG legislation, unified measurement methods are used to analyse EG components and harmful substances:

- measurement of CO and CO_2 concentrations by NDIR non-dispersive infrared analysers;
- measurement of NO_x concentration by CLD chemiluminescent instruments;
- determination of the mass of particles in the EG (by weighing the filters before and after sampling);

- measuring the concentration of total hydrocarbons C_mH_n by the flame ionisation method FID.

The AVL-Zollner roller simulator (Fig. 7) type RPL1220/12C23M17/APM150 (serial No. R1305) is designed to provide the required traction force and speed during the test, as provided for in the driving cycle programme. The main technical characteristics of the stand are shown in Table 9.

The fuel consumption during the test was determined by a dynamic liquid mass meter AVL LIST GmbH type 733S.18, which is designed to measure the mass of fuel consumed by a car engine (petrol, diesel fuel) in the range of mass flow rates from 0 to 150 kg/h with the largest mass of liquid passage of 1800 g, the maximum value of the relative error of measuring the mass of liquid in the weighing range from 50 to 1800 g according to the results of metrological studies does not exceed 0.4%.

The air flow rate measurement system was used as part of the universal particle emission analysis system "MT-010" (Fig. 9) with the limits of permissible relative error ±1.5% in the range of volume flow rate from 11.3 dm^3/min to 51.6 dm^3/min (total flow), and ± 2.5% in the range of volume flow rate from 0.4 dm^3/min to 25.8 dm^3/min (sample flow). Channels for measuring the air volume flow rate of the CVS system "EMMS-CVS-010" (Fig. 10) with the limits of permissible relative error ±2%.

Measurements of the volume content of carbon monoxide CO, carbon dioxide CO_2, hydrocarbons CmHn, methane CH_4, nitrogen oxides NOx and oxygen O_2 in the EG were carried out by the gas analytical complex MEXA-7400DEGR manufactured by Horiba Ltd (Japan) (Fig. 11), which includes gas analysers AIA-721 CO (order No. 6423004), AIA-722 CO/CO_2 (order No. 06420007), MRA-720 O_2 (order

Table 9 Technical specifications of the AVL-Zollner roller simulator

Parameter	Value
Maximum speed, km/h	200
Maximum pulling force, N	10,096
Weight of rotating parts, kg	1184
Minimum configurable weight of rotating parts, kg	454
Maximum adjustable weight of rotating parts, kg	5400
Drum diameter, mm	1219.2
Error in power measurement, %	<0.10
Error in speed measurement, %	<0.01
Acceleration measurement error, %	<1
Error in measuring mechanical losses, N	<5
Error in determining the time, ms	10
Error when setting a constant speed, %	<0.05
Error in setting the steady-state traction force, %	<0.2
Error when setting load simulation, %	<2
Error when setting the simulated moment of inertia, %	<1

Fig. 9 Emission analysis system of particles «MT-010»

Fig. 10 Air volume flow measurement system CVS «EMMS-CVS-010»

Fig. 11 Gas analysing complex MEXA-7400DEGR

No. 29416005), and the OVN-728A unit (order No. 430148001), which houses gas analysers FIA-725 A.H.THC, CLA-755 A, H.NO/NO$_x$, and FIA-712HA. H.THC/CH$_4$.

The principle of operation of the devices for determining the concentrations of harmful substances in the EG is as follows: carbon monoxide CO and carbon dioxide CO$_2$—non-dispersive gas analyser with infrared absorption (NDIR); hydrocarbons C$_m$H$_n$—flame ionisation gas analyser calibrated by propane; nitrogen oxides NO$_x$—chemiluminescent gas analyser (CLA) with NO$_x$/NO converter.

The main metrological characteristics of the gas analytical complex are shown in Table 10.

The particle content was determined by the gravimetric method. The particles are captured by two step filters installed on the analysed gas flow line. The surface of the filters is made of a hydrophobic material that is chemically inert to the components of the gas (polytetrafluoroethylene). Before testing, the particulate filters are subjected to special treatment (temperature, humidity) in a dustproof chamber for 24 h (Fig. 11), and then weighed. After the test, the filters are subjected to a second special treatment and re-weighed. The weighing is carried out in a special chamber on a Sartorius SE2-F electronic balance (Fig. 12) with a maximum weighing limit of 2.1 g and a resolution of 0.0001 mg.

Table 10 Main metrological characteristics

Indicator to be determined (designation of the gas analyser)	Measuring range for volumetric content (%)	Measuring range interval	Permissible error	
			Absolute	Relative
CO (AIA-721 CO)	0–0.5	0–0.2% over 0.2%	±0.01% –	– ±5%
CO (AIA-722 O/CO$_2$)	0–12	0–0.6% over 0.6%	±0.03% –	– ±5%
CO_2 (AIA-722 O/CO$_2$)	0–20	0–10% over 10%	±0.5% –	– ±5%
C_mH_n (FIA-725 A.H.THC)	0–5%	0–0.02% over 0.02%	±0.001% –	– ±5%
CH_4 (FIA-712 HA.H.THC/CH$_4$)	0–0.25	0–0.02% over 0.02%	±0.001% –	– ±5%
NO_x (CLA-755 A, H.NO/NO$_x$)	0–0.5	0–0.04% over 0.04%	±0.002% –	– ±5%
O_2 (MPA-720 O$_2$)	0–0.5	0–0.04% over 0.04%	±0.002% –	– ±5%

Fig. 12 Particle weighing chamber

Methodology for Calculating the Total Mass of Pollutant (Harmful) Substances Emitted

The determination of the mass of the i-th pollutant in grams per test is performed in accordance with the current standard [37].

The total mass of emissions of harmful substances is calculated by Eq. 1:

$$M_i = \frac{V_{mix} \cdot Q_i \cdot k_H \cdot C_i \cdot 10^{-6}}{d}, \tag{1}$$

where M_i–emitted mass of the i-th pollutant, g/test; V_{mix}–reduced to standard conditions (273.2 K and 101.33 kPa) volume of diluted EG, l/test; Q_i–density of the *i*-th pollutant, reduced to standard conditions (273.2 K and 101.33 kPa), g/l; k_H–coefficient that takes into account the effect of moisture. It is used only for calculating the mass of nitrogen oxides NO_x in EG; C_i–average value of the concentration of the *i*-th pollutant in diluted EGs, adjusted for the amount of the *i*-th pollutant contained in the air for dilution, mln^{-1}; d–distance conditionally travelled by the vehicle per cycle, km.

Bringing the volume of diluted EG to normal conditions. The volume of diluted EG is determined by the following relationship

$$V_{mix} = V \cdot k_1 \cdot \frac{p_b - p_i}{T_P}, \tag{2}$$

$$k_1 = \frac{273.2}{101.33} = 2.6961 \;\; \mathrm{K} \cdot \mathrm{kPa}^{-1}, \tag{3}$$

where V–is the volume of diluted EG (before adjustment), l/test; k_1–constant factor; p_b–barometric pressure in the test chamber, kPa; p_i–vacuum at the level of the air intake of the discharge pump, kPa; T_p–average temperature of diluted EG, K.

Calculation of the actual adjusted concentration of pollutants in the sampling chamber:

$$C_i = C_e - C_d\left(1 - \frac{1}{DF}\right), \tag{4}$$

where C_i–adjusted concentration of the i-th pollutant in diluted EG, mln^{-1}; C_e–measured concentration of the i-th pollutant in diluted EG, mln^{-1}; C_d–concentration of the i-th pollutant in the air to be diluted, mln^{-1}; DF–dilution coefficient.

The dilution factor is calculated according to the following formula:

$$DF = \frac{13.4}{C_{CO_2} + (C_{CmHn} + C_{CO}) \cdot 10^{-4}}, \tag{5}$$

where C_{CO2}–CO_2 concentration in diluted EG contained in the sampling chamber, %; C_{CmHn}–C_mH_n concentration of in diluted EG contained in the sampling chamber, mln^{-1}; C_{CO}–CO concentration in diluted EG contained in the sampling chamber, mln^{-1}.

The total mass of nitrogen oxides C_{NOx} in diluted EG is determined by formula (1). To correct the effect of moisture on the C_{NOx}, the following relationship was used:

$$k_H = \frac{1}{1 - 0.0329(H - 10.71)}, \tag{6}$$

where H–absolute moisture, g (water)/kg (air);

$$H = \frac{6.211 \cdot R_a \cdot p_d}{(P_B - P_d) \cdot R_a \cdot 10^{-2}}, \tag{7}$$

where R_a–relative moisture content of the ambient air, %; p_d–saturated water vapour pressure at ambient air temperature, kPa; p_B–atmospheric pressure in the room, kPa.

Features of determining the concentration of hydrocarbons C_mH_n. For vehicles equipped with diesel engines, the concentration of total hydrocarbons CmHn is determined as an average value during continuous analysis of diluted EG. When calculating the mass of hydrocarbons C_mH_n for diesel engines, the average integrated concentration value C_e is determined by the following dependence:

$$C_e = \frac{\int_{t_1}^{t_2} C_{CmHn} \cdot dt}{t_2 - t_1}, \tag{8}$$

where $C_{CmHn} \cdot dt$–integral of the dataset of instantaneous concentration values in the heated dilute EG during the test *(t_2–t_1)*; C_e–average integrated value of the concentration of hydrocarbons C_mH_n in diluted EG, mln^{-1};

Determination of particle mass. Particle emissions M_p are calculated according to the following relationship (in our case, gas samples are taken outside the channel), g/km

$$M_p = \frac{\left(V_{mix} + V_{ep}\right) \cdot P_e}{V_{ep} \cdot d}, \tag{9}$$

where V_{mix}–volume of diluted EG under standard conditions (273.2 K and 101.33 kPa), l/test; V_{ep}–volume of EG that has passed through the particle trapping filters under normal conditions, l/test; P_e–mass of particles, g; d–distance conditionally travelled by the vehicle per cycle, km.

Test Results of the Škoda Octavia 1.9Tdi

The study of fuel efficiency and environmental performance of a car engine is carried out according to the MNEDC. The normalised parameters for the test cycle are: mass fuel consumption per cycle, g/km; mass emissions of harmful substances from the engine: carbon monoxide, hydrocarbons, nitrogen oxides, and particles, g/km [37].

Figure 13 shows the programme for changing the speed $V = f(t)$ in the modified European driving cycle and the actual change in the speed $Vy = f(t)$ of the car on the simulation roller stand. Figures 14, 15, 16, 17 and 18 show examples of instantaneous values of fuel consumption $G_f = f(t)$ and concentration of harmful substances: carbon monoxide C_{CO}; hydrocarbons C_{CmHn}; nitrogen oxides C_{NOx} carbon dioxide C_{CO2} in diluted EG when performing the European driving cycle by a car running on regular fuel [38]. The results of tests with different types of fuels are summarised in Tables 11 and 12.

The consumption of regular diesel fuel during the test of the car on the modelling roller stand is 484.781 g/cycle, and according to the data obtained during the calculation on the mathematical model–481.68 g/cycle, which once again confirms the adequacy of the calculation of fuel consumption on the mathematical model.

As previously noted, the incommensurability of the quantitative results of mass emissions of HS with exhaust gases obtained by direct analysis and in diluted EG makes it possible only to qualitatively compare the results of their change.

Table 13 shows a comparison of the qualitative change (%) in mass emissions of HS with exhaust gases when operating on three-component biodiesel fuel (20% MERO) when calculated on a mathematical model and when testing a car on a simulation roller stand.

Table 13 shows that the pattern of change in mass emissions of carbon oxides, hydrocarbons, nitrogen oxides, particulate matter and total toxicity obtained from the results of the calculation on the mathematical model is practically the same as the pattern of change in mass emissions obtained during the test of the car on the simulation roller stand (Figs. 13, 14, 15, 16, 17 and 18).

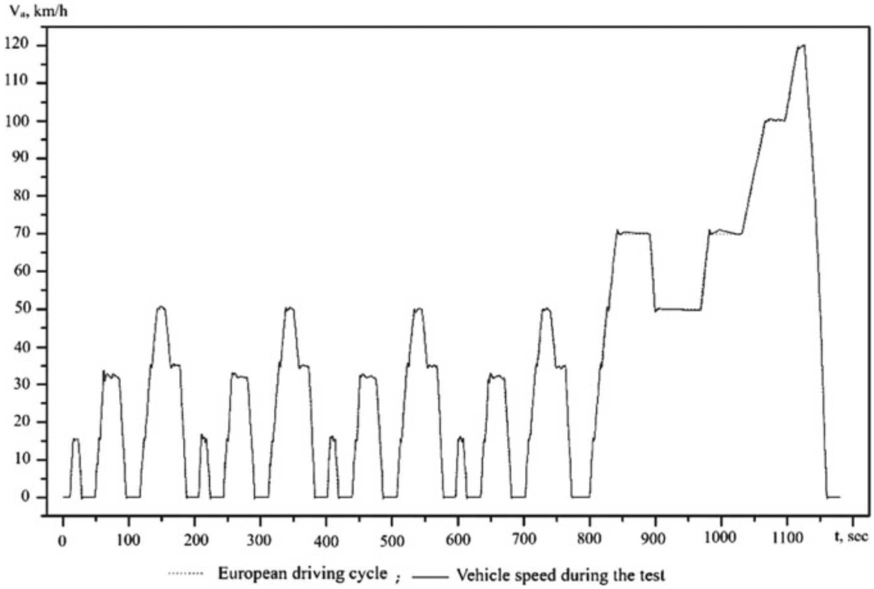


Fig. 13 Modified European Driving Cycle programme and actual change in vehicle speed

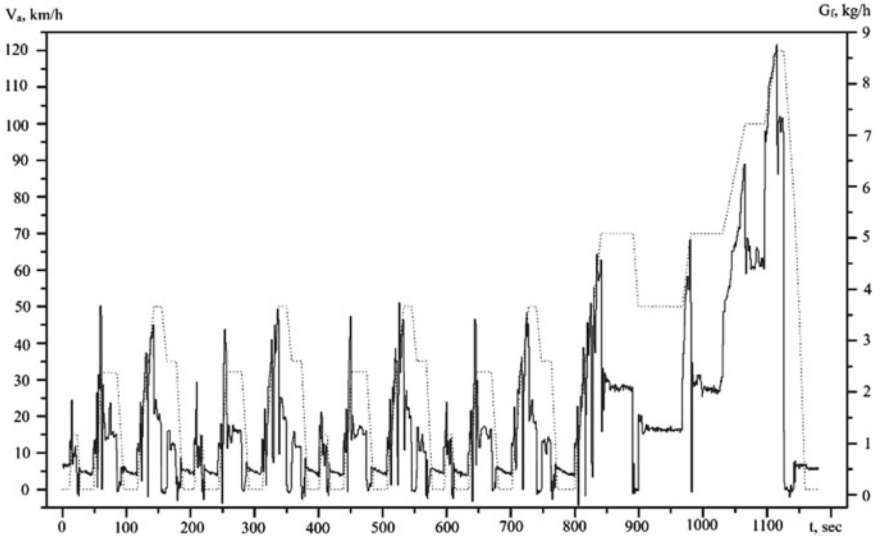


Fig. 14 Instantaneous fuel consumption of a car

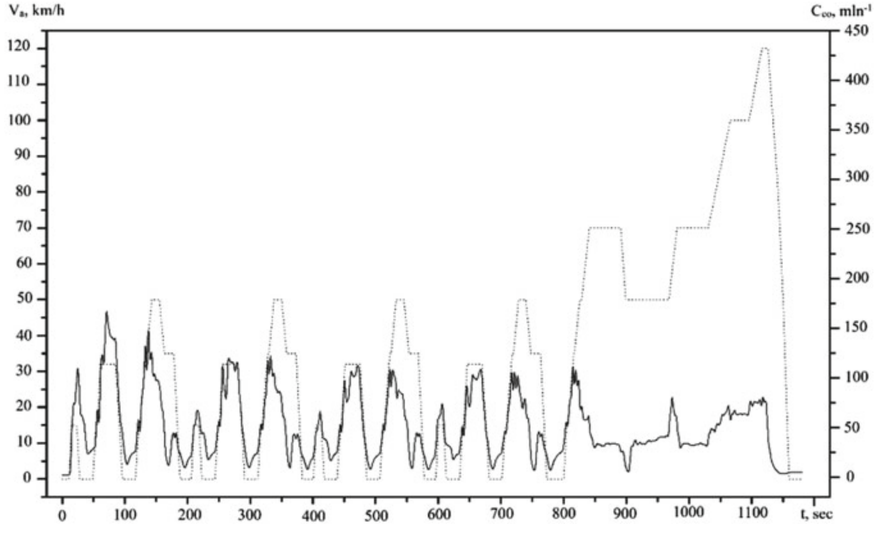


Fig. 15 Instantaneous concentration of carbon monoxide in dilute exhaust gases C_{CmHn}, mln^{-1}

The analysis of the results of car tests on a modelling roller stand under the conditions of the modified European driving cycle when running on regular and mixed biodiesel fuels shows that when the engine runs on biodiesel fuels, the consumption (g/cycle) increases by 4.6% when running on two-component biodiesel, and by 1.8% when running on three-component biodiesel. The fuels used in the research

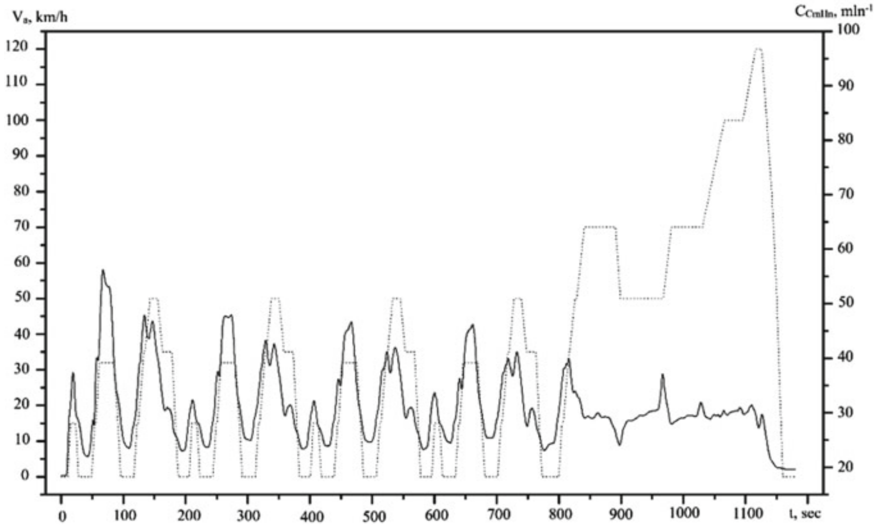


Fig. 16 Instantaneous hydrocarbon concentration in dilute exhaust gases

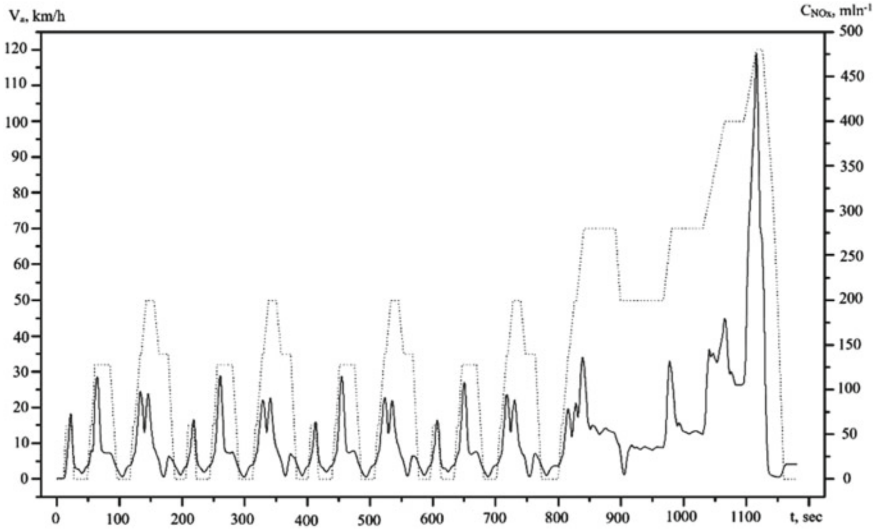


Fig. 17 Instantaneous concentration of nitrogen oxides C_{NOx} in diluted exhaust gases

have different lower heating values, so the quality of their heat use is assessed by the heat consumption (MJ/cycle) to perform equivalent work. Table 10 shows that when the engine runs on two-component biodiesel, there is a 2.12% increase in heat consumption compared to the heat consumed when running on regular diesel fuel to perform work in the driving cycle. When the engine runs on three-component

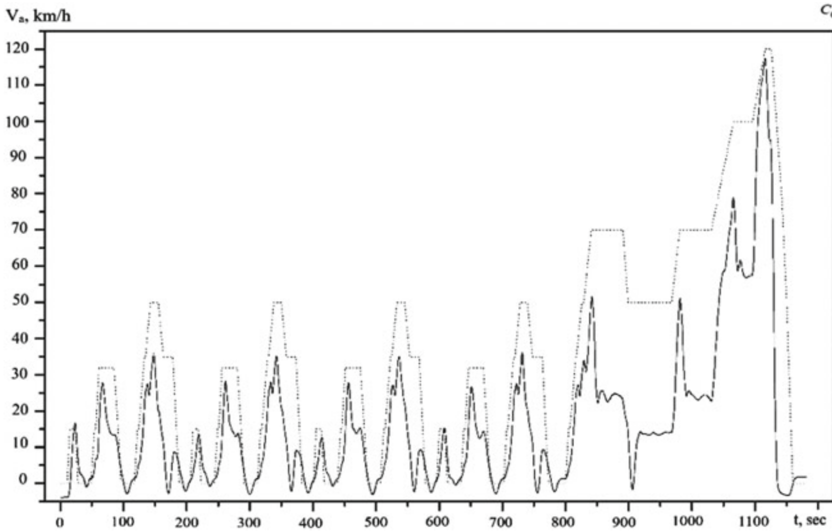


Fig. 18 Instantaneous concentration of carbon monoxide C_{CO2} in dilute exhaust gases

Table 11 Fuel consumption during testing of a car on a simulation roller bench in modified European driving cycle driving modes

Fuel	g/cycle	g/km	Change, %[a]	MJ/cycle	MJ/km	Change, %[a]
Regular diesel fuel	484.781	44.043	–	20.615	1.8729	–
2-component BF (20% MERO)	507.125	46.073	+4.6%	21.051	1.9125	+2.12%
3-component BF (20% MERO)	493.718	44.855	+1.8%	20.544	1.8674	−0.34%

[a] Change, %: + increase in fuel consumption or heat consumption; − decrease in fuel consumption or heat consumption

biodiesel fuel, there is a slight decrease in heat consumption (by 0.68%) to perform the same work.

Mass emissions of products of incomplete combustion: carbon monoxide G_{CO}, hydrocarbons G_{CmHn} and particles G_c. At the same time, mass emissions of nitrogen oxides G_{NOx} from the EG when the engine runs on two-component fuel (the kinematic viscosity of which is slightly higher) increase by 5.3% compared to mass emissions of nitrogen oxides G_{NOx} from the EG when the engine runs on regular DF. Mass emissions of nitrogen oxides G_{NOx} during operation on three-component biodiesel fuel are reduced by 6.2% (the kinematic viscosity of three-component fuels is equal to the kinematic viscosity of regular DF).

According to the test results, it was found that the total mass emissions of harmful substances from EG, reduced to CO, in the modified European driving cycle when

Table 12 Mass emissions of harmful substances during testing of a car on a simulator roller bench in modified European driving cycle driving modes

Mass of emissions of harmful substances	Fuel		
	Regular DF	2-comp. BF (20% MERO)	3-comp. BF (20% MERO)
G_{CO}, g/km	0.3568	0.2893	0.2808
		−18.9%[a]	−21.3%[a]
G_{CO2}[b], g/km	133.26	124.07	118.47
		−6.9%[a]	−11.1%[a]
G_{CmHn}, g/km	0.0854	0.0697	0.0687
		−18.4%[a]	−19.6%[a]
G_{NOx}, g/km	0.6095	0.6418	0.5717
		+5.3%[a]	−6.2%[a]
G_C, g/km	0.0421	0.0372	0.0365
		−11.8%[a]	−13.2%[a]
$G_{\Sigma CO}$, conv. g/kg	34.096	34.326	31.294
		+0.68%[a]	−8.22%[a]

[a] change, %: + increase in emissions; − decrease in emissions

[b] CO_2 is a non-toxic substance

Table 13 Relative change in emissions of harmful substances when testing a car on a simulation roller bench and calculating on a mathematical model when running on three-component biodiesel fuel (20% rapeseed oil methyl ester)

Type of research	Change in emissions compared to standard diesel fuel, %.*				
	CO (%)	C_{mHn} (%)	NO_x (%)	Particulate matter (%)	$G_{\Sigma CO}$ (%)
Calculation based on a mathematical model	−20.1	−21	−11.5	−8.8	−10.93
Tests on a simulated roller stand	−21.3	−19.6	−6.2	−13.2	−8.22

operating on two-component biodiesel fuel increase by 0.68%, and when operating on three-component fuel—decrease by 8.22% compared to standard diesel fuel.

4 Conclusions

1. The tests of the car on the modelling roller stand according to the modified European driving cycle, when running on two- and three-component biodiesel fuels, indicate that the mass emissions of incomplete combustion products are reduced: carbon monoxide G_{CO}; hydrocarbons G_{CmHn}; particles G_C. At the same time, the mass emissions of nitrogen oxides G_{NOx} rom the EG when the engine

runs on two-component fuel increase by 5.3% compared to the mass emissions of nitrogen oxides G_{NOx} from the EG when the engine runs on regular diesel fuel, and the mass emissions of nitrogen oxides G_{NOx} when running on three-component biodiesel fuel decrease by 6.2%.

2. Tests of a modern diesel car equipped with a regulated gas turbine supercharger, a EG recirculation system and an electronic crankshaft speed regulator showed that when the engine runs on three-component biodiesel fuel, mass emissions of the main harmful substances are reduced: carbon monoxide G_{CO} by 21,3%; total hydrocarbons G_{CmHn} by 19,6%; nitrogen oxides G_{NOx} by 6,2%; particles G_C by 13,2%; Improved efficiency of biodiesel use, reduced heat consumption by 2.46% to perform equivalent work compared to two-component biodiesel.
3. According to the test results, it was found that the mass emissions reduced to carbon monoxide in the modified European driving cycle when running on two-component biodiesel fuel increase by 0.68%, and when running on three-component fuel–decrease by 8.22% compared to regular diesel fuel.

References

1. Fischer, G., Prieler, S., van Velthuizen, H., Berndes, G., Faaij, A., Londo, M., de Wit, M.: Biofuel production potentials in Europe: sustainable use of cultivated land and pastures, Part II: Land use scenarios. Biomass Bioenerg. **34**(2), 173–187 (2010). https://doi.org/10.1016/j.biombioe.2009.07.009
2. Yakovlieva, A., Boichenko, S.: Energy efficient renewable feedstock for alternative motor fuels production: solutions for Ukraine. Stud. Syst. Decis. Control **298**, 247–259 (2020). https://doi.org/10.1007/978-3-030-48583-2_16
3. Panchuk, M., Kryshtopa, S., Shlapak, L., Kryshtopa, L., Panchuk, A., Yarovyi, V., Sladkowski, A.: Main trends of biofuels production in Ukraine. Transp. Probl. **12**(4), 15–26 (2017). https://doi.org/10.20858/tp.2017.12.4.2
4. Meyer, M.: Der Traum von Rudolf Diesel wirt wahr. Schweizer Landtechnik **59**(2), 16–19 (1997)
5. Hollo, J.: Trends in der Aufarbeitung von Olsamen. Fett Wissenschaft Technologie = Fat Sci. Technol., **89**(1), 2–7 (1987)
6. Korbitz, W. et al.: Status and development of biodiesel production and projects in Europe. SAE Technical Paper Series, vol. 952768, pp. 249–254 (1995)
7. Directive (EU) 2018/2001 of the European Parliament and of the Council of 11 December 2018 on the promotion of the use of energy from renewable sources (recast), 11.12.2018
8. He, D., Wang, M.: Contribution feedstock and fuel transportation to total fuel–cycle energy use and emissions. SAE Technical Paper Series, 2000–01–2976, pp. 1–15 (2000)
9. Zhou, W., Boocock, D.G.B.: Phase behavior of the base-catalyzed transesterification of soybean oil. J. Am. Oil Chem. Soc. **83**(12), 1041–1045 (2006)
10. Zhou, W., Boocock, D.G.B.: Phase distributions of alcohol, glycerol, and catalyst in the transesterification of soybean oil. J. Am. Oil Chem. Soc. **83**(12), 1047–1052 (2006)
11. Popa, M.G., Neguresc u, N., Pana, C.: Results obtained by methanol fuelling diesel. SAE Technical Paper Series, 2001-01-3748, pp. 1–12 (2001)
12. Aslan, V.: An overview of biodiesel produced from 2nd generation feedstock: mustard seed types. Bioenergy Res. (2022). https://doi.org/10.1007/s12155-022-10536-9
13. Namba, K., Kimoto, K., Ochi, T.: The combustion mechanism and combustion promotion of coal-water mixture fuel. Trans. JSME. Part B **58**(548), 1221–1227 (1992)

14. Wenzel, G., Lammers, P.S.: Vergleich des Siedeverhaltens von Pflanzenolen zur Beurteilung der Kraftstoffeignung. Fett Wissenschaft Technologie **97**(1), 475–481 (1995)
15. Bose, P.K. et. al.:Performance and emissions characteristics of a naturally aspirated diesel engine with esterified vegetable oil. SAE Technical Paper Series, 2001-01-3386, pp. 1–6 (2001)
16. Duggal, V.K. Kuo, T.W., Lux, F.B.:Review of multi fuel engine concepts and numerial modeling of in–cylinder flow processes in direct injection engines. SAE Technical Paper Series, vol. 840005, pp. 1–27 (1984)
17. Lamaisri, C., Punsuvon, V., Chanprame, S., Arunyanark, A., Srinives, P., Liangsakul, P.: Relationship between fatty acid composition and biodiesel quality for nine commercial palm oils. Songklanakarin J. Sci. Technol. **37**(4), 389–395 (2015)
18. Rabinovich, A., Bromberg, L., Cohn, D.R., et al.: Onboard plasmatron reforming of biofuels, gasoline and diesel fuel. SAE Technical Paper Series, vol. 981920, pp. 1–5 (1998)
19. Canakci, M., Van Gerpen, J.: Biodiesel production from oils and fats with high free fatty acids. Trans. ASAE **44**(5), 1429–1436 (2001)
20. Solis, J.L., Berkemar, A.L., Alejo, L., Kiros, Y.: Biodiesel from rapeseed oil (Brassica napus) by supported Li_2O and MgO. Int. J. Energy Environ. Eng. **8**(1), 9–23 (2017). https://doi.org/10.1007/s40095-016-0226-0
21. Kargiiev, V.: Legislative initiatives of the European Union on stimulation of use of alternative kinds of fuels for transport and energy saving. In: Autogas Fueling Complex + Alternative Fuel, vol. 5, pp. 56–59 (2005).
22. Ziejewski, M., Goettler, H.J., Gook, L.W.: Polycyclic aromatic hydrocarbons emissions from plant oil based alternative fuels. SAE Technical Paper Series, vol. 911765, pp. 1–8 (1991)
23. Noureddini, H., Teoh, B.C., Davis, L.: Clements densities of vegetables oils and fatty acids. J. Am. Oil Chem. Soc. **69**(12), 1184–1188 (1992)
24. Tat, M.E., Van Gerpen, J.H.: The specific gravity of biodiesel and its blends with diesel fuel. J. Am. Oil Chem. Soc. **77**(2), 115–119 (2000)
25. School, K.W., Sorenson, S.C.: Combustion of soybean oil methyl ester in a direct injection diesel engine. SAE Technical Paper Series, vol. 930934, pp. 211–223 (1993)
26. Demirbas, A., Karslioglu, S.: Biodiesel production facilities from vegetable oils and animal fats. Energy Sources, Part A: Recover. Util. Environ. Eff. **29**(2), 133–141 (2007). https://doi.org/10.1080/009083190951320
27. DSTU 4840:2007: Diesel fuel of improved quality. Specifications. National standard of Ukraine, Kyiv (2007)
28. Grimaldi, C.N., Postrioti, L., Battistoni, M., et al.: Common rail HSDI diesel engine combustion and emission with fossil/bio–derived fuel blends. SAE Technical Paper Series, 2002-01-0865, pp. 1–9 (2002)
29. Boichenko, S.V., Leida, K., Yakovleva, A.V., Vovk, O.A., Kuzhevskii, K.: Influence of rapeseed oil ester additives on fuel quality index for air jet engines. Chem. Technol. Fuels Oils **53**(3), 308–317 (2017). https://doi.org/10.1007/s10553-017-0807-5
30. Dolinskyi, A., Grabov, L., Mershchyi, V. et al.: High-technology production of alternatyive biofuel from plant feedstock. In: Autogas Fueling Complex + Alternative Fuel, vol. 3, pp. 62–64 (2005)
31. Bamgboye, A.I., Hansen, A.C.: Prediction of cetane number of biodiesel fuel from the fatty acid methyl ester (FAME) composition. Int. Agrophys. **22**(1), 21–29 (2008)
32. Iakovlieva, A., Vovk, O., Boichenko, S., Lejda, K., Kuszewski, H.: Physical-chemical properties of jet fuel blends with components derived from rapeseed oil. Chem. Chem. Technol. **10**(4), 485–492 (2016). https://doi.org/10.23939/chcht10.04.485
33. Moreno, F.: Sunflower methyl ester as a fuel for automobile diesel engines. Trans. ASAE **42**(5), 1181–1185 (1999)
34. Automotive fuels–Fatty acid methyl esters (FAME) for diesel engines–Requirements and test methods: EN 14214:2008 (2008)
35. DSTU: Fatty acid methyl esters of fat and oil for diesel engines. Technical requirements. National standard of Ukraine, Kyiv (2009)

36. Lange, W.W.: The effect in fuel properties on particulates emission in heavy–duty truck engines under transient operating conditions. SAE Technical Paper Series, vol. 912425, pp. 1–24 (1991).
37. Regulation No 83 of the Economic Commission for Europe of the United Nations (UN/ECE)—Uniform provisions concerning the approval of vehicles with regard to the emission of pollutants according to engine fuel requirements. (2006).
38. Govorun, A.G., Klimenko, O.A., Pavlovskyi, M.V.: Results of the vehicle test on roller modelling stand at European driving cycle using diesel fuel and blended biodiesel fuels. Autoshliahovyk Ukrainy **6**, 3–6 (2011)

Absorption Technologies for Biomethane Production from Biogas to Replace Natural Gas in Gas Distribution Networks and Use as Motor Fuel

Hennadiy Zhuk, Yuriy Ivanov, Liliya Onopa, Serhii Krushnevych, and Mehrzad Soltanibereshne

1 The Current State of Biogas and Biomethane Production in the EU Countries and Ukraine

Ukraine is a significant consumer of natural gas (NG). It is mined in Ukraine, but the volume of mining does not always ensure its consumption. Significant part of the demand is met through imports.

The volumes of use and import of natural gas in Ukraine from 1991 to 2019 [1] is shown in Fig. 1. For the period from 1991 to 2011, the imported gas share was ~80%, with the exception of 2009. From 2012 to 2019, the natural gas consumption in Ukraine gradually decreased from 54.8 to 29.8 billion cubic meters, and the imported gas share decreased from 32.9 to 14.3 billion cubic meters.

In 2020, the supply of imported natural gas to Ukraine increased by 12% compared to 2019–up to 15.9 billion m3.

Natural gas production and consumption in 2014–2021 are given in Table 1 Ukraine's domestic gas production for eight years, from 2014 to 2021, remained practically at the same level of ~ 20 billion cubic meters per year. A trend of decreasing of natural gas consumption volumes has been observed in recent years. In 2014, the consumption was 42.6 billion m3, and in 2021-26.8 billion m3, i.e. a 1.6-fold decrease, which led to increase in the share of domestic natural gas production from 48 to 71% of the total consumed natural gas.

Thus, in recent years, gas supply of domestic production is about 65 ÷ 70%, and it is obvious that the replacement of imported gas, including biogas and biomethane, is a particularly urgent task.

Over the past decades, there has been a significant depletion of traditional fossil fuel deposits, therefore it is important to search for and use alternative sources of

---

H. Zhuk (✉) · Y. Ivanov · L. Onopa · S. Krushnevych · M. Soltanibereshne
Gas Institute of NAS of Ukraine, Kyiv, Ukraine
e-mail: hen_zhuk@ukr.net

S. Boichenko et al. (eds.), *Modern Technologies in Energy and Transport*, Studies in Systems, Decision and Control 510, https://doi.org/10.1007/978-3-031-44351-0_5

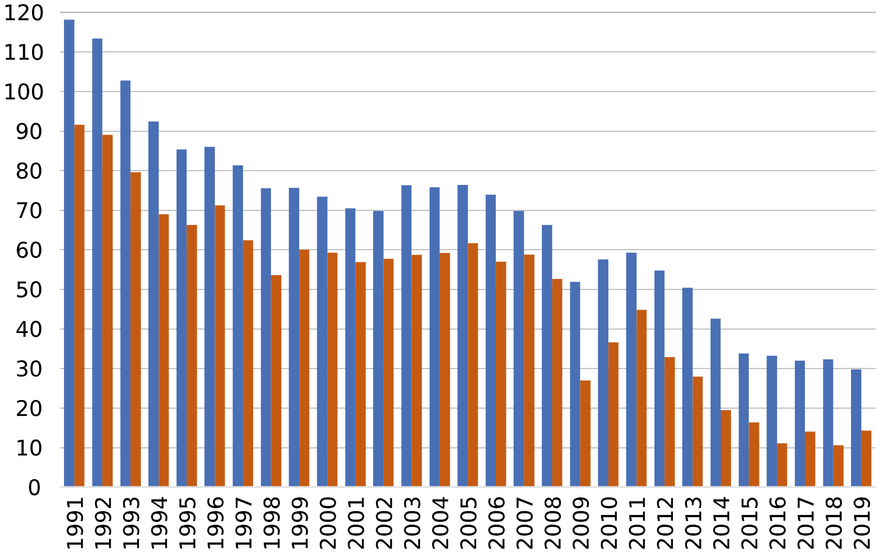


Fig. 1 Statistics of natural gas consumption and import in Ukraine, billion m^3/year [1]: 🟦 gas consumption; 🟧 gas import

Table 1 Natural gas production and consumption in Ukraine from 2014 to 2021

NG production and consumption [1–4]	2014	2015	2016	2017	2018	2019	2020	2021
Gas production, bln.m^3	20.5	19.9	20.1	20.5	21	20.7	20.2	19.8
Gas consumption bln.m^3	42.6	33.8	33.2	32	32.3	29.8	30.9	26.8
Gas production/Gas consumption, %	48	59	61	64	65	69	65	74

energy, such as biogas, which, as a fuel, is obtained from biological raw materials-biomass. Organic waste from the light and food industry, municipal sewage and solid household waste (MSW) can be the biogas source. The first three types of waste are processed in special devices for the production of biogas according to a strictly regulated technology [5]. MSW is a significantly wider class of waste, and in Ukraine alone, about 12 million tons of such waste are generated annually, which are buried in special landfills. Biogas from landfills consists mainly of methane (CH_4) and carbon dioxide (CO_2). As a result of natural processes of anaerobic fermentation, each ton of household waste releases 120–200 m^3 of biogas [6].

The main use of biogas is the production of electricity with its supply to the electrical network. Germany is the leader in the development of biogas technologies in Europe. At the end of 2019 in Germany, about 9.500 biogas plants with a total capacity of about 5.000 MW of electricity were operating [7]. In 2021, the number of biogas plants in Germany was 9,770, and their installed capacity increased to 5,860 MW [8].

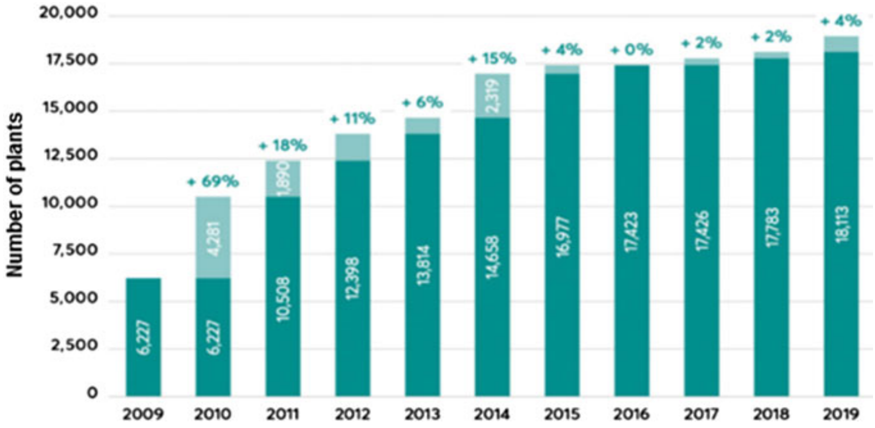


Fig. 2 Growth in the number of biogas plants in Europe in 2009–2019 [11]: ■ existing plants; 🟦 new plants

According to the statistical report of the European Biogas Association (EBA), at the end of 2017, 17.783 biogas plants were operating in all EU countries. The total installed electrical capacity of biogas plants reached 10.532 MW, and the production of electrical energy was 65.179 GWh [9].

In 2018, the number of biogas plants in Europe increased by 419 plants compared to 2017 and amounted to 18.202 [10]. The largest number of biogas plants operates in Germany–about 9.400, Italy has about 1700 plants, France has 837, Great Britain has 715, and Switzerland has 634 biogas plants. The total installed power generation from biogas complexes increased by 5% in 2018 and reached 11.082 MW. At the end of 2019, there were 18.943 biogas plants in Europe with a total biogas production of 15.8 billion m3.

Biogas plants number growth in Europe in 2009–2019 is shown in Fig. 2 [11].

To date, mainly in the EU countries, biomethane is produced and.

- supplied to NG distribution networks with subsequent production of electric and/or thermal energy;
- used at gas filling stations as motor fuel, including in a mixture with natural gas.

The number of biomethane stations in the European Union increased from 187 to 510 from 2011 to 2016, while biomethane production increased from 0.08 to 1.7 billion m3 per year, i.e. 21 times [12]. According to [9], in 2017, about 540 biomethane stations operated in Europe, which produced 1.94 billion m3 of biomethane. The EBA 2020 statistical report data [11] on the growth rate of biomethane plants in Europe in the 2011–2019 is shown in Fig. 3.

The leaders of the European biomethane market are: Germany–200 biomethane plants, Great Britain–93 biomethane plants, France–76 biometh ne plants, Sweden–72 biomethane plants. Totally in 2018, 22.877 GW·h or 2.28 billion m^3 of biomethane was produced in Europe [13].

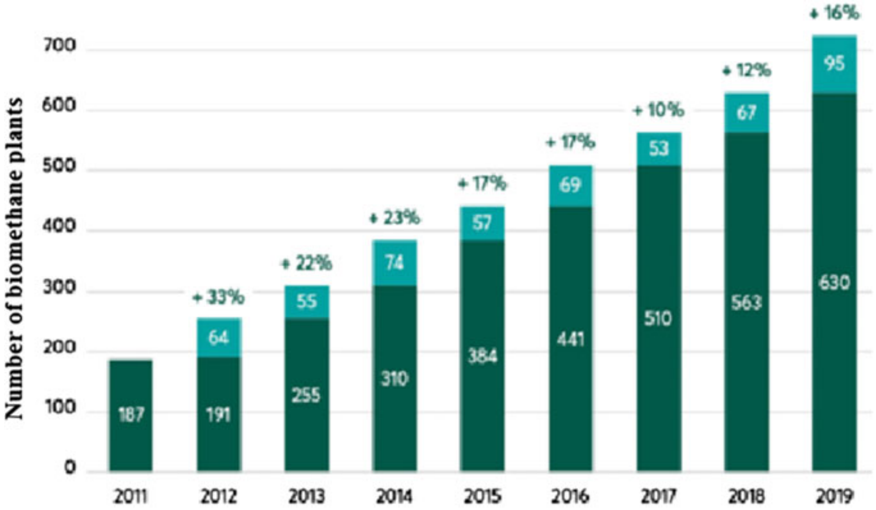


Fig. 3 Growth of the number of biomethane plants in Europe in 2011–2019 [11]: ■ existing plants; □ new plants

By 2020, the number of biomethane plants in Europe was 729.232 biomethane plants were operating in Germany, 131 in France, and 80 in Great Britain [14].

In Ukraine, there are about six thousand legal landfills and landfills with a total area of more than 10 thousand hectares [15]. The total amount of solid household waste exceeds 12 billion tons. About 12 million tons of MSW are generated annually, and the share of household waste processing in Ukraine, for example, in 2019 does not exceed 3–4% [16], which opens a perspective niche for increasing the share of processing into biogas waste.

The development of municipal solid waste (MSW) management in Ukraine in 2014–2018 is shown in Fig. 4. Figure 4 illustrates that from 2014 to 2018 the specific weight of incinerated for the purpose of obtaining energy and recycled of MSW is generally insignificant compared to the volume of generated MSW (1.4% in 2014 and 1.87% in 2018). That points to the huge possibilities of using waste as a raw material for the generation of biogas and energy, and at the same time, to a significant reduction of the negative impact on the environment.

Solid domestic waste is, on the one hand, a significant resource for biogas extraction and biomethane production, on the other hand, landfills are a real environmental problem. The above volume of solid waste (~12 million tons/year) in the process of anaerobic processing emits approximately 700–800 thousand tons of CH_4 and 1800 thousand tons of CO_2 per year. Since methane has a 21 times greater greenhouse effect than carbon dioxide, this amount is equivalent to 15 million tons of carbon dioxide. Collecting at least part of the produced biogas will make a significant contribution to the fight against the greenhouse effect. In addition, control over the emission

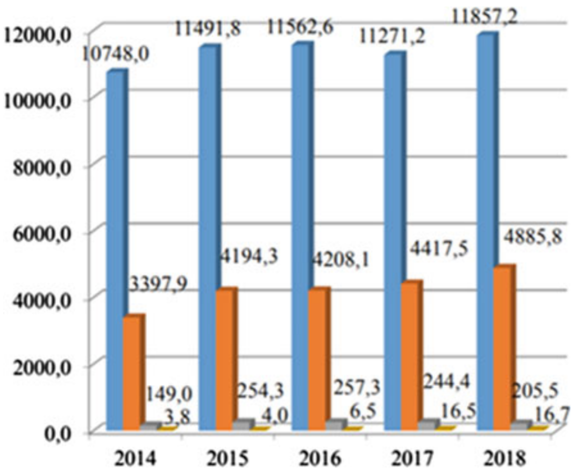


Fig. 4 Municipal solid waste management in Ukraine in 2014–2018 [17]: 🟦 formed MSW, thousand tons; 🟧 removed to landfills; ■ burned for energy; 🟨 reworked MSW

of methane will practically exclude spontaneous combustion of landfills, in which especially toxic substances–dioxin and furan–are released into the atmosphere.

Unlike other types of renewable energy sources, biogas power plants do not depend on sunny weather, gusts of wind, etc., but are uninterrupted alternative energy sources with access to stable supplies of raw materials. This fact is important for the stability of the power system as a whole when the biogas power plant is connected to the grid and for the operation on the balancing capacity market. Ukraine has a sufficiently high biomass potential for biofuels, in particular, the potential for biogas production of various origins, according to estimates [18], can be up to 30–40 billion m3.

In Fig. 5 the dynamics of the biogas capacities growth in Ukraine, namely, the number of biogas plants and their installed capacity in 2012–2019 are given, according to the data of the State Energy Efficiency Agency [19].

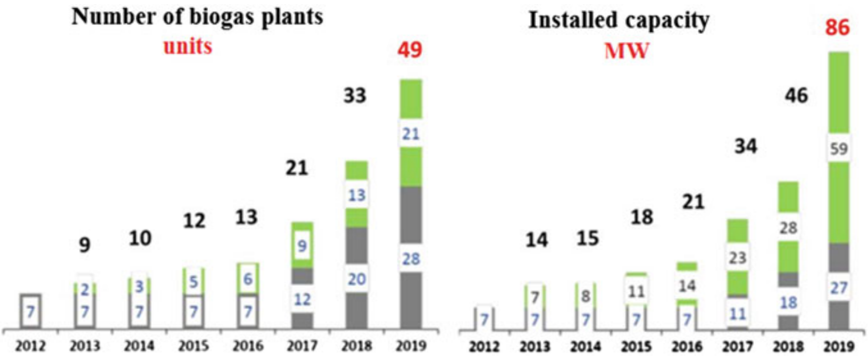


Fig. 5 Dynamics of biogas capacities growth in Ukraine operating under the green tariff [19]: 🟩 biogas from agriculture; ⬛ biogas from solid waste landfills

As of the end of 2019, 49 biogas plants were installed, 28 of which operate at solid household waste landfills. The total capacity of the installations was 86 MW, which is almost 2 times more than in 2018 (46 MW). In 2020, 68 biogas plants with a total installed electrical capacity of about 105 MW were commissioned in Ukraine [20].

The potential for biomethane production in Ukraine is estimated at about 8 billion m^3 per year, which is more than 50% of natural gas imports (~14 billion m3/year) and more than 25% of the total volume (~30 billion m3/year) of NG consumption [21].

In Fig. 6 the projected structure of biofuels uses in Ukraine until 2050 according to the types of energy obtained during the recent production of thermal and electrical energy from solid biofuels, biogas and biomethane, as well as the production of motor biofuels (biomethane, biodiesel, bioethanol) is shown [22].

In December 2020, at a joint meeting of the Bioenergy Association of Ukraine, the Ministry of Energy, the State Energy Efficiency Agency, Gas Transmission System Operator of Ukraine LCC, a draft Law of Ukraine “On Amendments to the Law of Ukraine “On Alternative Energy Sources” regarding the development of electricity production from biomethane” was developed. The draft law provides for the introduction of the biomethane market in Ukraine.

By stimulating the production of electric energy from biogas, the production of biomethane to replace natural gas in gas distribution networks and use as motor fuel, the state also increases the level of environmental safety on the territory of Ukraine,

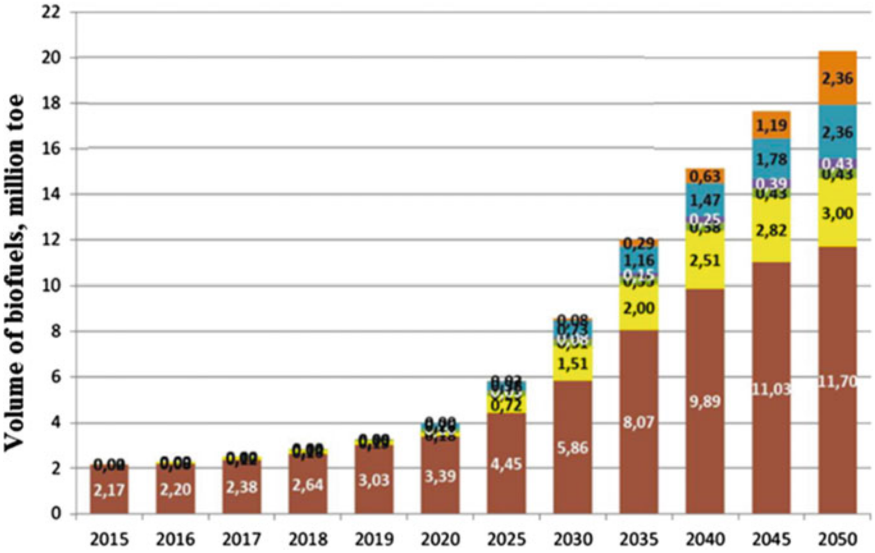


Fig. 6 The projected structure of biofuels use in Ukraine until 2050 by types of energy sources [22]: 🟫 solid biofuels (heat); 🟨 solid biofuel (electricity); 🟩 liquid biofuels of the Ist generation; 🟪 liquid biofuels of the IIst generation; 🟦 biogas; 🟧 biomethane

since waste from agriculture, communal services, food and processing industries negatively affects the state of air and soil, groundwater and, as a result, pose a threat to the health of the population.

2 Analysis of Biogas Purification Methods from Acidic Components for the Purpose of Biomethane Production

It is known that in the process of biogas production, the final phase of anaerobic biodestruction of waste is methanogenesis, i.e. synthesis of biogas. The methanogenic phase of anaerobic decomposition includes two stages: active and stable. In the active stage, the enzymatic decomposition of the acids formed in the acetogenic phase takes place, which is accompanied by a significant release of gases (methane, carbon dioxide, mercaptans, ammonia, etc.). The concentration of methane in biogas increases to 40–60%. The maximum release of biogas occurs after a two-year aging of the waste in the layer of the landfill and stabilization of the decomposition processes.

A stable stage of methanogenesis limits the overall rate of organic substances decomposition in the body of the landfill. A characteristic sign of the onset of this phase is the presence of more than 50% methane in biogas. If the conditions of solid waste storage are not violated, the process of anaerobic decomposition of waste is stabilized with an almost constant volume and composition of biogas.

At the temperature of the fermentation process of 30–40 °C, biogas is released in a water-saturated state and contains, along with methane and carbon dioxide, significant amounts of hydrogen sulfide (up to 3%). In order to protect the gas treatment units from severe wear and tear and to meet the requirements of the following purification stages, water vapor, hydrogen sulfide, and carbon dioxide must be removed from the biogas. Moreover, if biogas is used in heating systems and internal combustion engines, pre-treatment and purification of biogas from harmful and ballast impurities is mandatory.

Currently, the most common technologies for biogas enrichment to biomethane are the following:

- membrane method of purification;
- method of short-cycle adsorption;
- physical absorption;
- chemisorption processes of CO_2 and H_2S extraction.

Membrane Purification Method

The diagram of the membrane method for extracting acidic components from gas mixtures is shown in Fig. 7 and its essence is as follows. Biogas moving along the separation membrane loses separated particles (CO_2, H_2S and others) that pass

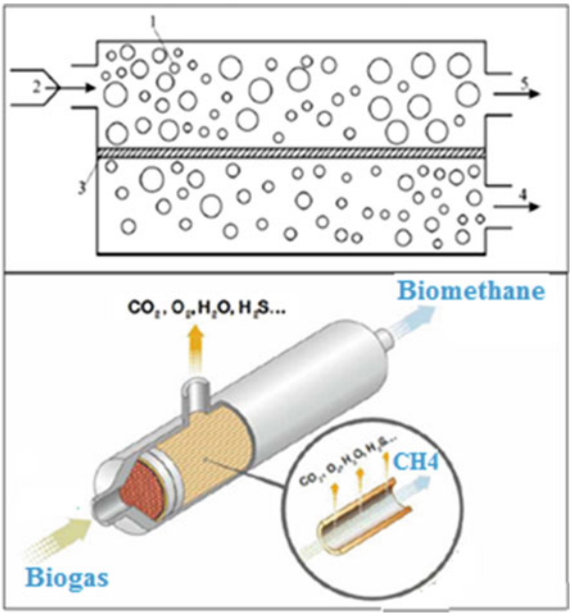


Fig. 7 Scheme of the biogas membrane separation process [23]

through the porous separation membrane. At the same time, the concentration of CH_4 gas (biomethane), which remains in the flow, increases.

Due to the hydrostatic pressure gradient 2, the concentration of ballast gases passing through membrane 3 increases in filter 4, and the gases of the initial mixture form gas concentrate 5. The separation process takes place under the condition that the smallest particles pass through the pores of the separation membrane, and large particles remain in initial gas flow. The degree of separation and productivity of the process depends on the properties of the membrane (material, structure), the design of the devices, and so on.

The effectiveness of membrane separation depends on the pressure, which is significant–up to 2–3 MPa and requires preliminary treatment of the gas mixture before submitting it for separation, namely: removal of solid particles (dust, resin, ash), removal of light hydrocarbons, removal of water vapor. This leads to an increase in the cost of installations, a sagas dehydration unit, separator, and filter are additionally required.

Method of Pressure Swing Adsorption (PSA)

The development of the technological process of pressure swing adsorption uses the fact that gas adsorption by the adsorbent is a function of pressure. Therefore, the specific adsorption process is built in such a way that a mixture of gases is fed into the

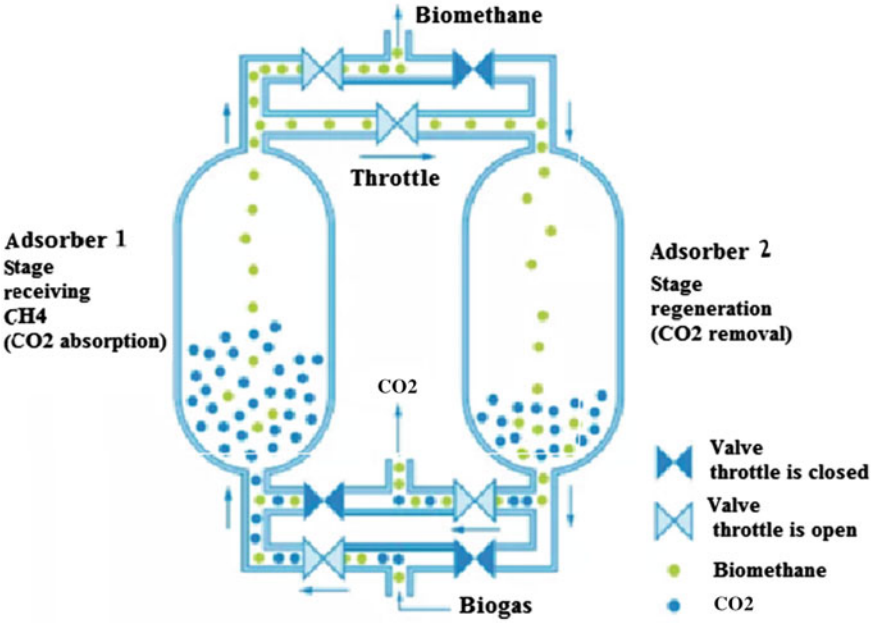


Fig. 8 Schematic diagram of PSA

adsorber at elevated pressure and temperature of the external environment, and in the process, easily adsorbing components of the mixture are absorbed by the adsorbent, while weakly adsorbing or non-adsorbing ones pass through the apparatus, due to which the gas mixture is separated. The principal diagram of PSA is given in Fig. 8.

The PSA process is carried out at high pressure (up to 3 MPa and above), which requires additional energy consumption for gas flow compression. Other disadvantages of most adsorption plants are the periodicity of the process and the associated low intensity of the reactors, the high cost of periodic regeneration of adsorbents. The use of uninterrupted methods of purification in a moving and fluidized bed of adsorbent partially eliminates these disadvantages, but requires high-strength industrial sorbents, the development of which for most processes has not yet been completed. But it should be noted that improving the quality of biogas with the help of adsorption processes is a promising direction in biogas utilization technologies.

Physical Absorption

Absorption processes with the use of physical, chemical absorbents and their combination have become the most widespread for cleaning of process gases from acidic components [24, 25]. During physical absorption, the extraction of carbon dioxide occurs at increased pressure due to its physical solubility in organic: methanol

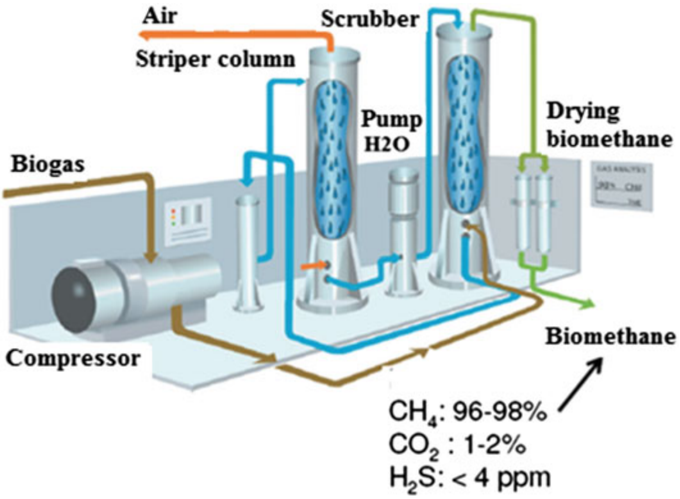


Fig. 9 Illustration of water scrubber technology

(“Rectisol” process), N-methylpyrrolidone (“Purizol” process), propylene carbonate (“Fluor” process) and inorganic-water absorbents. The cleaning method is based on the different solubility of carbon dioxide, hydrogen sulfide and other gases in the absorbent. Complex purification from CO_2 and organic sulfur compounds is also carried out with the help of processes using chemical and physical absorbents in the “Sulfinol” and “Amizol” processes. In Fig. 9 the process of biogas enrichment to biomethane using water scrubber technology is shown schematically.

Physical absorbents have a number of limitations:

- increased solubility of hydrocarbons (for example, biogas methane) in the absorbent, which leads to its loss and worsens the quality of the obtained acid gases, for example, the production of commercial liquid carbon dioxide or dry ice;
- difficulty in achieving a deep level of cleaning;
- high cost compared to ethanolamine’s.

Chemosorption Processes of CO_2 and H_2S Extraction

Chemosorption processes are devoid of the disadvantages of physical absorption. They are based on the chemical interaction of CO_2 and H_2S with the active part of the absorbent.

Amine absorption processes of biogas purification use ethanol amine sorbents. Most often, CO_2 and H_2S absorption processes are used with aqueous solutions of monoethanolamine (MEA), the strongest base among ethanolamines. The process of absorption of carbon dioxide and hydrogen sulfide is accompanied by the release of heat, and the process of the absorbent solution regeneration is accompanied by the absorption of heat.

The absorbing properties of MEA increase with decreasing temperature and increasing pressure. With an increase in temperature and a decrease in pressure, the equilibrium of chemical reactions shifts to the left. This is the basis for the regeneration of the MEA solution saturated with acid gases during absorption. When a saturated solution is heated, chemical compounds decompose and acid gases are desorbed from the solution.

In the MEA process of gas purification from CO_2, side reactions occur, which lead to an irreversible change in the composition of the absorbent (oxidation and thermal decomposition), a decrease in the absorption capacity, as well as serious corrosion of the equipment. Therefore, the recommended degree of saturation of the absorbent with carbon dioxide is limited to 0.30–0.35 mol CO_2/mol MEA at the usual its concentration in a solution with water of 15–20% by mass.

In recent decades, a more effective absorbent based on methyldiethanolamine (MDEA) has been used. Table 2 characterizes the effectiveness of CO_2 extraction methods from gases using amine absorbers.

The advantage of MDEA compared to MEA:

- the partial pressure is lower and the boiling temperature is significantly higher, which reduces absorbent losses during its regeneration;
- the heat of reaction with CO_2 is 1.43 times less, which leads to a decrease in the heat load of the desorber boiler and allows deeper regeneration of the sorbent;
- the corrosion activity is lower and therefore a more concentrated solution (up to 50% by weight) and a higher degree of carbonation (0.55–0.6 mol CO_2/mol MDEA) is used, which allows to reduce the amount of circulating absorbent;
- significantly reduced thermochemical degradation of the absorbent and, as a result, there are practically no deposits on the internal surfaces of the equipment, which increases the efficiency of heat exchange and reduces energy costs;
- low toxicity and significantly lower degree of biodegradability of the absorbing solution;
- reduced foaming.

However, MDEA, like a tertiary amine, does not have a mobile H+ atom in the amine group (N), so the direct carbonate-type reaction (as in the case of MEA) is slow. This deficiency is compensated by the introduction of activating additives such as piperazine, ethylenediamine, monoethanolamine, diethanolamine and others.

Methyldiethanolamine with the addition of piperazine (PZ) has a lower desorption energy compared to MEA, which allows saving up to 10% of energy for solution regeneration, while the evaporation losses for MDEA and PZ are significantly lower than for MEA [27, 28]. Aminomethylpropanol (AMP) is a promising solvent for CO_2 removal due to its absorption properties: absorption rate, selectivity and resistance to decomposition [29]. Studies have shown that AMP effectively affects the solubility of CO2 in MDEA solution, the rate of absorption increases with increasing concentration of AMP in MDEA aqueous solution [30]. The authors [31] suggest

Table 2 Efficiency of CO_2 extraction by amine absorbents [26]

Purification method	Reagents, purification conditions	Regeneration conditions	Residual content
Monoethanolamine	Aqueous 13–17% solution of MEA.P-up to 4 MPa $T = 35 \div 40$ °C	$P = 0.15 \div 0.2$ MPa $T = 115 \div 130$ °C	CO_2 from 1% vol. to 5 ppmv
Methyldiethanolamine	Aqueous $40 \div 50\%$ MDEA solution with activator P-up to 12 MPa.$T = 35 \div 90$ °C	$P = 0.05 \div 0.24$ MPa $T = 130$ °C	CO_2 up to 50 ppmv

using a mixture of MDEA/MEA with a concentration of each component of 20% (by weight) as an absorbent.

Activated additives have, as a rule, higher values of saturated vapor pressures than MDEA and are volatile components, which can lead to instability of the absorbent composition. It is obvious that while preserving the activating properties of these additives, their concentrations in MDEA solutions should be minimized.

Today, the MDEA process is the most widespread method of gas purification.

3 Modeling of Aqueous and Amine Processes of Acidic Components Extraction from Biogas and Production of Biomethane

The Code of the Gas Transportation System of Ukraine [32] establishes that the heat of combustion (lower) of natural gas supplied to the gas transportation system should not be lower than 32.66 MJ/m3 (7800 kcal/m^3). According to NJSC "Naftogaz Ukraine", the lower calorific value of natural gas on the territory of Ukraine varies between 8000–8250 kcal/m^3, i.e. higher (better for the consumer) than prescribed by the norm. The concentration of carbon dioxide and hydrogen sulfide in natural gas should be no more than 2% (vol.) and 0.006 g/m^3, respectively.

When using natural gas as motor fuel in transport, according to the Interstate Standard for Internal Combustion Engines [33], the concentration of hydrogen sulfide should not exceed–0.02 g/m^3.

The most widespread technologies of biogas enrichment to biomethane in EU countries are water scrubber technology and amine absorption. Therefore, it is relevant to carry out evaluation comparative calculations of energy indicators of aqueous and amine processes of extraction of acidic components from biogas.

Modeling of Water Absorption

The project of biomethane production and use it at CNG stations is under consideration [34]. It is proposed to enrich 20 nm^3/h of biogas composition: CH_4–63%, CO_2–34% (vol.) to biomethane ($CH_4 \approx 90\%$ and higher) using water scrubber technology. Schematically, the water scrubber technology is shown in Fig. 10.

The solubility of CO_2 and CH_4 in water is directly proportional to pressure. High operating pressure complicates the selection and manufacture of equipment and requires higher electricity costs for gas compression. Very low pressure leads to excessive water consumption and, as a result, to an increase in the size of the column. Thus, the optimal value of the working pressure was chosen–1.0 MPa. To extract CO_2 from 20 nm^3/h of biogas, an absorbent - water in the amount of 4 m^3/h is fed into

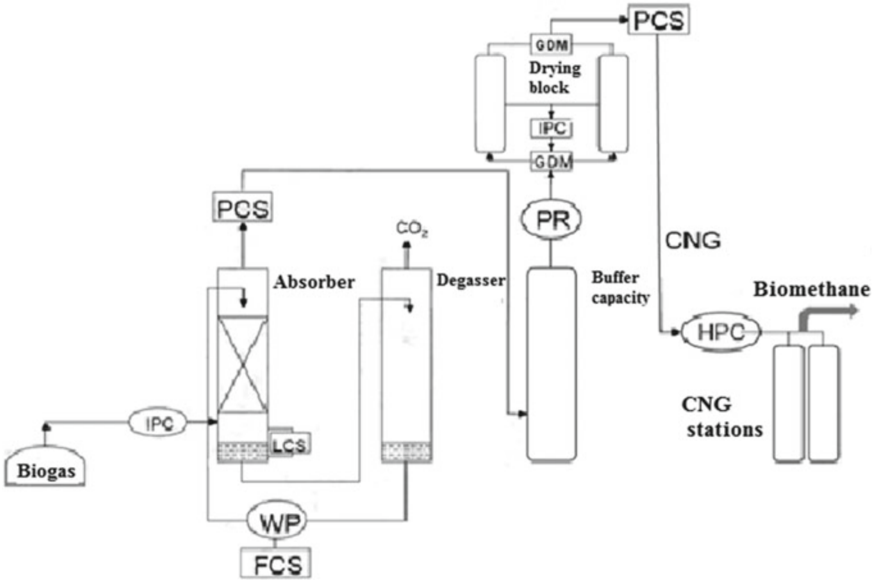


Fig. 10 Water absorption of CO_2 from biogas [34]: IPC–intermediate compressor; HPC–high pressure compressor; PCS–pressure control system; FCS–flow control system; LCS–level control system; GDM–gas distribution mechanism; WP–water pump; PR–pressure regulator

the absorber with a diameter of 0.15 m and a height of 3 m. The total energy costs in this case are 5.25 kW, and taking into account the supply to CNG stations–8.25 kW.

The software system GazCondOil (GCO) was used to model the process of water absorption of CO_2 and H_2S [35–40]. Testing of the methods for calculating phase balances of the main components of biogas with H_2O, i.e. CO_2-H_2O and CH_4-H_2O systems, laid down in GCO, is shown in Table 3. The results of calculations of solubility of CH_4 and CO_2 in H_2O based on GCO and their comparison with data [41] show their almost complete coincidence.

The technological scheme water absorption of CO_2 from biogas, biomethane production and its supply to CNG stations is presented in Fig. 11.

Table 3 Results of calculations of the solubility of CH_4 and CO_2 in H_2O

Temperature, °C	Solubility of CH_4 and CO_2 in H_2O, g/kg_H_2O			
	Data [41]		Software GCO	
	CH_4	CO_2	CH_4	CO_2
0	0.04	3.3	0.045	3.1
20	0.023	1.7	0.024	1.6
40	0.016	0.95	0.016	0.97

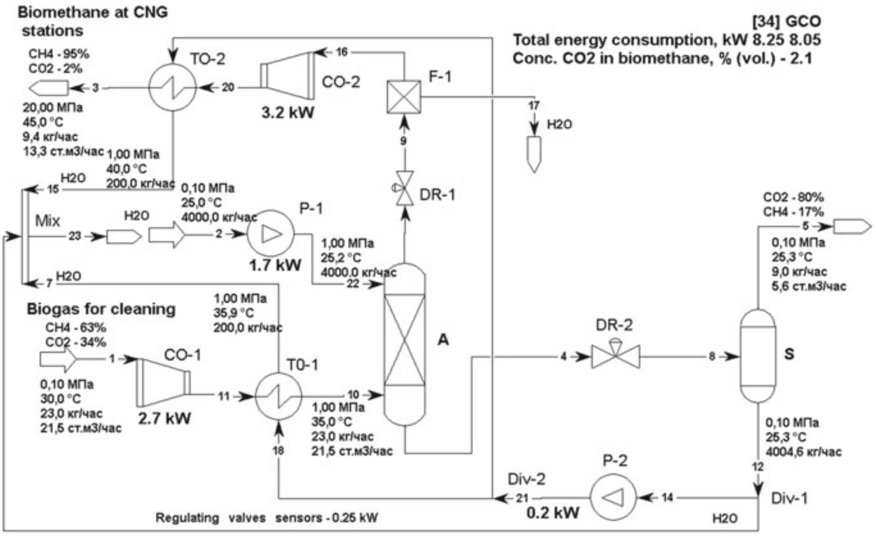


Fig. 11 The technological scheme of water-based CO_2 absorption from biogas: A–absorber; S-1–separator; CO-1, CO-2–compressors; TO-1, TO-2–recuperative heat exchangers; F–filter; Mix–mixer; P-1, P-2–pumps

Biogas (stream 1) in the amount of 20 nm^3/h with a concentration of CH_4–63%, CO_2–34% at P = 0.1 MPa and T = 30 °C is compressed in the CO-1 compressor to 1.0 MPa, cooled in the recuperative heat exchanger TO-1 by water flow 18 and enters the absorber A. The absorber is irrigated with water flow 22 at T = 25 °C. In the absorber column, the CO_2 concentration in biogas decreases to ~ 2% (vol.). Residual water is removed from purified biogas-biomethane (stream 9), then biomethane (stream 16) is compressed in the CO-2 compressor to 20 MPa, cooled in the TO-2 recuperative heat exchanger by water flow 15 and directed (stream 3) to the consumer-CNG stations. The CO_2-saturated aqueous solution (stream 4) is throttled in DR-2 to a pressure of 0.1 MPa and then enters the S separator, where the gas phase (stream 5) and water (stream 12) are separated from it. Flow 12 is divided into three flows, two of which enter the recuperative heat exchangers TO-1 and TO-2, and then they are mixed in the Mix mixerand the flow 23–2-22 is fed to the upper part of the absorber A by pump P-1.

The estimated total energy consumption, taking into account the control valves and sensors, was 8.05 kW, which differs from the data of the water scrubber project–8.25 kW by 2.5%.

Modeling the Process of Amine Absorption

It is known that up to 80% of the capital investment for an amine CO_2 absorption plant from biogas is related to the amount of circulating amine solution, which determines the size of the absorber, desorber, heat exchange equipment, etc. 70% of the operating costs consist of energy costs for the regeneration of the saturated amine solution, i.e., they are largely dependent on the efficiency of the absorbents used and the optimal parameters of the absorption/desorption processes, such as pressure, temperature, and the extent of CO_2 extraction from the saturated absorbent during its regeneration in the desorber.

In Fig. 12 the basic technological scheme of amine purification of biogas, production of biomethane and gaseous carbon dioxide is presented. Process modeling was carried out using the HYSYS software.

Biogas (stream 1) at $P = 0.26$ MPa and $T = 40$ °C enters absorber A-1. The absorber is irrigated with an aqueous solution of the chemosorbent at $T = 45$ °C (stream 9). In the absorber column, the concentration of carbon dioxide in the biogas decreases to ~2% (vol.). Purified biogas (stream 2) is sent to the consumer. The saturated chemosorbent solution (stream 3) enters the recuperative heat exchanger TO-1, where it is heated to a temperature of ~100 °C by the hot return flow 7 of the regenerated sorbent solution, which comes from the desorber D-1. The heated saturated sorbent solution (stream 4) enters the upper part of the D-1 desorber, where the absorbed carbon dioxide is vaporized to the required concentration. The regeneration process is carried out at the chemosorbent boiling temperature of 114–118 °C. The steam-gas mixture that leaves the upper part of the desorber is cooled in the condenser to 25–30 °C, while water vapor condenses and enters the desorber as irrigation (phlegma) in its upper part, and the gas leaves the condenser (stream 5) and contains, in mainly carbon dioxide (~98% vol.). The regenerated chemosorbent solution (stream 6) is fed by the H-1 pump to the TO-1 recuperativeheat exchanger (stream 7), then to the OH-1 cooler (stream 8). After the OH-1 cooler, it enters (stream 9) in the upper part of the absorber A-1.

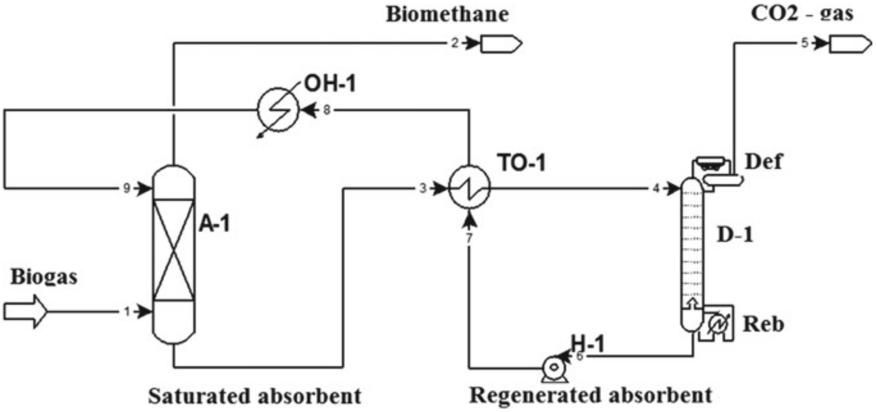


Fig. 12 The basic technological scheme of amine purification of biogas: A-1–absorber; D-1–desorber; Def–dephlegmator; Reb–reboiler; TO-1–recuperative heat exchanger; OH-1–heat exchanger (cooler); H-1–pump

Determination of the Amine Absorbent Effective Composition

In the Table 4 comparative indicators of the CO_2 extraction process from biogas with amine sorbents of different compositions are given. In order to provide an objective evaluation of the tests, absorbents of unchanged composition were used, that is, the calculations were performed for an open cycle of the technological scheme.

In further calculations, the results obtained for the open cycle provided good starting values for modeling the closed cycle using regenerated absorbent.

The $MDEA_{mod}$ absorbent was the most effective-an aqueous solution of methyldiethanolamine (40% MDEA) and monoethanolamine (10% MEA), the use of which reduces the heat load of the desorber reboiler by 1.3 ÷ 2.5 times compared to the use of traditional solutions of monoethanolamine [42–44].

In the Table 5 calculations of the energy indicators of the CO_2 extraction process from 600 st.m^3/h of biogas are given when using: absorbent of unchanged composition (A) = MDEAmod and regenerated absorbent-(B) ≠ MDEAmod. Calculations show that for the extraction degree of CO_2 from the saturated chemosorbent $\mathcal{E} = 0.7$ when absorbent (B) is used, the thermal loads of the desorber reboiler increase by up to 35% due to carbon dioxide contamination of the absorbent compared to absorbent (A). When the degree of CO_2 extraction increases to $\mathcal{E} = 0.9$, the thermal loads for compositions (A) and (B) increase by ~ 3 times, but the difference between the latter significantly decreases (to ~10%) due to the reduction of the content of CO_2 in the regenerated sorbent and, thus, bringing the latter closer to the initial composition.

Table 4 Comparison of the main indicators of the CO_2 extraction process from biogas with amine absorbents[a]

Indicators	Biogas Composition, % (vol.): CH_4-50, CO_2-45, N2-3, H_2O-2 G = 360 st. m^3/h, T = 40 °C, Pabs. = 0.26 MPa, Pdes. = 0.16 MPa CO_2 concentration in biomethane-2% (vol.)					
	Absorbent composition, % (wt.)					
	15%MEA	18%MEA	20%MEA	7%MEA + 30%MDEA	8%MEA + 40%MDEA	$MDEA_{mod}$
Absorbent consumption, kg/h	4800	4215	3940	4380	3730	**3120**
Thermal load of the desorber reboiler, kW	375	400,0	425	200	180	**160**

[a]Calculations with non-regenerated absorbent

Table 5 Comparison of calculated energy indicators of the CO_2 extraction from biogas using $MDEA_{mod}$ absorbent: unchanged composition (A) and regenerated (B)

Biogas Composition, % (vol.): CH_4-50, CO_2-45, N_2-3, H_2O-2 G = 600 st.m3/h	Flow absorbent, kg/h	Power pump, kW	Heat load, kW	
			Reboiler desorber	Deflegmator desorber
CO_2 extraction degree = 0.7				
(A) (B) δ, [(B)−(A)/(A)]*100%	5200 6890 32.5%	0,20 0,26 30,0%	281.0 380,0 35.2%	146.5 191.3 30,6%
CO_2 extraction degree = 0,8				
(A) (B) δ, [(B)−(A)/(A)]*100%	5200 6690 28.7%	0,20 0,25 25.0%	365.0 453.3 24.2%	202.5 255.4 26.1%
CO_2 extraction degree = 0,9				
(A) (B) δ, [(B)−(A)/(A)]*100%	5200 5830 12.1%	0,20 0,22 10,0%	606.4 670,0 10,5%	418.5 460,4 10,0%

Determination of the Amine Absorption Process Optimal Parameters

When determining the optimal temperature and pressure in the absorber and desorber in calculations [45, 46] biogas in the amount of 600 st.m3/h and composition: CH_4–48% (vol.), CO_2–45% (vol.), H_2S–2% (vol.), N_2–3% (vol.) and H_2O–2% (vol.) biogas was adopted. MDEAmod was used as an absorbent. The temperature in the absorber varied from 35 to 55 °C at a pressure of 0.26, 0.28 MPa. The pressure in the desorber varied from 0.14 to 0.2 MPa with an interval of 0.02 MPa. In the Table 6 the calculated absorbent consumption, CO_2 and H_2S concentrations at the absorber outlet are shown. At the maximum permissible concentration of H_2S in biomethane–5 mg/st.m^3, the optimal temperature at which the aqueous solution of the chemosorbent is supplied to the absorber is determined to be T = 45 °C.

Table 6 Calculated absorbent consumption, concentrations of CO_2 and H_2S at the absorber outlet

Pressure, MPa	Temperature, °C	Absorbent flowrate, kg/h	Concentration of the components at the absorber outlet	
			CO_2, % (vol.)	H_2S, mg/st.m^3
0,26 0,26 0,26	35 45 55	6720 6720 6720	2.0 1.1 0,65	3.5 4.5 7.0
0,28 0,28 0,28	35 45 55	6260 6260 6260	2.0 1.1 0,7	3.6 4.8 8.9

The Table 7 shows the calculated energy indicators of the CO_2 and H_2S extraction from biogas when using the MDEAmod absorbent. The pressure in the absorber varied from P = 0.24 to 0.3 MPa, in the desorber–from P = 0.14 to 0.2 MPa with an interval of 0.02 MPa. Permissible concentration at the absorber outlet: CO_2–1% (vol.), H_2S–5 mg/st.m^3.

Figure 13 illustrates the dependence of the heat load of the desorber reboiler on the pressure at carbon dioxide extraction degree from a saturated amine solution $\varepsilon = 0.7$ and 0.8. The heat load of the desorber reboiler at the CO_2 extraction degree $\mathcal{E} = 0.7$ is on average 30% less than at $\mathcal{E} = 0.8$.

The dependence of the desorber reboiler heat load on the residual concentration of CO_2 in biomethane at P = 0.16 and 0.18 MPa and $\mathcal{E} = 0.7$ and 0.8 is shown in Fig. 14. It can be seen that the load decreases when the CO_2 content in biomethane increases to 2.5%. A further increase in CO_2 concentration has practically no effect on the reboiler load. Obviously, the optimal degree of CO_2 extraction from a saturated amine solution is $\mathcal{E} \leq 0.7$.

When the pressure in the desorber is P = 0.14 MPa, the heat loads of the reboiler and dephlegmator, as well as the absorbent consumption, are the highest for all CO_2 extraction degrees. The lowest indicators are at P = 0.2 MPa. At the same time, the equilibrium solubility of carbon dioxide depends on the gas pressure and the concentration of the amine solution. Since $MDEA_{mod}$ absorbent uses 10% MEA as an activating additive, carbonates and bicarbonates are formed as a result of chemisorption, which decompose in the desorber when the flow is heated above 120 °C [47]. The completeness of hydrogen sulfide extraction from biogas also depends on the concentration of the amine used for this purpose, the quantitative ratio of the amine to the gas being purified, the temperature, and the completeness of the regeneration of its solution. It is necessary that the content of sulfides in the regenerated solution is minimal and the

Table 7 Estimated energy indicators of extracting CO_2 and H_2S from 600 st.m^3/h biogas[a]

Pressure, MPa		Absorbent flow rate, kg/h	Power pump, kW	Heat load, kW		
Absorber	Desorber			Reboiler desorber	Deflegmator desorber	Heat exchanger/ cooler
CO_2 extraction degree $\mathcal{E} = 0.7$						
0.24	0.14	7790	0,30	509	349	217
0.26	0.16	6720	0,26	372	219	211
0.28	0.18	6260	0,24	323	183	199
0.30	0.20	5955	0,23	296	166	189
CO_2 extraction degree $\mathcal{E} = 0.8$						
0.24	0.14	7790	0,30	830	647	221
0.26	0.16	6720	0,26	510	332	217
0.28	0.18	6260	0,24	413	245	208
0.30	0.20	5955	0,23	370	209	201

[a]–Calculations with admissible concentration at the absorber outlet: CO_2–1% (vol.), H_2S–5 mg/ st.m^3

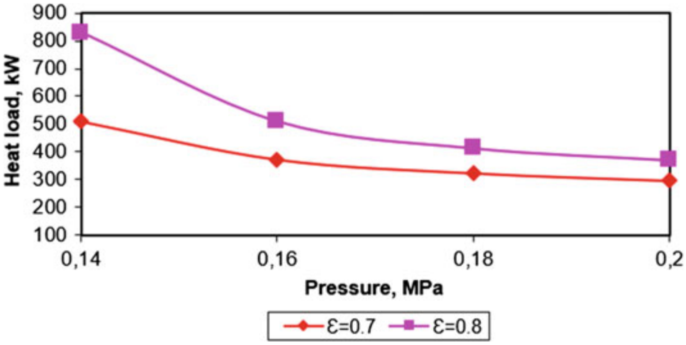


Fig. 13 Dependence of the heat load of the desorber reboiler on the pressure in the desorber with CO_2 extraction degree from the saturated amine solution Ɛ = 0.7 and 0.8

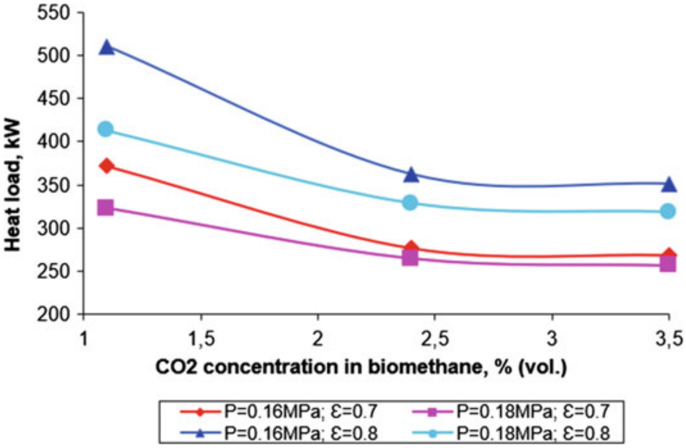


Fig. 14 Dependence of the desorber reboiler thermal load on the residual concentration of CO_2 in biomethane at P = 0.16; 0.18 MPa and Ɛ = 0.7; 0.8

temperature of the bottom of the desorber is not higher than 120 °C, since at a higher temperature MEA partially decomposes [48]. The temperature of the bottom of the desorber varies depending on the pressure from 113 °C at P = 0.14 MPa to 121 °C at P = 0.2 MPa, which is higher than the permissible 120 °C, therefore the pressure range P = 0.16–0.18 MPa is considered optimal.

Combined Water-Amine Absorption Processes of CO_2 Extraction from Biogas

As noted, water and amine absorption are fairly common technologies for obtaining biomethane from biogas in EU countries. Calculation comparisons of water and amine absorption processes of CO_2 extraction from biogas are given in publications [49, 50].

In work [51], it is proposed to use a combined water-amine method for cleaning biogas from CO_2, in which the preliminary CO_2 extraction from biogas occurs with the help of water absorption at a pressure close to atmospheric or increased to 0.2–0.3 MPa. For the final purification of biogas to biomethane, amine absorption is used.

Obviously, it is relevant to carry out comparative calculations of water, amine and combined water-amine absorption processes for a wide range of CO_2 concentrations in biogas. Such calculations were carried out [52, 53], the results and comparison are given below.

Figure 15 shows a two-stage technological scheme of water purification of 250 nm^3/h of biogas from CO_2 using two options. When using variant A (Var A), the obtained aeration gas is mixed with the input biogas in order to increase the yield of methane in the purified gas. According to option B (Var B), degassing gas (aeration gas) with a relatively high concentration of CH_4 ($\geq 30\%$) in it can be used as fuel gas. Below is a brief description of the technological process of preliminary purification of biogas from CO_2.

Biogas enters absorber A-1 at a pressure of 0.26 MPa. Absorbent–fresh water–is supplied to the absorber in the counterflow of the gas. In this process, carbon dioxide dissolves in water, and enriched methane gas leaves the absorber for further amine purification at a pressure of 0.26 MPa. Water saturated with CO_2 leaves the absorber and enters the A-2 evaporation column, where it is blown with air under a pressure of 0.12–0.15 MPa, while the dissolved methane is almost completely removed from H_2O. The aeration gas leaving column A-2 can be mixed with the biogas flow fed to absorber A-1 (Var A) or used as fuel gas (Var B). In column A-3 at close to atmospheric pressure the aqueous solution in the countercurrent is blown with aeration air, while CO_2 is almost completely removed from the absorbent – H_2O, which then enters the absorber A-1 again.

Modeling of absorption water processes was carried out using the GasCondOill program. The description of the technological scheme of amine absorption of carbon dioxide from biogas was considered in the subsection "Modeling of water absorption" (Fig. 12).

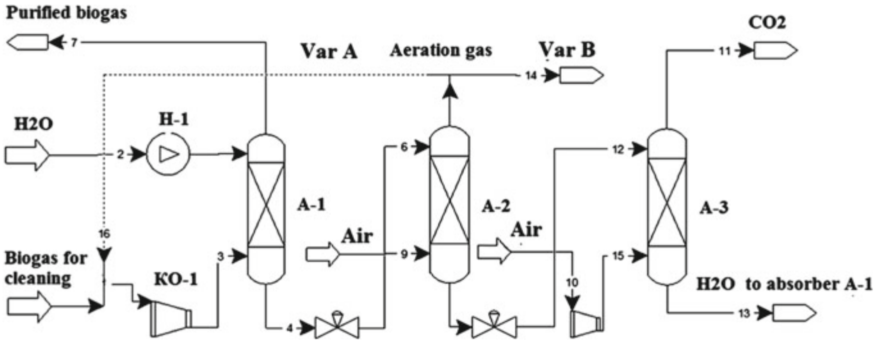


Fig. 15 The basic two-stage technological scheme of water absorption purification of biogas from CO_2: A-1, A-2, A-3–absorbers; KO-1–biogas compressor; H-1–water pump

Results of Comparative Calculations of Water, Amine and Combined Water-Amine Absorption Processes

The results of simulation of CO_2 absorption/desorption processes with 250 nm^3/h of biogas of different composition are presented in Table 8. The concentration of CO_2 in BG varied from 32 to 42% (vol.). Such concentrations of CO_2 are the most common for biogas, in particular, biogas from solid household waste landfills (~30 ÷ 40%).

The specific energy consumption of the water process compared to amine absorption is lower, on average, by ~2.0 times, but the total losses of CH_4 during water absorption amounted to 7.1 ÷ 7.6% with practically zero losses of CH_4 when using amine technology. It should also be noted that during the water absorption of CO_2 at $P = 1.0$ MPa, the methane contained at the outlet of the evaporation column A-2 due to its low concentration (10.7–15.6%) can be used as fuel only with the help of an auxiliary combustion system, therefore it is considered as losses.

According to the Var A scheme (Fig. 15), where the degassing gas of the evaporation column A-2 is mixed with biogas in order to increase the potential content of CH_4 in obtained biomethane and is fed to the input of the KO-1 compressor, the combined water-amine absorption has an excess of energy costs by ~ 50% compared to water, and methane losses are insignificant and amount to −0.14–0.24%.

When using Var B (Fig. 15) in the aeration gas–degassing gas of column A-2, the concentration of CH_4 is, on average, about 30–35% and this gas can be used as a fuel for the production of both electricity and heat and, to a large extent, to compensate for the energy costs of the biogas compressor during the previous water absorption of CO_2 or heat costs for the regeneration of a saturated amine solution. Thus, in case compensating the compressor power when compressing biogas to 0.26 MPa, the specific energy consumption amounted to an average of 0.42 $kWh/nm^3\_CH_4$, which is 1.2 times higher than the energy consumption of traditional water absorption at $P = 1.0$ MPa. For the option of compensation of heat consumption of the amine desorber reboiler, the specific energy consumption was, on average, 0.29 kWh/ nm^3_CH_4, which is 20% less than the water technology. Methane losses for both variants of the water-amine process with compensation of energy consumption are the same and range from 2 to 2.8%.

Figure 16 illustrates the specific energy consumption in the biomethane production from 250 nm^3/h of biogas of different composition using water, amine and water-amine absorption processes. It can be seen that with a decrease in CO_2 concentration in BG there is a sharp decrease in specific energy consumption in the amine process, while water and water-amine absorption has an almost insignificant decrease in energy consumption for all BG compositions.

Figure 17 shows losses (%, vol.) of methane in the obtained biomethane in the considered processes. The most significant losses occur during water absorption, which is associated with increased solubility of CH_4 in H_2O. The content of CH_4 in biomethane when applying the technology of amine and water-amine absorption practically corresponds to its potential content in biogas.

Technological schemes of the most common processes of amine and water extraction of CO_2 and H_2S from biogas were developed using computer modeling. For the amine process, an effective absorbent is proposed–MDEAmod, the use of which reduces the load of the desorber reboiler by 1.5–2.5 times compared to the use of traditional aqueous solutions of MEA. The optimal parameters of amine absorption/desorption processes were determined: the temperature of the absorbent in the inlet to the absorber is −45 °C at a pressure of $0.26 \div 0.28$ MPa, the pressure in the desorber is $0.16 \div 0.18$ MPa, the degree of extraction of carbon dioxide in the desorber is $\varepsilon \leq 0.7$.

Energy consumption when using amine absorption of CO_2 from biogas is ~ 2 times higher compared to water absorption, but the output of biomethane is 7–8% higher due to the absence of methane losses, as in the case of its dissolution in H_2O. This biomethane difference can be used to compensate for the energy costs of regenerating the circulating amine absorbent.

The energy efficiency of combined water-amine absorption is commensurate with the energy consumption when using water absorption due to a significant reduction in the work of biogas compression during the initial water absorption of CO_2 from biogas and a reduction in heat costs for the regeneration of saturated amine absorbent, since part of CO_2 has already been previously removed from biogas.

4 Extraction of Carbon Dioxide from Process Gases Using MDEAmod Absorbent

In Ukraine, until now, the energy costs per unit of manufactured products, and therefore, the resource intensity, are 2–3 times higher than in similar productions of industrially developed countries of the West. Therefore, by reducing energy consumption during modernization or when developing new technological processes, several

Table 8 Results of simulation of water, amine and water-amine CO_2 absorption processes from 250 nm^3/h of biogas

Indicators	CH_4/CO_2 concentration in biogas, % (vol.)		
	55/42	60/37	65/32
CH_4 content in biogas, nm^3	137.5	150	162.5
Water Pabs = 1.0 MPa (Var B)		139	151
CH_4 content in biomethane, nm^3	127	12.9	15.6
CH_4 concentr. in degassing gas, % (vol.)	10.7	47.7	47.7
Energy consumption, kWh	47.7	0.34	0.32
Energy consumption, kWh/nm^3_CH_4	0.38	7.3	7.1
CH_4 losses,%	7.6		
Amine Pabs = 0.26 MPa			
CH_4 content in biomethane, nm^3	137.5	150	162.5
Energy consumption, kWh	119	110	101
Energy consumption, kWh/nm^3_CH_4	0.86	0.73	0.62
CH_4 losses,%	–	–	–
Water–Amine Pabs = 0.26 MPa (Var A)			
CH_4 content in biomethane, nm^3	137.3	149.7	162
Energy consumption, kWh	72.8	76.3	79.5
Energy consumption, kWh/nm^3_CH_4	0.53	0.51	0.48
CH_4 losses,%	0.15	0.2	0.3
Water–Amine Pabs = 0.26 MPa (Var B)[a]			
CH_4 content in biomethane, nm^3	133.7	146.5	159.2
CH_4 concentr. in degassing gas, % (vol.)	33.7	33.9	35.6
Energy consumption, kWh	57.8	62.5	67.5
Energy consumption, kWh/nm^3_CH_4	0.43	0.43	0.42
CH_4 losses,%	2.8	2.3	2.0
Water–Amine Pabs = 0.26 MPa (Var B)[b]			
CH_4 content in biomethane, nm$_3$	133.7	146.5	159.2
CH_4 concentr. in degassing gas, % (vol.)	33.7	33.9	35.6
Energy consumption, kWh	36	42	48.5
Energy consumption, kWh/nm^3_CH_4	0.27	0.29	0.3
CH_4 losses, %	2.8	2.3	2.0

[a] Combined water-amine CO_2 absorption from biogas using potential energy of degassing gas (CH_4 > 30%) to compensate for power consumption of biogas compressor during preliminary water absorption

[b] Combined water-amine CO_2 absorption from biogas using potential energy of degassing gas (CH_4 > 30%) to compensate for heat costs for regeneration of saturated amine absorbent

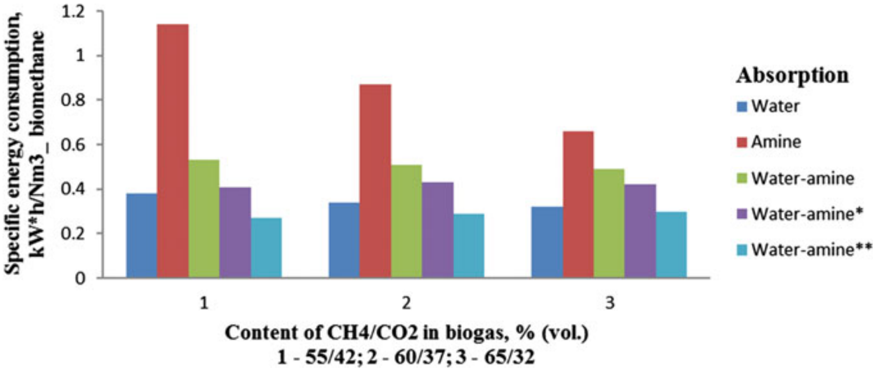


Fig. 16 Specific energy consumption in the production of biomethane from 250 nm^3/h biogas of different composition using water, amine, water-amine and combined water-amine absorption using potential energy of degassing gas ($CH_4 > 30\%$) to compensate for the power consumption of biogas compressor during preliminary water absorption (*) and heat costs for regeneration saturated amine absorbent (**)

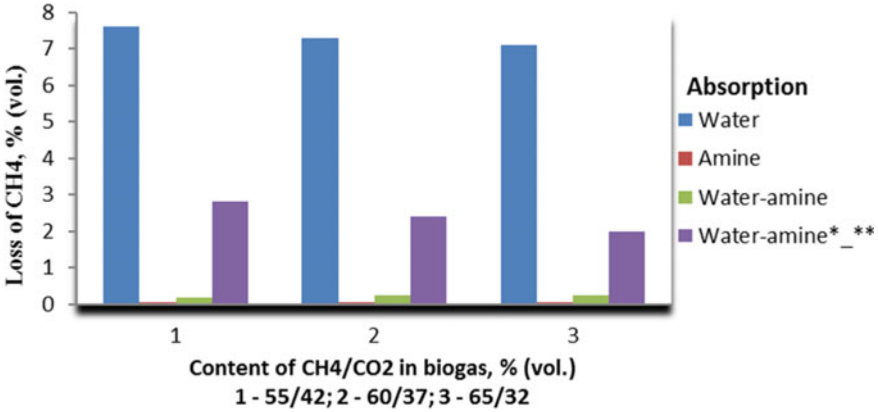


Fig. 17 CH_4 losses during production of biomethane from 250 nm^3/h of biogas of different composition using water, amine, water-amine and combined water-amine absorption (*_**) using potential degassing gas energy ($CH_4 > 30\%$)

problems are simultaneously solved: reducing the use of resources, increasing the economic efficiency of production, reducing harmful effects on nature.

One of the energy-intensive processes is the technology of extracting carbon dioxide from process gases. Moreover, CO_2 can be the object of both targeted allocations, for example, in the production of urea, and ballast or a “polluting” admixture in process gases, which is a poison at later stages, for example, in the production of some types of mineral fertilizers. The main raw material for the production of nitrogen-containing fertilizers is ammonia, the production of which includes the stage of absorption purification of synthesis gas from carbon dioxide, the costs of which make up to 30% of the cost price of ammonia.

A reduction in resource intensity can also be achieved in technologies where CO_2 affects the overall efficiency of the process. For example, it is known that in the blast furnace process, the utilization degree of the coke carbon reducing potential is less than 50%. Iron reduction reactions stop when the carbon dioxide concentration increases to the thermodynamically equilibrium one. Removing CO_2 from the blast furnace gas allows unused carbon monoxide to be returned to the blast furnace. The consumption of coke in this case will decrease in proportion to the increase in the degree of use of its regenerative potential, i.e., more than twice. The number of harmful emissions will decrease proportionally.

The gas obtained during the gasification of hard coal with oxygen and water vapor should first be freed from the main part of CO_2, and only then the gas, consisting mainly of CO and H_2, should be subjected to methanation.

Synthesis gas from hydrocarbon gases (natural, associated gas, gases of processing of other fuels) is currently the main source of ammonia production. Oxygen-containing compounds are poisons for ammonia and methanol synthesis catalysts. CO_2 impurities in synthesis gas have a negative effect on the ammonia synthesis catalyst, reducing its productivity, and therefore it is necessary to reduce their content in the nitrogen–hydrogen mixture sent to ammonia synthesis as much as possible.

The authors conducted calculation studies on CO_2 extraction from flue gases [54] using $MDEA_{mod}$ absorbent. But the simulation of CO_2 extraction from biogas and flue gases was carried out at a sufficiently low pressure–up to 0.3 MPa. Therefore, it is important to carry out calculation studies on the use of $MDEA_{mod}$ absorbent at elevated pressure and for the carbon dioxide extraction from other gases, such as synthesis gas, generator gas.

The process of CO_2 extraction from the following process gases is considered below [55, 56]:

- flue gas, combustion products at $\alpha = 1$ of natural gas;
- generator gas, brown coal gasification process;
- synthesis gas, gas purification from CO_2 in the AM-70/76 unit;
- biogas, purification of biogas from landfill No. 5 (Pidgircy village, Kyiv region).

The principle technological scheme of CO_2 extraction from process gases by amine absorbents is shown in Fig. 12. The composition of process gases is given in Table 9. For comparison, aqueous solutions of amines of the composition: $MDEA_{mod}$ and 18% MEA were used as absorbents (Table 10).

Figure 18 shows the relative difference δ (%) of the thermal loads of the reboiler, the desorber dephlegmator and the heat exchanger-cooler for the two absorbents-18% of MEA (I) and MDEAmod(II). õ = 100% *(I-II) / II.

As can be seen from the figure, the thermal load of the circuit elements in the scheme above for all types of gas in the case of an 18% MEA absorbent. In this case, the relative difference δ reaches 220%, that means, the thermal load I exceeds II in 3 times.

Table 9 Composition of process gases

Components	Concentration, % (vol.)			
	Flue gas	Generator gas	Synthesis gas	Biogas
Hydrogen	–	25.0	60.0	–
Nitrogen	72.0	6.0	20.0	3.0
Carbon monoxide	–	48.0	0.5	–
Carbon dioxide	9.3	15.9	19.0	45.0
Methane	–	5.0	0.5	50.0
Water	18.7	0.1	–	2.0

5 Experimental Biomethane Production

For the practical study of the separation process of the biogas into CH_4 and CO_2, a project of a laboratory installation using the amine process of CO_2 absorption was developed at the Gas Institute of the National Academy of Sciences of Ukraine. The installation scheme includes an absorbent regeneration system, which allows you to heat the saturated absorbent to the temperature at which intensive release of carbon dioxide from the saturated absorbent begins. During these experiments, the process of CO_2 absorption and absorbent regeneration was studied.

Output data:

- absorber diameter (internal)–76 mm;
- diameter of the desorber (internal)–129 mm;
- the temperature of the saturated absorbent at the inlet to the desorber is 80–100 °C;
- the temperature of the regenerated absorbent at the outlet from the desorber is 100–120 °C;
- the maximum load of the desorber reboiler is 2 kW;
- biogas consumption 0.5–2 nm^3/h;
- absorbent consumption–0.2–1.2 l/min.

The base scheme for extracting CO_2 and H_2S from biogas using aqueous amine solutions is shown in Fig. 12.

The laboratory installation scheme for the separation of biogas into biomethane and carbon dioxideis presented in Fig. 19.

The filling of the laboratory installation with the amine solution is carried out through the upper fitting of the absorber, after which, due to the operation of the circulation pump, it also enters the desorber. After filling both columns with a solution of amines, the filling fitting is closed and the heating of the lower part of the desorber is turned on. The circulation pump works constantly, and due to the presence of the flowmeter F, a constant flow of the amine solution in the system is maintained by adjusting the number of revolutions of the pump. To reduce energy consumption for heating the saturated solution in the desorber, a recuperative heat exchanger is installed in the laboratory unit. Post-cooling of the regenerated solution after the

Table 10 Comparison of the main indicators of the absorption process of CO_2 recovery from process gases by absorbents[a] : $MDEA_{mod}$/18% MEA

Indicators	Flue gas	Generator gas	Synthesis gas	Biogas
Absorption unit				
Gas consumption, m^3/h	1470	46,000	100,000	600
Pressure, MPa	0.12	0.5	2.5	0.26
Inlet gas temperature, ºC	40	30	30	40
Absorbent temperature at the inlet, ºC	45	35	35	45
Concentration of CO_2 at the inlet, % (vol.)	9.3	15.9	19.0	45.0
Absorbent consumption, kg/h	2710/3170	156,700/181,400	301,600/396,200	5200/6930
Absorbent temperature at the outlet, ºC	62/59	64/63	73/68	77/74
Concentration of CO_2 at the outlet, % (vol.)	0.03/0.03	0.19/0.19	0.2/0.19	2.0/2.0
Desorption unit				
Pressure, MPa	0.16	0.2	0.2	0.16
The temperature of the saturated solution at the inlet, ºC	101/98	107/104	100/101	100/100
The temperature of the regenerated solution at the outlet, ºC	116/114	123/121	121/120	116/114
The content of CO_2 in a saturated solution, mol CO_2/mol solution	0.42/0.61	0.38/0.56	0.52/0.67	0.42/0.54
The content of CO_2 in the regenerated solution, mol CO_2/mol solution	0.08/0.12	0.08/0.11	0.1/0.13	0.08/0.11
Concentration of CO_2 at the outlet from the reflux condenser, % (vol.)	98	98	98	98
Thermal load, kW				
Reboiler desorber	196/488	9625/13,150	18,850/13,150	365/675
Desorber's reflux condenser	118/384	4831/7132	7702/12,420	203/470
Heat exchanger-cooler of the regenerated adsorbent	58/70	5648/7170	13,960/17,020	203/257

[a] The calculation was carried out using the software system of technological modeling HYSYS, the composition of absorbents was adopted unchanged

recuperative heat exchanger, before it enters the absorber, is performed in an air-cooled heat exchanger. The desorber is equipped with: a heater and a level sensor, which automatically turns off the heater when the level drops below the critical level, as well as a dephlegmator–a reflux condenser in the upper part of the column.

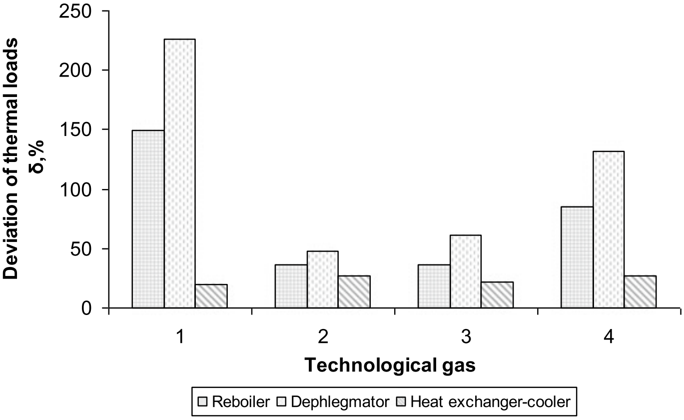


Fig. 18 Comparative evaluation of the thermal loads of the reboiler, desorber dephlegmator and heat exchanger-cooler of the regenerated absorbent for various gases: 1–flue gas; 2–generator gas; 3–synthesis gas; 4–biogas

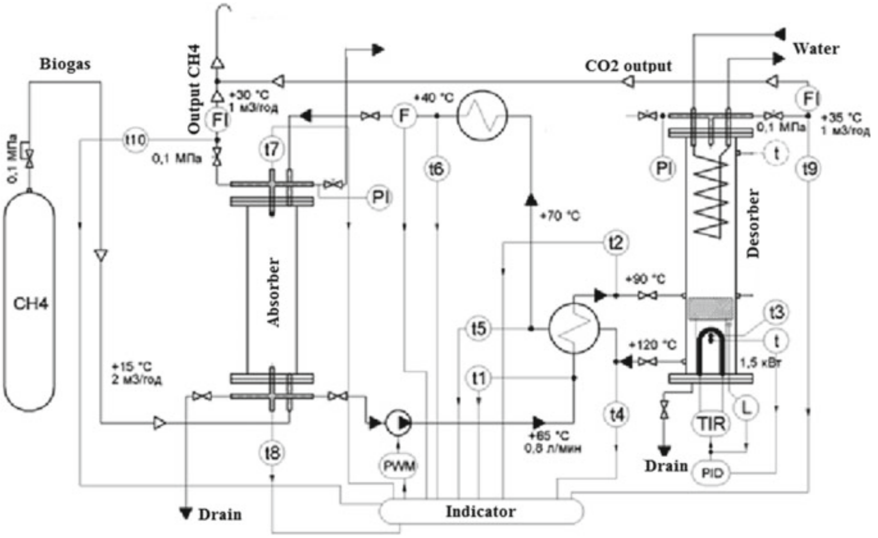


Fig. 19 Scheme of the laboratory installation

To control the process, a special controller of technological processes was developed, which allows to monitor all temperatures, consumption of the amine solution and pump control.

Comparison of Indicators of CO_2 Extraction by Aqueous Amine Solutions from Biogas by Computer Simulation and Those Obtained on a Laboratory Setup

During the testing of the laboratory installation for the CO_2 extraction from biogas, it was planned to use amine absorbents $MDEA_{mod}$ and 20% MEA. But since it is currently impossible to purchase officially methyldiethanolamine in Ukraine, testing was carried out using 20% monoethanolamine. A number of biogas composition samples were taken from the Kamianets-Podilskyi landfill and the average composition of biogas was obtained with the content of CH_4–62% (vol.), CO_2–37% (vol.).

Comparison of indicators of calculations and those obtained on a laboratory setup is given in Table 11. The maximum deviation of the calculated from the experimentally obtained concentration of CH_4 in biomethane at the pressure in the absorber Pabs = 0.12–0.2 MPa is 2.8%. The content of CO_2 in the obtained biomethane at the laboratory installation is within the range of 3.3–6.6% (vol.), which exceeds the maximum permissible 2%, therefore, further work is planned to improve the laboratory installation.

The results of the above calculations and experimental studies can be used for the design, creation and testing of amine absorption technologies for the CO_2 extraction from biogas and the production of biomethane and carbon dioxide.

Design of Pilot Plant for Extraction of Target Fractions of Biomethane and Carbon Dioxide from Biogas

Today, the biogas market has significant development among countries that are actively implementing programs for the transition to alternative energy sources and systematically support initiatives aimed at introducing new technologies.

The production of biomethane from biogas and its use for partial direct replacement of natural gas in distribution networks, as well as the use of biomethane as motor fuel at gas filling stations, is relevant both from an energy point of view and from an environmental point of view. Ozone-destroying carbon dioxide extracted from biogas can also be a commercial product that is used: for the production of fertilizers, in the food industry as a preservative, in welding as a protective medium, as a coolant and working fluid in thermal power plants, etc.

Therefore, at the Institute of Gas of the National Academy of Sciences of Ukraine, work was carried out on the design of a research and industrial installation for the extraction of target fractions of biomethane and carbon dioxide from biogas using amine absorbents. The results of this work are presented below.

The basic technological scheme of cleaning 250 nm^3/h of biogas by 20% MEA and $MDEA_{mod}$, obtaining biomethane and gaseous carbon dioxide is shown in Fig. 12.

Table 11 Comparison of calculated and laboratory indicators of the amine process of CO_2 extraction from biogas

Absorption/desorption process indicators Absorbent–20%MEA	Biogas G = 1.0 nm^3/h. Content, % (vol.): CH_4-62, CO_2-37		
	Pressure in the absorber P_{abs}, MPa		
	0,12	0,16	0,2
	exp/calc	exp/calc	exp/calc
Absorbent consumption, kg/h	18/19	15/15	14/13
The temperature of the regenerated absorbent at the inlet to the absorber, °C	39/39	52/55	53/55
The temperature of the saturated absorbent at the outlet of the absorber, °C	47/52	76/71	76/73
Temperature of the saturated absorbent at the inlet to the desorber, °C	83/83	92/92	98/98
The temperature of the regenerated absorbent at the outlet from the desorber, °C	97/100	113/112	117/118
Concentration in biomethane, % (vol.)[a]:			
CH_4	95.5/95.4	93.8/95.7	92.6/95.2
CO_2	3.3/4.3	5.5/4.0	6.6/4.6
Thermal load of the reboiler desorber, kW	1.5	2.0	2.0

[a] Concentrations of components in biomethane are given taking into account drying to the temperature of the dew point according to humidity minus 8 (−8) °C (at P = 3.92 MPa)

The main results of calculations of the technological scheme of the CO_2 extraction process from biogas and biomethane production are summarized in Table 12.

The results of the calculations show that the energy consumption when using MDEAmod is 1.5 times lower than when using 20% MEA, therefore, the properties of the absorbent MDEAmod were used in the design of pilot plant for the extraction of target fractions of biomethane and carbon dioxide from biogas.

According to the Table 12 and with the application of the methodology [57], the working documentation of the project of an experimental-industrial plant for extracting target fractions of biomethane and carbon dioxide from biogas was developed.

The technological scheme of the research and industrial plant for biogas separation is presented in Fig. 20.

The technological scheme of the experimental-industrial plant of amine-based CO_2 recovery absorption from biogas and production of biomethane from 250 nm^3/h of biogas has been developed. Technological and structural calculations of the devices

Table 12 The main indicators of biogas purification from CO_2

Indicators $P_{abs} = 0.26$ MPa, $T_{abs} = 45$ °C Absorber $P_{des} = 0.16$ MPa	250 nm^3/h of biogas, composition % (vol.): CH_4–50, CO_2–45, N_2–3, H_2O–2	
Absorber	20% MEA	$MDEA_{mod}$
Absorbent outlet temperature, °C	62	61
Absorbent consumption, kg/h saturated regenerated	5044 4827	5095 4876
Absorbent density, kg/m^3 saturated regenerated	1045 1018	1052 1039
Output of biomethane, nm^3/h	140	140
CH_4 concentration at the outlet, % (vol.)	90	90
CO_2 concentration at the outlet, % (vol.)	1.6	1.7
Desorber		
Absorbent inlet temperature, °C	100	105
Absorbent outlet temperature, °C	114	115
The degree of carbonation of the absorbent, mol CO_2/mol amine saturated regenerated	0,54 0,19	0,32 0,11
CO_2 output, nm^3/h	114	113
CO_2 concentration at the inlet from dephlegmator, % (vol.)	98	98
Load, kW reboiler dephlegmator	350 226	235 141

of the process unit were carried out. The working documentation of the pilot plant project and drawings of the main devices of the technological process unit were developed: absorber, desorber and recuperative heat exchanger for heating saturated amine absorbent.

6 Enrichment of Biogas with High Air Content

With intensive pumping of landfill gas, the concentration of methane can drop to 30% or less. At the same time, the critical CH_4 content in fuel for gas piston engines is 28%. To solve the problem, biogas enrichment (through CO_2 extraction) with increased air content was investigated. The results of calculations of CO_2 extraction process from biogas of different composition with increased air content ($N_2 = 20$–40%) are given in Table 13. The concentration of methane increased by 1.2–1.4 times, and the heat of release of 1 kg of CO_2 was 1.0 kW for the entire spectrum of biogas compositions.

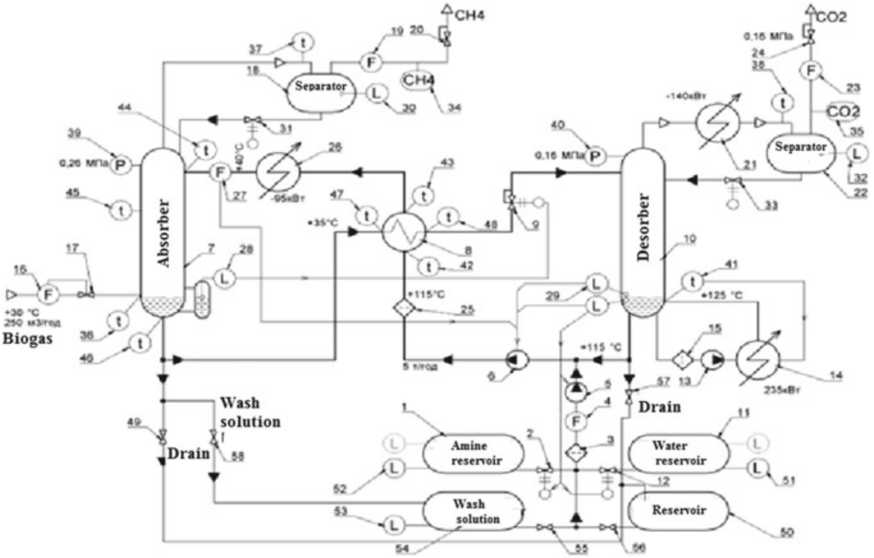


Fig. 20 Technological scheme of the pilot biogas separation plant

Table 13 Indicators of the CO_2 extraction process from 250 nm^3/hour of biogas of different composition with increased air content ($N2 = 20 \div 40\%$)

Indexes	Composition of biogas, % (vol.):		
	CH_4-50 CO_2-30 N_2-20	CH_4-45 CO_2-25 N_2-30	CH_4-40 CO_2-20 N_2-40
Consumption of $MDEA_{mod}$ absorbent, kg/h	2318	1733	1346
Content in methane gas, % (vol.):			
CH_4	68.3	57.3	47.8
CO_2	1.2	1.2	1.1
CO_2 concentration at the desorber outlet, % (vol.)	98	98	98
Output of gaseous CO_2, kg/h	143	118	92
Thermal load of reboiler desorber, kW	159	118	93
Specific consumption when obtaining gaseous CO_2, kW/kg_CO_2	1.1	1.0	1.0

7 Study of Landfill Biogas

The first stage of industrial utilization of biogas was the study of landfills. Employees of the Gas Institute drilled test wells at 17 landfills of solid waste of Ukraine with different terms of waste disposal. Experimental wells were drilled, an imitation of industrial gas extraction from a well with the help of a special device developed for these purposes, was performed (Fig. 21) and gas samples were taken.

The obtained gas samples were analyzed in the Institute's laboratory using an Agilent 6890N gas chromatograph. The methane content in biogas in all samples exceeded 50%, so it can be fed directly into internal combustion engines. Biogas also contains 20–40% carbon dioxide and less than 6.5% nitrogen (Fig. 22).

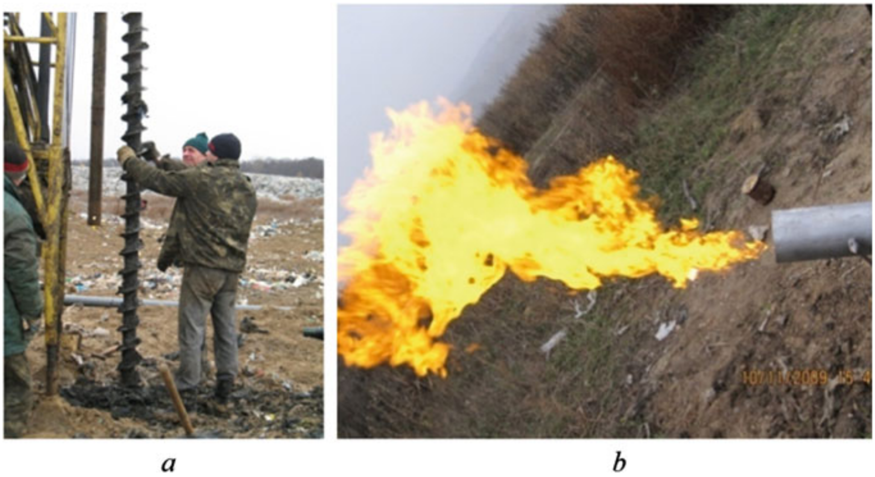


Fig. 21 Study of the debitage and chemical composition of the well. Drilling test wells (**a**), flaring biogas (**b**)

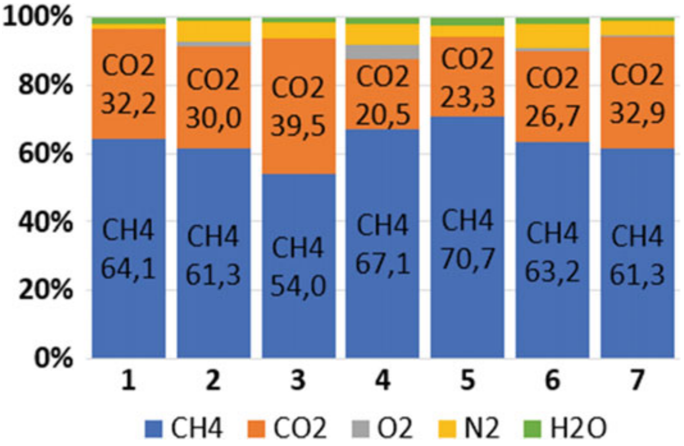


Fig. 22 Results of chemical analysis of biogas from different landfills (average data)

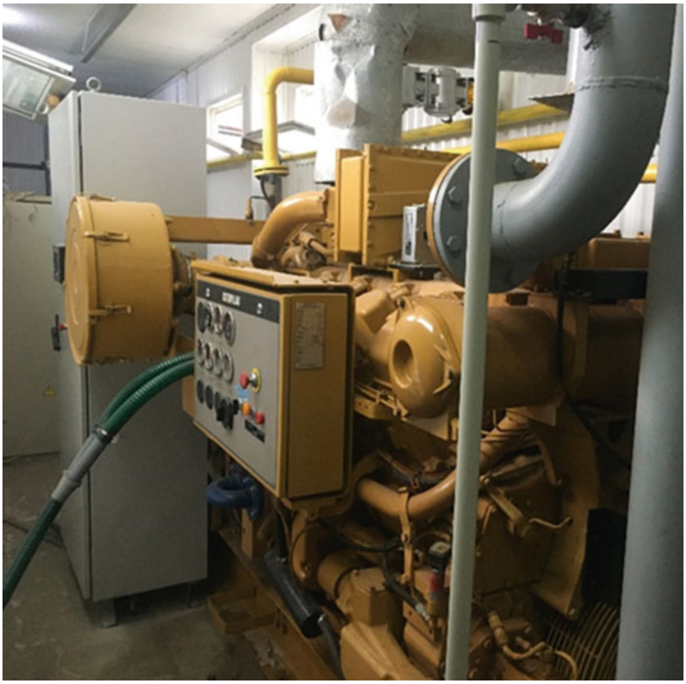


Fig. 23 Landfill gas to power generator on the base of a Caterpillar G3508 engine with electric power 500 kW

The first implementation of biogas collection and use technology at a power plant with a 1 MW engine was carried out at the municipal landfill near Kyiv in 2012. In 2015, the installed capacity here was increased to 2 MW.

At one of the landfills equipped with the participation of the Gas Institute in the city of Kamianets-Podilskyi (operating company LLC "International Center of Gas Technologies") with a Caterpillar G3508 engine with a capacity of 500 kW, (Fig. 23) parameters were measured over the past 2 years. This made it possible to execute a statistical analysis of changes in various parameters, including specific fuel consumption due to changes in methane concentration. The data show the power generated by the machine and its effectiveness rising at a constant biogas consumption (300 nm^3/h) with methane concentration rising (Fig. 24).

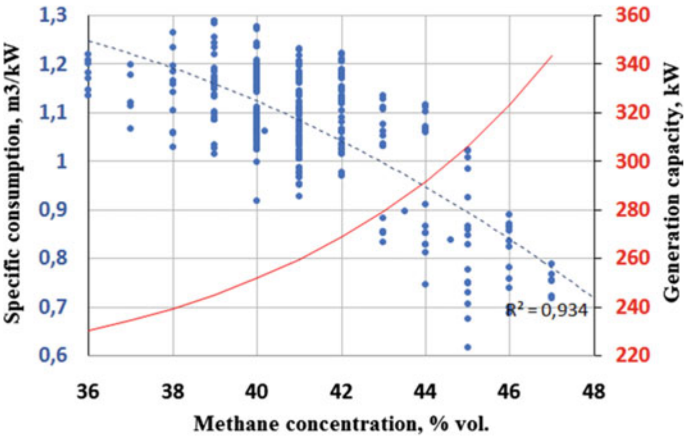


Fig. 24 The influence of methane concentration on the specific consumption of biogas (blue points), the approximate value of the specific consumption (dotted curve) and the production of electricity with a constant consumption of biogas in the volume of 300 m^3/h (red solid curve)

References

1. How the volumes of zazu extraction in Ukraine changed during the years of independence. “Word and Deed”, Analytical portal (2021). https://www.slovoidilo.ua/2021/02/05/infografika/ekonomika/yak-zminyuvalysya-obyemy-vydobuvannya-hazu-ukrayini-roky-nezalezhnosti
2. Gas in Ukraine: import, production, price for the population. Analytical portal “Word and Deed” (2020). [ukr], https://www.slovoidilo.ua/2020/04/28/infografika/ekonomika/haz-ukrayini-import-vydobutok-czina-naselennya/
3. Gas production in Ukraine decreased by 2%-to 19.8 billion cubic meters. EXPRO CONSULTING (2022). [ukr], https://expro.com.ua/novini/vidobuTok-gazu-v-ukran-znizivsya-na-2-do-198-mlrd-kub-m/
4. Gas consumption in Ukraine decreased by 7% during the year-GTS Operator. Economic truth (2022). [ukr], https://www.epravda.com.ua/news/2022/01/14/681457/
5. Soufera, E., Zaborski, S.O.:Biomass as a source of energy, M: Mir, p. 368 (rus) (1985)
6. Pyatnichko, A.I., Zhuk, G.V., Bannov, V.E.: The results of the survey of solid waste landfills in Ukraine to determine the volume of production and composition of biogas (rus) Technical gases-2010. - No. 2, pp. 63–66 (rus) (2010)
7. Investments in alternative energy: how Ukraine makes money on biogas (rus). https://getmarket.com.ua/ru/news/investicii-v-al-ternativnuyu-energetiku-kak-v-ukraine-zarabatyvayut-na-biogaze/
8. The number of biogas plants is growing in Germany. Farmer (2022). (ukr), https://minagro.gov.ua/news/u-nimechchini-zrostaye-kilkist-biogazovih-ustanovok/
9. Statistical report of the European Biogas Association (EBA) (2018). (ukr). https://saf.org.ua/library/537/
10. Report of the European Biogas Association (2020). (ukr), https://uabio.org/materials/7524/
11. By 2030, the biogas and biomethane sector could practically double production, and by 2050, production could more than quadruple-EBA forecast. 2021. (ukr). https://uabio.org/materials/9740/
12. Studying the possibilities of production and use of biomethane. Seminar of the Sustainable Agribusiness Forum (SAFUkraine) on April 26, (2018). (ukr), https://www.slideshare.net/GeorgiiGeletukha/ss-149292540

13. He report "EBA Statistical report 2019: European Overview" from the European Biogas Association (2020).25.05.2020. (ukr), https://www.facebook.com/uabio/posts/2865179810271355/
14. European Biogas Association (EBA) (2020). (ukr), https://www.europeanbiogas.eu/wp-content/uploads/2021/01/Annual-ReporT-2020-new.pdf/
15. Extraction of biogas from landfills. Ecodevelop company, 26.03.2020 (2020). (ukr), https://ecodevelop.ua/vidobuvannya-biogazu-zi-zvalishh/
16. GETMARKET: Investments in alternative energy: how Ukraine makes money on biogas (2018). (rus), https://getmarket.com.ua/ru/news/investicii-v-al-ternativnuyu-energetiku-kak-v-ukraine-zarabatyvayut-na-biogaze/
17. Website of the State Statistics Service in Ukraine (2019). (ukr), http://www.ukrstat.gov.ua
18. Polyashenko, S.O.: Prospects for the production and use of biogas in Ukraine Materials of the All-Ukrainian Scientific and Practical Conference of the Institute of Mechanotronics and Management Systems (2020)
19. The field of biogas in Ukraine: great prospects and reality. "Energy Transition" (2020). (ukr), https://energytransition.in.ua/sfera-biohazu-v-ukraini-velyki-perspektyvy-ta-real-nist/
20. Website of the State Statistics Service in Ukraine AgroPortal, 03.11.2020. (ukr), http://agroportal.ua/news/novosti-kompanii/nazvany-krupneishie-proizvoditeli-biogaza-v-ukraine/
21. Biogas production in 2020 is an up-to-date and reliable statistic. UABIO (2021). https://uabio.org/materials/10904/
22. Geletukha, G.G., Zhelezna, T.A., Matveev, Y.B., Kucheruk, P.P., Kramar, V.G.: Road map of bioenergy development in Ukraine until 2050. EBA analytical note No. 26/2020 (2020). (ukr), https://uabio.org/wp-content/uploads/2020/11/PP-UABIO-26_UA_26-11-2020.pdf
23. Grebenyuk, V.D., Ponomaryov, E.I.: Electromembrane separation of mixtures (ukr). Kyiv, Nauk. Dumka, pp. 183 (1992)
24. Semenova, T.A., Leites, I.L., Axelrod, Yu.V., Markina, M.I., Sergeev, S.P. Kharkovskaya, E.N.: Purification of technological gases. (rus) M.: Khimiya, pp. 488 (1977)
25. Bekirov T.M.: Industrial and factory processing of natural and petroleum gases. (rus) M.: Nedra, pp. 293 (1980)
26. Ratushnyak, G.S., Jezhula, V.V., Anokhin, K.V.: Energy-saving renewable sources of heat supply: study guide. Vinnytsia: VNTU, pp. 170 (2010). (ukr)
27. Khan, S.N., Hailegiorgis, S.M., Man, Z., Shariff, A.M.: High pressure solubility of carbon dioxide in aqueous solution of piperazine activated N-methyldiethanolamine solvent for CO2 capture. In: AIP Conference Proceedings 1891. 020081-020086 (2017). https://doi.org/10.1063/1.5005414
28. Anuchin, K.M., Miroshnichenko, D.A.: The possibility of using piperazine-activated methyldiethanolamine as an absorbent for deep gas purification from CO2 based on calculations in the Petro-SIM program. In: Modern Technologies for Processing and using Gas, vol. 1, pp. 9–16 (2015)
29. Al-Masabi, F.H., Castier, M.: Simulation of carbon dioxide recovery from flue gases in aqueous 2-amino-2-methyl-1-propanol solutions. Int. J. Greenhouse Gas Control. **5**, 1478–1478 (2011). https://doi.org/10.1016/j.ijggc.2011.08.005
30. Liua, G., Kou, L., Li, C.: Absorption performance for CO2 capture process using MDEA-AMP aqueous solution. In: IOP Conference Series: Earth and Environmental Science, vol. 59, pp. 1–4 (2017). /https://doi.org/10.1088/1755-1315/59/1/012011
31. Capraa, F., Fettarappab, F., Maglia, F., Gattib, M., Martellib, E.: Biogas upgrading by amine scrubbing: solvent comparison between MDEA and MDEA/MEA blend. Energy Procedia. **148**, 970–977 (2018). https://doi.org/10.1016/j.egypro.2018.08.065
32. Kodeks gas transportation system (2022). (ukr), https://zakon.rada.gov.ua/laws/show/z1378-15#Text
33. Compressed natural fuel gas for internal combustion engines. Specifications. OST 27577–2000 (rus). http://docs.cntd.ru/document/1200017921
34. Vijay, V.K.: A fit option for low cost small scale applications water scrubbing based biogas enrichment technology by IIT Delhi (2013). http://www.valorgas.soton.ac.uk/Pub_docs/Delhi_Aug_2013/Biogas%20Vehicle%203/biogas%20upgrading8-13.pdf

35. Kalashnikov, O.V., Budnyak, S.V., Ivanov, Y.V.: Engineering calculation models of technological environments of oil and gas fields. 5. Software system GazCondOil. (rus). In: Ecotechnologies and Resource Saving. #2, pp. 50–51 (1996).
36. Kalashnikov, O.V., Ivanov, Yu.V., Budnyak, S.V.: Questions of the adequacy of the thermophysical base of the software systems HYSYS, PRO-2 and GazCondOil. 1. Hydrocarbon mixture. In: Ecotechnologies and Resource Saving. #6, pp. 13–18. (rus) (1999).
37. Kalashnikov, O.V., Ivanov, Y.V., Budnyak, S.V.: Questions of the adequacy of the thermophysical base of the software systems HYSYS, PRO-2 and GazCondOil. 2. Mixtures of hydrocarbons, water, methanol and glycols (rus). In: Ecotechnologies and Resource Saving. #1, pp. 31–35 (2000).
38. Kalashnikov, O.V. Ivanov, Y.V., Onopa, L.R.: Questions of the adequacy of the thermophysical base of] the software systems HYSYS, PRO-2 and GazCondOil. 5. Problems of choosing computational models for gas and oilfield technological environments and the data bank “SiBDM-hydrocarbons” (rus). In: Ecotechnologies and Resource Saving #2, pp. 10–13 (2006)
39. Kalashnikov, O.V.. Ivanov, Y.V.: Questions of the adequacy of the thermophysical base of the software systems HYSYS, PRO-2 and GazCondOil. 6. Additional comparisons of calculated and experimental data on the mutual solubility of the components of industrial process media (rus). In: Ecotechnologies and Resource Saving. #3, pp. 12–15 (2007).
40. Kalashnikov, O.V., Budnyak, S.V., Ivanov, Y.V., Belyansky, Y.M., Aptulina, N.O., Zobnin, A.O.: Comparison of the software systems of GasCondNaft and HYSYS in the computer simulation of oil and gas industry technologies (rus). In: Ecotechnologies and Resource Saving #3, pp. 4–22 (2021). https://doi.org/10.33070/etars.3.2021.01.
41. Solubility of some gases in water. Technical tables. https://tehtab.ru/Guide/GuidePhysics/Solvability/SolvabilityOfSomeGases/
42. Pyatnichko, A.I., Ivanov, Y.V., Krushnevich, T.K.: Optimization of the composition of absorbents water-amines of the installation for the extraction of biomethane from bioga. (rus). In: Technical Gases #3, pp. 26–29 (2010)
43. Pyatnichko, A.I., Ivanov, Y.V., Zhuk, G.V., Budnyak, S.V.: Absorption extraction of methane and carbon dioxide from biogas (rus). In: Ecotechnologies and Resource Saving #1, pp. 4–10 (2012)
44. P’yatnichko, O.I., Zhuk, G.V., Ivanov, Y.V.: Dosvid utilizatsiy gas in power plants in Ukraine (rus). K. Agrar Media Group, pp. 126 (2015)
45. Pyatnichko, A.I., Ivanov, Y.V., Zhuk, G.V., Onopa, L.R.: Optimization of parameters of the absorption desorption plant for the production of biomethane from biogas (rus). In: Technical Gases #2, pp. 58–63 (2015)
46. Pyatnichko, A.I., Ivanov, Y.V., Zhuk, G.V., Onopa, L.R.: Optimization of the parameters of the technological scheme of amine biogas purification from CO2 and H2S (rus). In: Ecotechnologies and Resource Saving #1, pp. 121–19 (2015).
47. Lapidus, A.L., Golubeva, I.A., Zhagfarov, F.G.: Gas chemistry. Part 1. Primary processing of hydrocarbon gases (rus). In: Tutorial. - M.: Nedra, pp. 246 (2004)
48. Prokopyuk, S.G., Masagutov, R.M.: Industrial installations of catalytic cracking (rus). In: M., “Chemistry” pp. 176 (1974)
49. Ivanov, Y., Pyatnichko, O., Zhuk, H., Onopa, L., Krushnevich, S., Verbovsky, A.: The simulation of CO2 and H2S extraction processes from biogas using amine and water absorption (ukr). In: Ecotechnologies and Resource Saving, pp. 11–22 (2018). https://doi.org/10.33070/etars.4.2018.02
50. Pyatnichko, A.I., Ivanov, Yu.V., Zhuk, G.V., Onopa, L.R., Soltanibereshne, M.A.: Comparative analysis of the energy performance of amine and water absorption processes for extracting CO2 and H2S from biogas (rus). In: Ecotechnologies and Resource Saving #4, pp. 29–38 (2016)
51. Method and system for the purification of raw gases, in particular biogas, to produce methane (rus). RF patent No. 2508157. https://patents.google.com/patent/RU2508157C2/ru
52. Ivanov, Y.V., Pyatnichko, A.I., Zhuk, G.V., Onopa, L.R.: Comparative analysis of the effectiveness of absorption methods for extracting carbon dioxide from biogas (rus). In: Technical Gases #2, pp. 27–35 (2019)

53. Ivanov, Y.V.: Amine absorption processes for the production of CO2 from biogas (ukr). In: Ecotechnologies and Resource Saving. #4, pp. 17–26 (2021)
54. Lavrenchenko, G.K., Kopytin, A.V. Pyatnichko, A.I., Ivanov, Y.V.: Optimization of the composition of the absorbent "amines-water" of the unit for extracting CO2 from flue gases (rus). In: Technical Gases #1, pp. 16–25 (2011)
55. Pyatnichko, A.I., Ivanov, Yu.V., Zhuk, G.V., Onopa, L.R.: Comparative analysis of the efficiency of methods for extracting carbon dioxide from process gases (rus). In: Technical Gases #4, pp. 58–66 (2014)
56. Ivanov, Y., Pyatnichko, O., Zhuk, H., Onopa, L., Soltanibereshne, M.: Extraction of carbon dioxide from gas mixtures with amines absorbing process. In: International Scientific Conference "Environmental and Climate Technologies", CONECT 2017, 10–12 May 2017, Riga, Latvia. EnergyProcedia, vol. 128, pp. 240–247 (2017)
57. Kuznetsov, A.A., Sudakov, E.N.: Calculations of the main processes and apparatus for the processing of hydrocarbon gases (rus). In: Reference Manual.-M.: Chemistry, pp. 224 (1983)

Solutions for Reducing Negative Impact of Energy and Transport on Environment

Forecasted Petroleum Products Consumption in Ukraine and Estimated Greenhouse Gas Emissions from Their Use

Olena Maliarenko, Natalia Ivanenko, Natalia Maistrenko, Oleksandr Teslenko, and Artur Zaporozhets

1 Introduction

The petroleum products supply is great importance for the country's economy, since so far the transport and agricultural machinery of any country consume mainly gasoline, diesel fuel, kerosene, liquefied gas (i.e. petroleum products). During the cold winter season, boilers and thermal power plants (TPPs and CHPs) can use fuel oil or diesel fuel as back-up fuel in the case of a shortage of natural gas. Fuel oil is also used as an additional high-calorie fuel at the start-up of coal-fired boilers. The application area for petroleum products is therefore transport, agriculture, energy and industrial energy.

In Ukraine, during 2014–2020, the consumption of gasoline (taking into account sales through petrol-gas stations) decreased from 3.1 to 1.8 million tons and fuel oil from 0.1 to 0.09 million tons [1]. However, during 2017–2020, the consumption of diesel fuel (including sales through petrol-gas stations) increased from 5.4 to 6.1 million tons and liquefied gas (including sales through petrol-gas stations) from 0.9 to 1.3 million tons [1]. This is clearly the result of high fuel prices and the availability of low-cost second-hand diesel cars from Europe.

According to the data of the State Statistics Service of Ukraine, the total consumption of petroleum products in Ukraine has increased, while the consumption of crude oil for petroleum processing has significantly decreased (Fig. 1) [2].

The export of oil refining products from Ukraine in January–June 2021 increased to 203 thousand tons (a 1.8-fold increase compared to the same period in 2020), including 126.1 thousand tons of fuel oil [3]. The share of oil exports of the

---

O. Maliarenko (✉) · N. Ivanenko · N. Maistrenko · O. Teslenko · A. Zaporozhets
General Energy Institute of NAS of Ukraine, Kyiv, Ukraine
e-mail: malyarenlena@gmail.com

A. Zaporozhets
Green Technology Research Center, Yuan Ze University, Taoyuan, Taiwan

S. Boichenko et al. (eds.), *Modern Technologies in Energy and Transport*, Studies in Systems, Decision and Control 510, https://doi.org/10.1007/978-3-031-44351-0_6

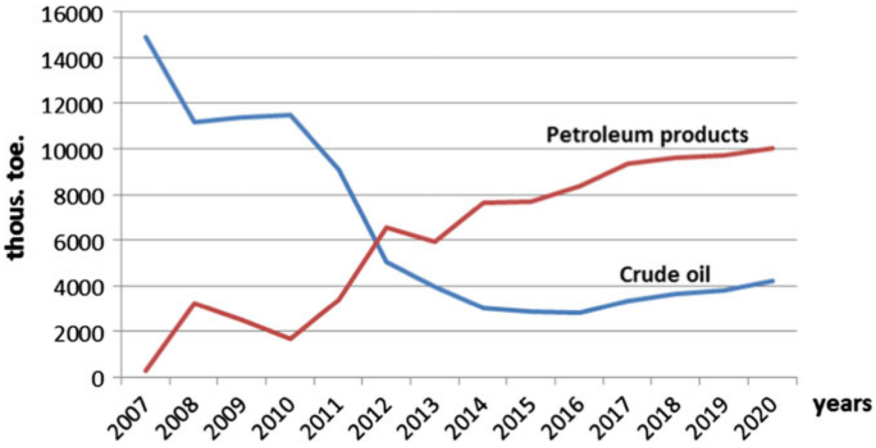


Fig. 1 Total supply of crude oil and petroleum products to Ukraine in 2007–2020 [2]

Kremenchug oil refinery was 114.7 thousand tons, and that of the state-owned corporation “Ukrgazvydobuvannya” was 11.4 thousand tons. In June 2021, exports of petroleum refining products from Ukraine amounted to 34.5 thousand tons, which is three times more than in June 2020. At the same time, as a result of large-scale military operations, total exports of goods from Ukraine have been reduced by half [4].

In 2021, 5 million tons of petroleum products were sold at Ukrainian petrol-gas stations, which is 12% more than in 2020 (4.46 million tons of all types of fuels) [5]. In 2021, sales of A-95 gasoline saw the greatest growth from 1.76 (2020) to 2.1 million tons (23%). The sale of A-92 gasoline increased by 10% (from 0.60 to 0.66 million tons (data on the sale of A-98 gasoline stopped being published as of the end of 2019) [3]. The sale of diesel fuel increased significantly by 19% (from 1.76 to 2.1 million tons). However, the sale of liquefied gas decreased for the first time in seven years: in 2021, its sales were 3% less than in 2020 [3].

According to Ukraine’s product balance sheets [6], the consumption structure of petroleum products has changed with increasing fuel prices. Higher gasoline prices have stimulated the import of diesel vehicles into Ukraine and the upgrading of gasoline engines for the use of liquefied gas.

Taking into account the difficulty of forecasting price changes for certain types of fuel, this article first analyzes the total consumption of petroleum products in Ukraine and by types of economic activity. Then the trends of changes in the structure of consumption of types of petroleum products are determined. The forecast structure of consumption of petroleum products was evaluated, taking into account the military actions in Ukraine and the post-war recovery of the country. Expected changes in the structure of the country’s economy and small amounts of energy savings are taken into account. Energy saving involves reducing the specific consumption of fuel oil for the production of electricity at TPPs and CHPs, and the loss of petroleum products during their transportation and distribution.

Table 1 Actual and forecast consumptions for petroleum products in Ukraine for 2020 relative to 2015, million toe [6, 7]

Indicators	2020 actual	2020 forecast
Ukraine (total)	10.019	11.5–11.7
Agriculture, forestry and fishing	1.016	1.490
Mining and quarrying	0.127	0.305
Manufacturing industry	1.580	1.423
Supply of electricity, gas, steam and air conditioning; water supply; sewerage, waste management	0.154	0.577
Transport, warehousing, postal and courier activities	6.842	7.652
Other types of economic activity	0.159	0.286

The previous forecast of petroleum products was carried out in 2015 and is given in the publication [7]. A comparison of the accuracy of forecasts with actual data is considered using the example of 2020 (the latest available statistical data on the country's energy balance on the website of the State Statistics Service of Ukraine [6]). The results of the comparison of the forecast and actual data for 2020 are given in the Table 1.

As can be seen from the Table 1, the sections "Manufacturing industry" (up to 10%), "Transport" (11.8%), by country (14.8–16.8%) have a satisfactory forecasting error. Other sections of the economy have a significant difference. It is clear that the COVID pandemic has significantly affected economic indicators around the world, so there is an obvious expediency in reviewing forecasts made more than 5 years ago.

After February 24, 2022, the war in Ukraine made significant adjustments to the volumes of consumption of petroleum products according to the directions of their use, but there is still no state statistical reporting on these issues.

2 The Purpose of the Study and Methods

The aim of the study was to update petroleum product forecast (2015) for further balance forming, clarification of methodological approaches to obtaining activity data and projecting petroleum product demand in the energy sector under the destruction of energy facilities in the wake of Russian economic activity against Ukraine.

Many scientists have studied the problems of forecasting the consumption of fuel and energy resources, in particular Kulyk, Piriashvili, Rozen, Kasyanova, Podolets, Lear, Nechaeva, Leshchenko and others [8–20].

At the global level, research on the oil products market is presented in the analytical materials of international organizations (for example, the Organization of the

Petroleum Exporting Countries (OPEC), the International Monetary Fund (IMF), the International Energy Agency (IEA), the Organization for Economic Cooperation and Development (OECD)). At the same time, significant attention of scientists is given to the problems of evaluating monopolization, consideration of the structure of the world oil market, issues of pricing on the world oil market, the manifestation of crisis phenomena in this market and their consequences for Ukraine, analysis of global trends in energy, opportunities for the development of the oil refining industry in Ukraine, etc. However, in their research there is no calculation of the volumes of current consumption of oil and oil products in the sections of the economy of Ukraine and in the country as a whole, corresponding forecast volumes of consumption that depend on structural and technological changes (structural and technological potentials of energy saving), since for the formation of the price factor forecasts are decisive in the economy of Ukraine.

In the General Energy Institute of the National Academy of Sciences of Ukraine, Kulyk developed a complex method of forecasting energy resource consumption [8, 21, 22]. This method is also called two-stage, as it involves forecasting energy consumption by known methods at the same time on two hierarchical levels of the economy (TOP-level and DOWN-level) with further matching of the obtained forecasts by Kulyk's vector iterative-free method [21]. The two-stage method usually uses the traditional regulatory method or the direct account method. In this study, the traditional normative method was used to forecast petroleum products. Forecasts obtained at two levels were subsequently agreed using the Kulyk's method of forecasting decisions. The need for coordination arises when there is a significant discrepancy in statistical data by country and by type of economic activity. Since statistical reporting on types of economic activity in 2020 has not been published by the State Statistics Service of Ukraine, the initial data for economic sectors was formed from the Energy Balance of Ukraine in 2020. It should be noted that the energy balance of the country and the product balance of oil products have differences in the given data; therefore the initial data for the country and for the sectors of the economy were obtained from the same source—the Energy Balance of Ukraine in 2020.

3 Mathematical Model of Forecasting the Petroleum Products Consumption

In the paper [7], a comprehensive method [21] based on a two-stage method of forecasting the consumption of energy resources was used to forecast consumption of petroleum products (base year—2015). According to this method, two forecasts are made at the DOWN (types of economic activity) and at the TOP (country) levels of the economy with subsequent reconciliation using Kulyk's vector method [8, 21].

Two approaches can be used to determine the forecasted consumption of petroleum products. The first approach: separately determine the consumption of each type of petroleum product, and then sum them up in the same units, as in the energy balance according to the Eurostat format. ‘The second approach: immediately determine the consumption of petroleum products together, since the total volume of consumption of petroleum products is a fairly constant value, and only the structure of consumption changes, which is mainly affected by the price of fuel. The structure of petroleum product consumption for the future can be determined by the scenario method. The second approach is used in this paper.

For each economy section *i* (according to the classifier of types of economic activity) with the consumption of petroleum products for transport (in internal combustion engines) without conversion into other types of energy (electricity, heat), the forecast of the consumption of the each petroleum product type ***j*** is determined by formula:

$$E^t_{i,j} = \sum_i e^b_{GVAij} V^t_{GVAi} \mp \sum_i \Delta e^{b-t}_{GVAij} V^t_{GVAi} - \sum_i \Delta e^t_{GVAij} V^t_{GVAi} \pm E^t_{subtj}, \tag{1}$$

where e^b_{GVAij}—the energy intensity of GVA (Gross Value Added) of the energy resource type *j* of the economy section *i* in the base year *b*, MJ/UAH; V^t_{GVAi}—forecasted GVA of the economy section *i* in year *t* at constant prices (adjusted to the prices of the base year b according to [21–23], thousand UAH; $\sum_i \Delta e^{b-t}_{GVAij} V^t_{GVAi}$—total decrease or increase in energy consumption of the energy resource type *j* in year *t* due to changes in the structure of the economy and the structure of its sectors [21–26], MJ/UAH; $\sum_i \Delta e^t_{GVAij} V^t_{GVAi}$—decrease in consumption of energy resource type *j* in year *t* due to technological changes, MJ/UAH [21, 26]; E^t_{subsj}—volumes of substitution of energy resource of type *j* in year *t*, GJ [21].

The energy saving potential due to structural changes when determining the forecast consumption for all types of petroleum products was calculated based on the change in the structure of the economy in the forecast years. The calculation of the technological potential of energy saving for each consolidated type of economic activity takes into account the reduction in the consumption of petroleum products due to the reduction of losses during storage, transportation and distribution of petroleum products.

For the economy section *i*, which mainly use petroleum products for conversion into other types of energy in power plants: section D “Supply of electricity, gas, steam and air conditioning”, section C “Manufacturing industry”, partly other sections, forecast levels of consumption of the petroleum product type *j* are determined depending on the forecast structure of electricity and heat generation sources and the forecast consumption of electricity and heat energy by the economy [7, 21]:

$$\begin{aligned} E^t_{convj} &= \sum_j \left(\sum_{i=1}^n B^t_{wfj} + \sum_{m=1}^n B^t_{qmj} + B^t_{eothj} \right) = k_{fj} W^t_f b^t_{wj} + k_{mj} Q^t_m b^t_{qj} \\ &\quad + \sum k_{oth} B^t_{othj}, \end{aligned} \tag{2}$$

where B^t_{wfj}—consumption of petroleum products type *j* (diesel fuel, fuel petroleum) for electricity generation of type *f* (thermal power plant, thermal power plant, other electricity generators on petroleum fuel) in forecast year *t*; B^t_{qmj}—consumption of petroleum products type *j* for heat generation of type *m* (CHP, thermal power plants, other petroleum-fueled heat generators) in forecast year *t*; B^t_{eothj}—other needs of petroleum products type *j* in sections; k_{fj}—share of electricity produced by power generation facilities using petroleum products type *j*; W^t_f—the amount of electricity (gross) produced by power generation capacities of type *f* in year *t*; b^t_{wj}—specific consumption of petroleum products type *j* for the production of electricity in the power system in year *t*; k_{mj}—share of heat energy produced by heat generating facilities using petroleum products type *j*; Q^t_m—amount of thermal energy produced by heat-generating capacities of the type *m* in year *t*; b^t_{qj}—specific consumption of petroleum products type *j* for the production of thermal energy in the centralized heat supply system in year *t*; k_{oth}—share of petroleum products type *j* used in sections for other needs (lubricants, solvents, etc.); B^t_{othj}—consumption of petroleum products type *j* for other needs in sections in year *t*.

Only petroleum products (fuel petroleum, petroleum refinery gas) burned in heating furnaces of petroleum refineries are taken into account in the production of “Petroleum Refining”. The volumes of crude oil processing should be taken into account when determining the need for petroleum. This is a separate forecast.

The total consumption of petroleum products at the DOWN-level (consolidated sections of the economy) includes the sum of consumption according to Eqs. (1) and (2):

$$E^t = \sum_i E^t_{i,j} + E^t_{convj}. \tag{3}$$

It is necessary to note about the formation of the forecast of the consumption of petroleum products for the energy sector. To determine the forecast trend, the volumes of consumption of petroleum products were analyzed in separate directions according to the energy balances of Ukraine for 2015–2020 (Table 2).

Table 2 Consumption of petroleum products for conversion in the energy sector for the retrospective period, thous. toe

Conversion enterprises	2015	2017	2018	2019	2020	Average over 5 years
TPP	127	64	132	119	27	94
CHP	158	471	156	37	57	176
Boilers	141	46	37	32	34	58
Other conversion enterprises	3	120	118	135	10	77
Total for conversion	429	701	443	323	128	346.6

As can be seen from Table 2, petroleum products were used as a fuel substitute in the past period, especially this is evident from the dynamics of consumption of petroleum products at TPPs. Taking into account the uncertainty with the volumes of imported gas supplies, and we can expect an increase in the consumption of petroleum products in the energy sector in 2025. In any case, it is desirable to have a reserve. Therefore, in the forecast of the consumption of petroleum products for conversion at TPPs, CHPs, boiler rooms and other enterprises, the average value of the consumption of petroleum products for 5 years with a further decrease in their consumption to the level of 2020 was adopted for 2025.

The results of calculations by types of economic activity and by DOWN-level (country) according to the given model are shown in Table 3 [26].

The forecasted consumption of petroleum products for the country level (DOWN—level) is calculated according to the forecast indicators of the energy intensity of the country's GVA and the volume of the country's GVA:

$$E_{T_j}^t = e_{GVAT_j}^b V_{GVAT_s}^t \pm \Delta e_{GVA_{ij}}^{b-t} V_{GVAT_s}^t - \sum_{i=1}^{I} \Delta e_{GVA_{T_{sj}}}^t V_{GVAT_{is}}^t \pm \sum E_{subj}^t, \quad (4)$$

where $e_{GVAT_j}^b$—the GVA energy intensity of petroleum products type j at the country level in the base year b; $V_{GVAT_s}^t$—the forecast of GVA volumes of the country, created with the forecast economy structure s in year t; $\Delta e_{GVA_{ij}}^{b-t}$—change in the country's GVA energy intensity of petroleum products type j in the forecast year t under the structural chancing of the economy relative to the structure of the base year b; $\Delta e_{GVA_{T_{sj}}}^t$—change in the country's GVA energy intensity of petroleum products type j in the forecast year t under the technological restructuring of the economy; E_{subj}^t—volumes of substitution of petroleum products type j with other types of fuel due to its shortage or high price.

To the Eq. (4) for the selection of the forecast structure, a restriction on the country's GVA energy intensity is added $e_{GVAT_j}^t \leq e_{GVAT_j}^b$.

The impact of structural changes on the country's energy consumption level is determined by the second component of formula (4), which can have a "+" sign in the case of overspending of the economy under a certain structure or "−" in the case of fuel and energy savings. Technological potential (component 3) and replacement volumes are determined only by individual technologies and are summed up. Table 4 includes forecasted petroleum products consumption (low level) taking into account structural and technological energy saving potentials.

Forecasts obtained by the normative method at the upper and lower levels have minor differences of 1.41% in 2020 and 1.13% in 2040. Such minor differences can be ignored and not reconciled. The reason for the small difference is that since the State Statistics Service did not provide the form of statistical reporting by types of economic activity for 2020, the initial data for sectors of the economy were formed from the Energy Balance of Ukraine for 2020. Therefore, the received forecasts have a convergence of about 1% and do not need to be reconciled.

Table 3 Forecasted petroleum products demand by the KEA to 2040 (low level) under the updated GDP forecast with structural and technological changes in 2016 prices, thous. toe

Indicators	2015* actually	2020 actually	2025	2030	2035	2040
Agriculture. forestry and fishing						
Forecasted GWA with 2020 economy's structure in 2016 prices, bln UAH	263.0	266.0	343.9	435.1	521.8	590.3
Forecasted GWA with structural economy's changes in 2016 prices, bln UAH	263.0	266.0	317.0	451.7	597.7	681.6
Forecasted petroleum products consumption by section, thous. t						
I Consumption with 2020 economy's structure and petroleum products intensity	1278.0	1016.0	1313.4	1661.7	1992.8	2254.4
II Consumption with structural economy's changes and 2020 petroleum products intensity	1278.0	1016.0	1210.7	1725.1	2282.7	2603.1
Under and overconsumption due to structural changes	0.0	0.0	102.7	−63.4	−289.8	−348.7
Technological energy saving potential	0.0	0.0	13.1	33.2	59.7	112.7
III.I Consumption with 2020 economy's structure and technological changes	1278.0	1016.0	1300.3	1628.5	1933.0	2141.7
III.II Consumption with structural and technological changes	1278.0	1016.0	1197.5	1691.9	2222.9	2490.4
Forecasted petroleum products intensity of GVA, kg/UAH	0.0054	0.0038	0.0038	0.0037	0.0037	0.0036
Mining and quarrying						
Forecasted GVA with 2020 economy's structure in 2016 prices, bln UAH	94.8	120.6	181.6	229.8	275.5	311.7
Forecasted GVA with structural economy's changes in 2016 prices, bln UAH	94.8	120.6	153.9	163.6	172.8	158.5

(continued)

Table 3 (continued)

Indicators	2015* actually	2020 actually	2025	2030	2035	2040
Forecasted petroleum products consumption by section, thous. t						
I Consumption with 2020 economy's structure and petroleum products intensity	321.0	127.0	191.3	242.0	290.2	328.3
II Consumption with structural economy's changes and 2020 petroleum products intensity	321.0	127.0	162.1	172.3	182.0	166.9
Under and overconsumption due to structural changes	0.0	0.0	29.2	69.7	108.2	161.4
Technological energy saving potential	0.0	0.0	5.7	12.1	20.3	32.8
III.I Consumption with 2020 economy's structure and technological changes	321.0	127.0	185.5	229.9	269.9	295.5
III.II Consumption with structural and technological changes	321.0	127.0	156.4	160.2	161.7	134.1
Forecasted petroleum products intensity of GVA, kg/UAH	0.0034	0.0011	0.0010	0.00098	0.0009	0.0008
Manufacturing industry						
Forecasted GWA with 2020 economy's structure in 2016 prices, bln UAH	239.1	292.9	372.4	471.2	565.0	693.3
Forecasted GWA with structural economy's changes in 2016 prices, bln UAH	239.1	292.9	289.3	331.0	364.2	401.5
Forecasted petroleum products consumption by section, thous. t						
I Consumption with 2020 economy's structure and petroleum products intensity	1358.0	1570.0	1996.3	2525.9	3028.7	3427.0
II Consumption with structural economy's changes and 2020 petroleum products intensity	1358.0	1570.0	1550.8	1774.4	1952.3	2152.3
Under and overconsumption due to structural changes	0.0	0.0	445.5	751.6	1076.4	1274.7
Technological energy saving potential	0.0	0.0	99.8	176.8	302.9	514.0

(continued)

Table 3 (continued)

Indicators	2015* actually	2020 actually	2025	2030	2035	2040
III.I Consumption with 2020 economy's structure and technological changes	1358.0	1570.0	1896.5	2349.1	2725.9	2913.0
III.II Consumption with structural and technological changes	1358.0	1570.0	1451.0	1597.5	1649.4	1638.2
Forecasted petroleum products intensity of GVA, kg/UAH	0.0057	0.0054	0.0050	0.00483	0.0045	0.0041
Supply of electricity, gas, steam and air conditioning; water supply; sewerage, waste management						
Forecasted GWA with 2020 economy's structure in 2016 prices, bln UAH	83.1	56.7	96.5	122.0	146.3	165.6
Forecasted GWA with structural economy's changes in 2016 prices. bln UAH	83.1	56.7	110.8	148.0	182.1	211.3
Forecasted petroleum products consumption by section, thous. t						
Own energy sector consumption without conversion						
I With 2020 economy's structure and petroleum products intensity (own consumption)	121.0	36.0	61.3	77.4	92.9	105.1
II With structural economy's changes and 2020 petroleum products intensity (own consumption)	121.0	36.0	70.3	93.9	115.6	134.1
Energy saving potential with structural changes	0.0	0.0	−9.1	−16.5	−22.7	−29.0
Demand for conversion						
TPPs demand	127.0	27.0	93.8	90.0	45.0	25.0
Technological energy saving potential for TPPs	0.0	0.0	0.7	1.0	1.1	1.4
CHPs demand, including	158.0	57.0	176.0	150.0	100.0	50.0
–electricity production (0.328)	51.8	18.7	57.7	49.2	32.8	16.4

(continued)

Table 3 (continued)

Indicators	2015* actually	2020 actually	2025	2030	2035	2040
–heat production (0.672)	106.2	38.3	118.3	100.8	67.2	33.6
Technological energy saving potential for CHPs	0.0	0.0	3.2	4.9	5.3	7.0
Total technological energy saving potential for TPPs and CHPs	0.0	0.0	3.9	5.9	6.4	8.4
Total petroleum products demand for electricity production at TPPs and CHPs taking into account potential	178.8	45.7	147.6	133.3	71.4	33.0
Petroleum products demand for heat production at boilers	141.0	34.0	58.0	48.0	40.0	30.0
Total petroleum products demand for heat production at CHPs and boilers	247.2	72.3	176.3	148.8	107.2	63.6
Total petroleum products demand for electricity and heat production (conversion)	429.0	128.0	400.9	342.1	208.6	106.6
I. Consumption with 2020 economy’s structure and conversion in energy sector	550.0	164.0	462.2	419.6	301.5	211.7
II. Consumption with structural changes and conversion in energy sector	550.0	164.0	471.2	436.1	324.2	240.7
III.I Consumption with 2020 economy’s structure and conversion in energy sector with technological changes	550.0	164.0	458.2	413.7	295.0	203.2
III.II Consumption with structural and technological changes and conversion in energy sector	550.0	164.0	467.3	430.2	317.8	232.2
Forecasted petroleum products intensity of GVA under scenarios III.II, kg/UAH	6.6	2.9	4.2	2.9	1.7	1.1
Transport, warehousing, postal and courier activities						
Forecasted GWA with 2020 economy’s structure in 2016 prices, bln UAH	131.2	143.9	205.7	260.3	312.2	353.2

(continued)

Table 3 (continued)

Indicators	2015* actually	2020 actually	2025	2030	2035	2040
Forecasted GWA with structural economy's changes in 2016 prices, bln UAH	131.2	143.9	215.4	307.6	387.6	428.0
Forecasted petroleum products consumption by section, thous. t						
I Consumption with 2020 economy's structure and petroleum products intensity	6302.0	6842.0	9778.4	12,374.0	14,841.2	16,790.2
II Consumption with structural economy's changes and 2020 petroleum products intensity	6302.0	6842.0	10,239.5	14,622.5	18,425.5	20,346.0
Under and overconsumption due to structural changes	0.0	0.0	−461.1	−2248.5	−3584.3	−3555.8
Technological energy saving potential	0.0	0.0	205.3	410.5	547.4	684.2
III.I Consumption with 2020 economy's structure and technological changes	6302.0	6842.0	9573.2	11,963.5	14,293.8	16,106.0
III.II Consumption with structural and technological changes	6302.0	6842.0	10,034.3	14,212.0	17,878.1	19,661.8
Forecasted petroleum products intensity of GVA, kg/UAH	0.0480	0.0475	0.0466	0.0462	0.0461	0.0459
Other types of economic activity						
Forecasted GWA with 2020 economy's structure in 2016 prices, bln UAH	916.8	1256.0	1415.5	1791.1	2147.9	2430.1
Forecasted GWA with structural economy's changes in 2016 prices, bln UAH	916.8	1256.0	1569.6	2021.0	2442.3	2816.1
Forecasted petroleum products consumption by section, thous. t						
I Consumption with 2020 economy's structure and petroleum products intensity	253.0	159.0	179.2	226.7	271.9	307.6

(continued)

Table 3 (continued)

Indicators	2015* actually	2020 actually	2025	2030	2035	2040
II Consumption with structural economy’s changes and 2020 petroleum products intensity	253.0	159.0	198.7	255.8	309.2	356.5
Under and overconsumption due to structural changes	0.0	0.0	−19.5	−29.1	−37.3	−48.9
Technological energy saving potential	0.0	0.0	4.8	9.5	12.7	15.9
III.I Consumption with 2020 economy’s structure and technological changes	253.0	159.0	174.4	217.2	259.2	291.7
III.II Consumption with structural and technological changes	253.0	159.0	193.9	246.3	296.5	340.6
Forecasted petroleum products intensity of GVA, kg/UAH	0.0003	0.0001	0.0001	0.0001	0.0001	0.0001
Total KEA						
Forecasted petroleum products consumption by sections, thous. t						
I Consumption with 2020 economy’s structure and petroleum products intensity	10,062.0	9878.0	12,024.3	15,100.8	18,000.4	20,406.3
II Consumption with structural economy’s changes and 2020 petroleum products intensity	10,062.0	9878.0	13,733.2	18,809.4	23,173.0	25,351.4
III.I Consumption with 2020 economy’s structure and technological changes	10,062.0	9878.0	11,791.4	14,629.6	17,353.8	19,552.2
III.II Consumption with structural and technological changes—low level—E^t_{DOWN}	10,062.0	9878.0	13,500.4	18,338.1	22,526.4	24,497.4

* GVA for 2015 is given in 2015 prices

Table 4 Forecast of consumption of petroleum products by types of economic activity until 2040 based on the updated forecast of GDP in 2016 prices and for structural and technological changes, thousand toe

Indicators	2015* actually	2020 actually	2025	2030	2035	2040
Agriculture, forestry and fisheries	1278.0	1016.0	1197.5	1691.9	2222.9	2490.4
Mining and quarrying	321.0	127.0	156.4	160.2	161.7	134.1
Manufacturing industry	1358.0	1570.0	1451.0	1597.5	1649.5	1638.2
Supply of electricity, gas, steam and air conditioning; water supply; sewerage, waste management	550.0	164.0	467.3	430.2	317.8	232.2
Transport, warehousing, postal and courier activities	6302.0	6842.0	10,034.3	14,212.0	17,878.1	19,661.8
Other types of economic activity	253.0	159.0	193.9	246.3	296.5	340.6
Together for types of economic activity (DOWN-level)—E^t_{Down}	10,062.0	9878.0	13,500.4	18,338.1	22,526.4	24,497.3
Ukraine—(TOP-level)—E^t_{Ts}	10,062.0	10,019.0	13,504.3	18,441.7	22,704.7	24,777.0

* GVA for 2015 is given in 2015 prices

Table 5 includes the estimation of the emissions of greenhouse gases (GHG) from the forecasted petroleum products (gasoline, diesel, fuel oil, and propane-butane) consumption in 2040 of for the perspective of 2040 based on averaged indicators for. GHG emissions were determined according to the recommendations of the US Environmental Protection Agency [27, 28], Directive 2009/28/EC [29] and the methodological manual of the International Energy Agency [30] and the WRI/WBCSD manual [31, 32].

Table 5 Actual and forecasted GHG emissions from petroleum products consumption

Year	Petroleum products consumption, thous. toe	CO_2 emissions, thous. t	CH_4 emissions, thous. t	N_2O emissions, thous. t	GHG emissions, thous t CO2 eq
2015	10,062	30,493	1.3197429	0.277841	30,608.8
2020	10,019	30,362.7	1.3141029	0.276653	30,478
2025	13,504.3	40,924.9	1.7712387	0.372892	41,080.3
2030	18,441.7	55,887.8	2.4188334	0.509228	56,100
2035	22,704.7	68,806.8	2.9779732	0.626942	69,068.1
2040	24,777	75,087	3.2497783	0.684164	75,372.1

Determining directions for reducing the consumption of petroleum products and corresponding greenhouse gas emissions requires further additional research when forecasting the structure of consumption of petroleum products by individual species.

For forecasting petroleum products consumption by their types, it is necessary to analyze the consumption structure during the last years (Table 6).

Table 6 Petroleum products consumption by their types in 2015–2020 [33–38]

Petroleum product	2015 [33]	2016 [34]	2017 [35]	2018 [36]	2019 [37]	2020 [38]
Gasoline, thous. t	2360.8	2229.4	1985.9	1767.2	1711.6	1767.7
thous. toe***	2455.2	2318.6	2065.3	1837.9	1780.1	1838.4
Fraction in end use—$\boldsymbol{\beta}_1$	0.26	0.24	0.21	0.17	0.17	0.19
Diesel fuel, thous. t	4770.9	4968.6	5148.6	5366.1	5791.7	5173.9
Thous. toe	4866.3	5068.0	5251.6	5473.4	5907.5	5277.4
Fraction in end use—$\boldsymbol{\beta}_2$	0.51	0.53	0.52	0.52	0.56	0.54
Heavy fuel oil, thous. t	367.3	669.3	584.8	244.4	86.7	98.2
Thous. toe	374.6	682.7	596.5	249.3	88.4	100.2
Fraction in end use—$\boldsymbol{\beta}_3$	0.04	0.07	0.06	0.02	0.008	0.01
Liquefied propane and butane, thous. t	675.8	778.4	896.1	1014.1	1184.9	1384.1
Thous. toe	743.4	856.2	985.7	1115.5	1303.4	1522.5
Fraction in end use—$\boldsymbol{\beta}_4$	0.08	0.09	0.1	0.1	0.12	0.16
Total petroleum products, thous. toe	8439.6	8925.5	8899.1	8676.1	9079.4	8738.5
Fraction in end use—$\boldsymbol{\Sigma\beta}_{\mathbf{j}}$	0.89	0.93	0.89	0.81	0.858	0.9
End use* consumption of petroleum products according to Energy Balance—$\boldsymbol{\Sigma E}_{\mathbf{kj}}$	9455.0	9630.0	10,060.0	10,599.0	10,613.0	9695.0
Fraction in end use **—$\boldsymbol{\alpha}$	0.94	–	–	–	–	0.97

[*] End use does not include non-energy consumption, losses and consumption by energy sector for own

** Consumption is evaluated as the difference between resources (import + domestic production) and conversion to other fuel and energy types

*** Conversion factors from t to toe are as follows: gasoline—1.04, diesel and heavy oil—1.02, liquefied propane and butane—1.1 according to [39]

As can be seen from the Table 6, the final consumption of petroleum products, the sum of the consumption of the main types of petroleum products and their share of the final consumption are values that change slowly. Over 5 years, the final consumption of petroleum products increased by 2.5%. The amount of the main types of petroleum products increased during the same period by 3.5%, mainly due to the increase in the consumption of diesel fuel and propane-butane mixture. Most likely, such trends will persist for the next 5 years and stabilize by 2030. In the future, after the end of the war and post-war recovery, we can expect a decrease in diesel consumption and some growth of gas mixture and gasoline. Currently, it is difficult to predict the replacement of petroleum motor fuel with electricity, since the electric power system was destroyed during the war, and the term of its restoration can be up to 10 years.

It is possible to consider only forecast scenarios of the final consumption of the main types of petroleum products. At the same time, it should be noted that during the war, military equipment consumes diesel, and trucks, which are needed for post-war revival, mostly also consume diesel. Therefore, according to the basic scenario, it is assumed that until 2030 the volume of diesel consumption will be maintained at $\beta_2 = 0.55$, or even increase until 2025. After 2030, with the stabilization of the country's economy, the country's environmental policy will return to compliance with environmental requirements, i.e. a reduction consumption of heavy motor fuel—diesel to the volume of $\beta_2 = 0.44$ and stabilization of the final consumption of fuel oil $\beta 3 = 0.01$. The volume of gasoline may increase after 2030 to the volume of 2015: $\beta_1 = 0.25$. Propane-butane will also increase slightly to the fraction $\beta_4 = 0.2$.

Forecasted petroleum product consumption by country, except for formula (4), can be estimated as follows [40]:

$$E_{Ts}^{t} = \sum_{j} E_{kj}^{t} + E_{othj}^{t}, \tag{5}$$

where $\sum_j \mathrm{E}_{\mathrm{kj}}^{\mathrm{t}}$—total final petroleum product consumption; $\mathrm{E}_{\mathrm{othj}}^{\mathrm{t}}$—other petroleum product consumption, non-energy, own consumption and distribution losses.

Accordingly for forecasting petroleum products by fuel type, you the following dependence can be used:

$$\sum_{j} E_{kj}^{t} = \propto E_{Ts}^{t}, \tag{6}$$

where $\propto$—end use fraction from total consumption; according to energy balances $\propto = 0.94 \ldots 0.97$.

Therefore, the final consumption of the jth petroleum product will be determined by the dependence:

$$E_{kj}^{t} = \beta_j \sum_{j} E_{kj}^{t}, \tag{7}$$

where β_j—the fraction of the j-th petroleum product from the final consumption according to energy balances; $j = 1$—gasoline, $j = 2$—diesel, $j = 3$—heavy oil, $j = 4$—propane and butane mixture for road transportation. The calculated factors are given in Table 6.

The forecast of the main types of petroleum product consumption is given in Table 7.

The forecasted greenhouse gas emissions (GHG) up to were determined in accordance with the recommendations of the Intergovernmental Panel on Climate Change [41], the US Environmental Protection Agency [28], Directive 2009/28/EC [29] and the WRI/WBCSD manual [31]. The results of calculations of GHG emissions in thousand tons of CO_2 eq./year for the main types of petroleum products are shown at Figs. 2, 3, 4 and 5.

As can be seen from the Figs. 2, 3, 4 and 5, the largest emissions of greenhouse gases in thousand tons of CO_2-eq. provides diesel fuel, the emissions of which are almost twice as high as the emissions from gasoline consumption and greater than the total emissions from the consumption of gasoline and liquefied propane-butane together. To restore the war-damaged industry and infrastructure of Ukraine, diesel fuel will definitely be needed for transportation, but after the recovery of the economy, the volume of diesel fuel should be reduced and replaced by more environmentally friendly fuels.

Table 7 The forecast of the main types of petroleum product consumption in 2030–2040

Petroleum product type	2030	2035	2040
Gasoline, thous. t	3268.1	4658.8	5777.3
Thous. toe	3398.8	4845.2	6008.4
Fraction in end use—$\boldsymbol{\beta_1}$	0.19	0.22	0.25
Diesel fuel, thous. t	9470.3	10,579.9	10,367.5
Thous. toe	9659.7	10,791.5	10,574.8
Fraction in end use—$\boldsymbol{\beta_2}$	0.54	0.49	0.44
Heavy fuel oil, thous. t	175.4	215.9	235.6
Thous. toe	178.9	220.2	240.3
Fraction in end use—$\boldsymbol{\beta_3}$	0.01	0.01	0.01
Liquefied propane and butane, thous. t	2602.0	3603.8	4369.7
Thous. toe	2862.2	3964.2	4806.7
Fraction in end use—$\boldsymbol{\beta_4}$	0.16	0.18	0.2
Total petroleum products, thous. toe	16,099.7	19,821.1	21,630.0
Fraction in end use—$\boldsymbol{\Sigma\beta_j}$	0.9	0.9	0.9
End use consumption of petroleum products according to Energy Balance, thous. toe—$\mathbf{\Sigma E_{kj}}$	17,888.5	22,023.5	24,033.7
Fraction in end use from total—$\boldsymbol{\alpha}$	0.97	0.97	0.97

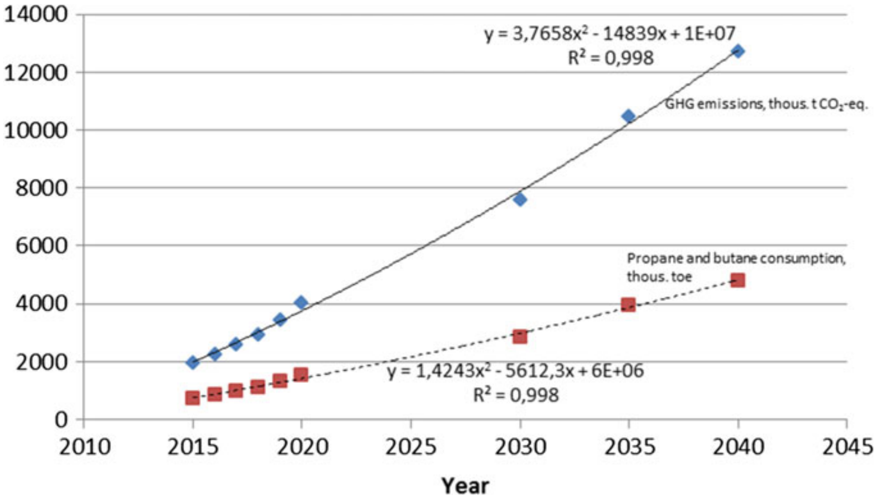


Fig. 2 Propane and butane consumption as well as GHG emissions in 2015–2020 and forecast in 2030–2040

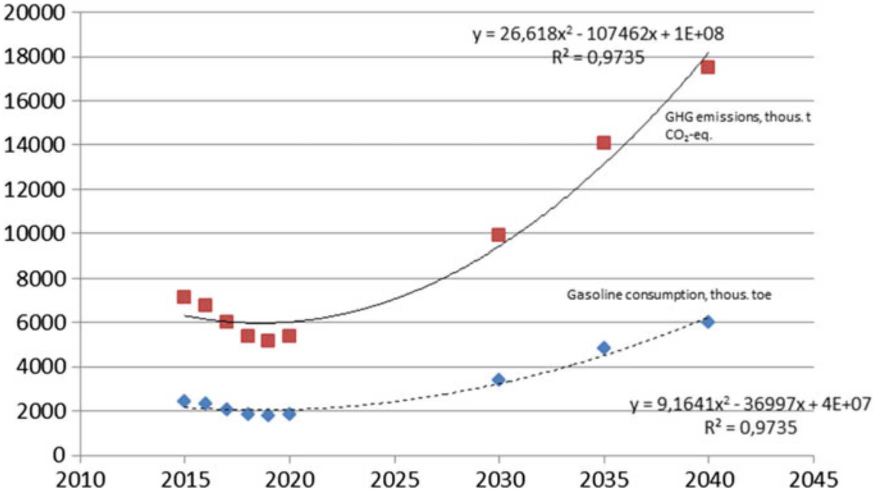


Fig. 3 Gasoline consumption as well as GHG emissions in 2015–2020 and forecast in 2030–2040

4 Results

The Table 4 contains the results of the calculation of forecasted consumption of petroleum products until 2040 by consumer groups (country, types of economic activity), adjusted relative to the actual consumption of petroleum products in 2020 (according to the energy balance).

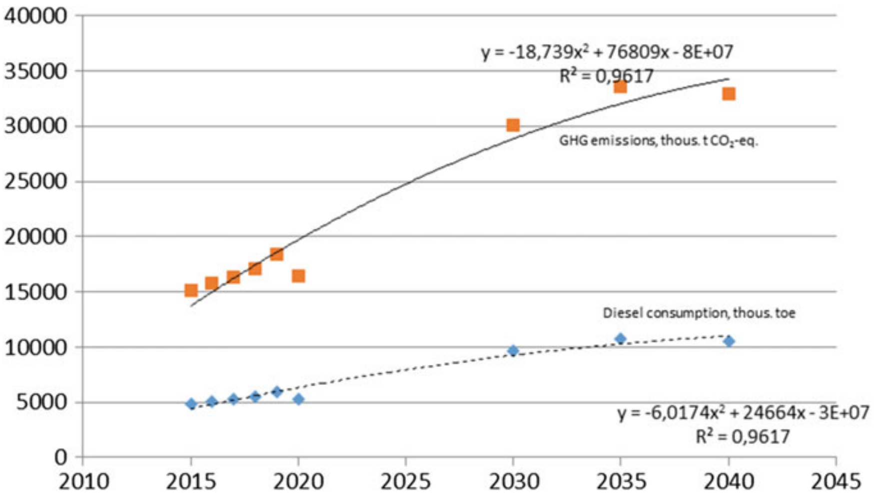


Fig. 4 Diesel fuel consumption as well as GHG emissions in 2015–2020 and forecast in 2030–2040

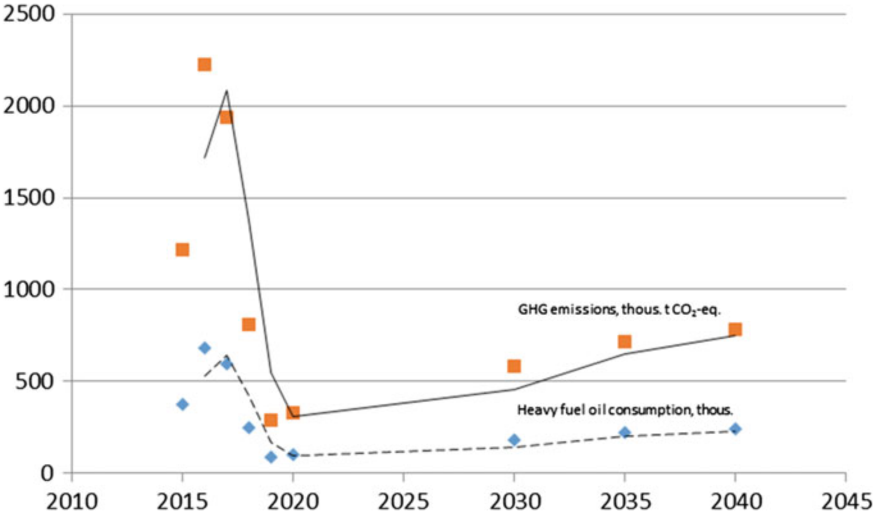


Fig. 5 Heavy fuel oil consumption as well as GHG emissions in 2015–2020 and forecast in 2030–2040

The 2019–2020 was marked by the COVID pandemic, which led to a drop in macroeconomic indicators almost all over the world. In this regard, the Institute of General Energy of the National Academy of Sciences of Ukraine has adjusted macroeconomic indicators, presented in the publication [42] on the base of analysis of the forecasts of the world's leading financial institutions (the International Monetary Fund, the World Bank, etc.).

The peculiarity of the forecast presented in the article is an increase in the consumption of petroleum products in the future in the energy sector of Ukraine, since more than 30% of the energy infrastructure facilities in Ukraine have been destroyed as a result of military operations in Ukraine, and the government must have a reserve of the necessary fuel. These volumes were estimated according to petroleum products consumption trends in the transformation sector of the energy balances of Ukraine transformation sector for 2015–2020 (Table 3). Since the energy infrastructure is being destroyed by the aggressor every day, the forecasts of the structure of electricity and heat generating capacities [18] made earlier at the Institute of General Energy of the National Academy of Sciences of Ukraine are not applicable now. They should be revised after the end of the war.

In the sections of the economy, a moderate technological potential of energy saving is assumed, because in wartime it is impossible to invest money in the reconstruction of enterprises. Based on the results of the forecasted petroleum products consumption, the total emissions of greenhouse gases were determined (Table 5), which are adjusted with the increase in the consumption of petroleum products. A methodical approach to determining the forecast structure of consumption of petroleum products by types of petroleum fuel is presented, and the forecast structure of consumption of petroleum products by individual types is determined, taking into account trends in their consumption that have developed in the retrospective period. The task of replacing oil fuel with other low-carbon fuels and electricity to reduce greenhouse gas emissions, especially from the consumption of diesel fuel, which produces the largest amount of these emissions, is also relevant.

5 Conclusions

The forecasted demand for petroleum products at the TOP and DOWN levels were carried out using the normative method and taking into account a separate algorithm for forecasting the demand for petroleum products in the section "Supply of electricity, etc.", in which the need for the conversion to other energy types is calculated according to the trend of consumption over the last five years. This is due to the impossibility of using the existing forecasts of structures of energy generating capacities as a result of military operations, damage and destruction of energy facilities. The forecasts obtained at the two levels have very close values with an error of about 1%, which can to some extent justify their reliability. Estimated overspending of oil products as a result of structural changes, which should ensure the development of key sectors of the economy: agriculture, industry, transport sector, will allow to restore the economy after the war and increase its energy efficiency. The forecasted greenhouse gas emissions are determined and the directions for their reduction are outlined.

References

1. Howthe consumption of fuel products changed in Ukraine in 2014–2021. https://www.slovoidilo.ua/2021/05/13/infografika/ekonomika/yak-zminyuvalosya-spozhyvannya-palyvnyx-produktiv-ukrayini-2014-2021-rokax
2. Total supply of primary energy for 2007–2020. https://www.ukrstat.gov.ua/
3. Ukrainian export of petroleum products increased by 1.8 times in six months. https://www.slovoidilo.ua/2021/07/24/novyna/ekonomika/ukrayinskyj-eksport-naftoproduktiv-pivroku-zbilshyvsya-18-raza
4. Ukraine halved exports due to the war unleashed by Russia—Ministry of Economy. https://agropolit.com/news/23560-ukrayina-udvichi-skorotila-eksport-cherez-viynu-rozvyazanu-rosiyeyu-mineoknomiki
5. Salesvolumesofpetroleumproductsincreasedby12%in2021. https://ua-energy.org/uk/posts/obsiahy-prodazhu-naftoproduktiv-v-2021-rotsi-zrosly-na-12
6. Energy balance of Ukraine for 2020. https://www.ukrstat.gov.ua/
7. Maliarenko, O.Y., Maistrenko, N.Y., Stanytsina, V.V., Bohoslavska, O.Y.: An improved comprehensive method of forecasting energy consumption for the long term. Energy: Econ., Technol., Ecol. **3**, 53–61 (2019)
8. Kulyk, M.M.: Methods of coordinating predictive solutions. Probl. Gen. Energy **2**(37), 5–12 (2014)
9. Pyriashvili, B.Z., Voronchuk, M.M., Galinovsky, et al.: Simulation modeling in energy; under the editorship BM Danylyshyn (Kyiv: Naukova dumka) 303 p. (2008)
10. Rosen, V.P., Kramarenko, E.R., Chernyavskyi, A.V.: Fuel-energy balance as a tool for energy efficiency analysis. Metallurgical Heat Engineering: Collection of Scientific Works of the National Metallurgical Academy of Ukraine. In two books. Book one. Dnipropetrovsk: Porogy, pp. 387–392 (2005)
11. Kasyanova, N.V., Levshova, Yu.O.: Complex model of energy consumption assessment in the region. Sci. Bull. Donbas State Mach.-Build. Acad. **2**, 164–171 (2014)
12. Podolets, R.Z.: Energy modeling: foreign experience and future research directions in Ukraine. Econ. Forecast. **1**, 126–140 (2006)
13. Lear, V.E.: Energy balance as a basis for economic analysis and forecasting of the state's energy supply. Econ. Forecast. **1**, 91–102 (2000)
14. Nechaeva, T.P.: Model and structure of the long-term development of generating capacities of the electric power system taking into account the dynamics of input-output of capacities and changes in their technical and economic indicators. Probl. Gen. Energy **3**, 5–9 (2018). https://doi.org/10.15407/pge2018.03.005
15. Ch, L.I., Spitkovskyi, A.I.: Application of the Pyramid-V system for solving the problems of forecasting the development of the gas industry of Ukraine. Probl. Gen. Energy **1**, 25–31 (2010)
16. Bezugla, K., Kostyuchenko, N.: Global market of petroleum products: current state and perspectives of development. Visnyk Sumy State University. Econ. Ser. **3**, 27–39 (2020). https://visnyk.fem.sumdu.edu.ua/en/3-2020
17. Omelchenko, V.: The crisis state of the oil products market: reasons, conclusions, recommendations (2022). https://razumkov.org.ua/statti/kryzovyi-stan-rynku-naftoproduktiv-prychyny-vysnovky-rekomendatsii
18. Vashchenko, V.V.: Forecasting the development of the state reserve in the long-term period.—Dissertation for obtaining the scientific degree of candidate of economic sciences on the specialty 08.00.03 "Economics and management of the national economy". National University of Bioresources and Nature Management of Ukraine. Kyiv (2020)
19. Yaroschuk, L.D., Tyurina, E.O.: Modeling and management of adsorptive purification of oils and lubricants in the mode of changing raw materials. In: Bulletin of NTUU "KPI named after Ihor Sikorskyi". Chemical Engineering, Ecology and Resource Conservation, Issue no 3, pp. 56–68 (2022). https://doi.org/10.20535/2617-9741.3.2022.265361

20. Khomenko, A.S., Gomelya, M.D., Shablii, T.O.: Evaluation of the effectiveness of alkylimidazolines in reducing the corrosive aggressiveness of oil-containing waters. In: Bulletin of NTUU “KPI named after Ihor Sikorskyi”. Chemical Engineering, Ecology and Resource Conservation, Issue no 2, pp. 60–71 (2022). https://doi.org/10.20535/2617-9741.2.2022.260350
21. Kulyk, M.M., Maliarenko, O.Y., Maistrenko, N.Y., Stanytsina, V.V., Kuts, H.O.: Energy Efficiency and Forecasting of Energy Consumption at Different Hierarchical Levels of the Economy: Methodology, Forecast Estimates until 2040 (Kyiv: Scientific Opinion) 234 p. (2021) ISBN 978-966-00-1739-9
22. Kulyk, M.M., Horbulin, V.P., Kyrylenko, O.V.: Conceptual approaches to the development of the energy industry of Ukraine (analytical materials) (Kyiv: General Institute of Energy of the National Academy of Sciences of Ukraine) 78 p. (2017)
23. Energy Strategy of Ukraine Until 2030, edition of 2013. http://www.energoatom.kiev.ua/ua/about/strategy_2030/
24. Shynkaruk, L.V., Baranovska, I.V., Bobukh, I.M., et al.: Structural transformations in the economy of Ukraine: dynamics, contradictions and impact on economic development scientific report; under the editorship L V Shinkaruk (Kyiv: Institute of Economics and Forecasting of the NAS of Ukraine) 304 p. (2015)
25. Skrypnychenko, M.I.: System of macro models in the program and analytical toolkit “Macroforecast of the economy of Ukraine”. Economist **4**, 85–96 (2014)
26. Maliarenko, O.: Consumption forecast of petroleum products in ukraine by the main types of economic activity. Syst. Res. Energy **2**(71), 31–41 (2022). https://doi.org/10.15407/srenergy2022.02.031
27. Greenhouse Gas Inventory Guidance. Direct Emissions from Stationary Combustion Sources. U.S. EPA Center for Corporate Climate Leadership (2014). https://www.epa.gov/sites/default/files/2015-07/documents/emission-factors_2014.pdf
28. Greenhouse Gas Inventory Guidance. Direct Emissions from Stationary Combustion Sources. U.S. EPA Center for Corporate Climate Leadership. 21 p. (2020). https://www.epa.gov/sites/default/files/2020-12/documents/stationaryemissions.pdf
29. Directive 2009/28/EC of the European Parliament and of the Council of 23 April 2009 on the promotion of the use of energy from renewable sources and amending and subsequently repealing Directives 2001/77/EC and 2003/30/EC 2009 Off. J. Eur. Union L **140**, 16–61. https://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2009:140:0016:0062:en:PDF
30. IEA.Emissionfactors2020DATABASEdocumentation43p.https://iea.blob.core.windows.net/assets/24422203-de22-4fe6-8d54-f51911addb8b/CO2KWH_Methodology.pdf
31. Michael Gillenwater 2005 Calculation tool for direct emissions from stationary combustion. WRI/WBCSD. GHG Protocol Stationary Combustion Guidance. 94 p. https://ghgprotocol.org/sites/default/files/Stationary_Combustion_Guidance_final_1.pdf
32. National strategy of approximation (approximation) of Ukrainian legislation to EU legislation in the field of environmental protection 2015 Kyiv 107 p. https://www.menr.gov.ua/docs/activity-adaptation/draft_NAS_FEB2015.pdf
33. Statistical Yearbook of Ukraine for 2015. Edited by Iryna M. Zhuk. State statistics service of Ukraine. Кyiv, 575 p. (2016). ISBN 978-966-8459-97-9. https://ukrstat.gov.ua/druk/publicat/Arhiv_u/01/Arch_zor_zb.htm
34. Statistical Yearbook of Ukraine for 2016. Edited by Ihor Yev. Verner. State statistics service of Ukraine. Кyiv, 611 p. (2017). ISBN 978-966-2224-90-0. https://ukrstat.gov.ua/druk/publicat/Arhiv_u/01/Arch
35. Statistical Yearbook of Ukraine for 2017. Edited by Ihor Yev. Verner. State statistics service of Ukraine. Кyiv, 541 p. (2018). ISBN 978-617-7551-15-6. https://ukrstat.gov.ua/druk/publicat/Arhiv_u/01/Arch_zor_zb.htm
36. Statistical Yearbook of Ukraine for 2018. Edited by Ihor Yev. Verner. State statistics service of Ukraine. Zhytomyr «Book-druk» LTD, 482 p. (2019). https://ukrstat.gov.ua/druk/publicat/Arhiv_u/01/Arch_zor_zb.htm
37. Statistical Yearbook of Ukraine for 2019 Edited by Ihor Yev. Verner. State statistics service of Ukraine. Кyiv, 465 p. (2020). ISBN 978-617-7551-24-8. https://ukrstat.gov.ua/druk/publicat/Arhiv_u/01/Arch_zor_zb.htm

38. Statistical Yearbook of Ukraine for 2020 Edited by Ihor Yev. Verner. State statistics service of Ukraine. Кyiv, 455 p. (2021). ISBN 978-617-7551-33-0. https://ukrstat.gov.ua/druk/publicat/Arhiv_u/01/Arch_zor_zb.htm
39. Oil fuel conversion coefficients from natural units to oil equivalent. https://uk.wikipedia.org/wiki/ton_ofoil_equivalent
40. Maliarenko, O.Y., Maistrenko, N.Y.: A methodical approach to forecasting the consumption of petroleum products by their main types. Energy Technol. Resour. Sav. **74**(1), 14–21 (2023). https://doi.org/10.33070/etars.1.2023.02
41. 2006 IPCC Guidelines for National Greenhouse Gas Inventories, Vol. 2. Energy, 51 p. (2006). https://www.ipcc-nggip.iges.or.jp/public/2006gl/vol2.html
42. Maliarenko, O.Y., Maistrenko, N.Y., Horskyi, V.V.: Forecast of fuel and coal consumption in Ukraine until 2040 by a complex method of forecasting energy consumption. Probl. Gen. Energy **3**(66), 28–35 (2021). https://doi.org/10.15407/pge2021.03.028

Adsorption of Oil Products by Natural Sorbents

Vira Sabadash

1 Introduction

Used oils are dangerous sources of environmental pollution. According to the Exxon-Mobil corporation, one litre of used oil can contaminate a million litres of drinking water. Ukraine consumes more than 1 million tons/per year of fresh oil. Without collection standards, it officially collects about 500,000 t/year of spent oil products; that is, it has a natural raw material resource approximately equal to Germany's similar resource of 660,000 t/year. However, in our country, 90% of the volume of this raw material is dumped into the environment or used unqualifiedly, which has a detrimental effect on all environmental objects—atmosphere, soil and water. The constant introduction of an increasing number of multifunctional additives to improve the operational characteristics and increase the service life of lubricating oils leads to the accumulation of compounds toxic to the environment in used motor oils (spent engine oils). More than 140 types of carcinogenic polycyclic hydrocarbons (PCHs) have been identified in spent engine oils. The amount of these compounds increases with the increase in the service life of the oils. Thus, for carbureted passenger cars, the average increase in the amount of KPV with 4–7 rings is 26.8 mg/kg per 1000 km of mileage. After 10,000 to 15,000 km of mileage, used oil contains from 270 to 400 mg/kg of CPV, formed from oil combustion and their entry into the oil from the fuel.

The purpose of the study is to develop a complex of legal, organizational and technological measures to prevent pollution of the natural environment by using motor oils.

To achieve this goal, it was necessary to solve the following tasks:

V. Sabadash (✉)
Ecology and Sustainable Environmental Management Department, Lviv Polytechnic National University, Lviv, Ukraine
e-mail: vira.v.sabadash@lpnu.ua

S. Boichenko et al. (eds.), *Modern Technologies in Energy and Transport*, Studies in Systems, Decision and Control 510, https://doi.org/10.1007/978-3-031-44351-0_7

- to establish the degree of pollution of used motor oils by determining the primary pollutants and the level of their concentrations in oils;
- propose a strategy for the collection and disposal of used motor oils;
- perform a comparative analysis of modern methods of cleaning used motor oils;
- to develop an ecologically safe, resource-saving complex technology for the regeneration of used oil;
- to establish optimal conditions for spent engine oils regeneration.

Pollution of the Environment with Used Oils

The most crucial factor of atmospheric pollution is the evaporation of lubricants. The tendency to evaporation depends on the chemical and fractional composition of oils and the operating temperature of the object being lubricated. An increase in the content of low-boiling fractions in the oil and the operating temperature increases oil losses from evaporation. This is also facilitated by the design features of the lubrication system of machines and mechanisms (lubrication with oil mist, spraying) [1, 2].

The burning of HMOs for their destruction, as well as the disposal of boiler and furnace fuel, leads to significant atmospheric pollution. Unwanted emissions arising from the burning of oils can be divided into the following groups:

- Lead and other metals usually in used oils, along with several oil-soluble lead halides from lead gasoline;
- other elements found in used oils: are sulfur, nitrogen, phosphorus, chlorine, and bromine; they can be present in the composition of both organic and inorganic compounds;
- polycyclic arenes present in all heavy fossil fuels and other polycyclic organics that can be released when waste oils are burned. In the literature, no information was found on the discrepancy between PAs released during the burning of fresh fuels and used oils;
- polychlorinated biphenyls (PCBs) are usually not present in used oils, but contamination with them is possible, especially in the case of possible mixing with transformer oils. If the combustion process achieves effective PCB decomposition, the expected end product is hydrogen chloride;
- other organic compounds, such as halogen-free solvents, glycolysis and gasoline, are usually explosive. Some impurities, such as gasoline, increase the volatility, saturated vapour pressure, and flash point of used oil, which requires special storage conditions.

If air pollution is affected by motor oils, oil mist and some industrial oils, other lubricants enter the biosphere mainly during spills and leaks. Falls of any volume is primarily related to accidents and cultural levels of exploitation. The compatibility of oils and lubricants with seal materials causes leaks.

Significant losses due to leakage are observed in the process of draining and filling operations, when refuelling equipment, changing the oil and collecting used products. Spent engine oils spilt on the water surface form dilutions, then emulsify films, as a result of which agglomerates are formed, which slowly biodegrade, thereby polluting the aquatic environment. Later, these films settle to the bottom of reservoirs. The entry of pollution into the body of fish leads to the destruction of gill and intestine tissues, mucus secretion, impaired breathing, and water and salt metabolism [3].

With a qualified oil change, only a small amount enters the environment. However, the share of complete services is relatively high: 10–15% abroad. Many motorists do not hand over spent engine oils to collection points but instead throw it into city dumpsters and down the drain. This waste accumulates mainly in parking lots, garages, and road ditches. Compared to oil and fuels, spent engine oils have low volatility and are much less prone to biodegradation in soil and water. Their pollution occurs mainly when they are absorbed into the ground and get into surface and groundwater during spills, leakage and evaporation with subsequent condensation. The primary pollution of the environment occurs along rivers. With rainwater, oils containing PA get into drains, reservoirs, and bottom sediments (the latter—especially in river mouths) [4].

Environmental pollution of the spent engine oils also applies to groundwater, which is the primary source of drinking water supply. Pollution of groundwater by oil products is observed in many cities of Ukraine (Kherson, Kremenchuk, Poltava, Lutsk) and other settlements. More than 120 water intakes with total reserves of 3.8 million m 3 /day (more than 25% of the volume of explored resources) are located in the areas of influence of sources of petrochemical pollution. At 54 water intakes, where the aquifers are covered by relatively permeable sand-clay rocks and are practically poorly protected from the surface, it is possible to foresee “hidden” pollution by oil products, that is, formally unrecorded penetration of oil products into the underground environment and their migration in the direction of water intake wells, as a result of contamination of water intakes is assumed.

The Main Types of Impurities in Used Motor Oils

In operation, oils are contaminated with products of the thermal decomposition of oils and their additives, solid particles, and water. Additionally, spent engine oils are contaminated with water and solid particles during collection and storage. Therefore, we considered the properties and methods of cleaning complex polyphase systems formed in spent engine oils due to operation.

Let’s start with the fact that during the operation of motor oils in internal combustion engines, oxidation products are formed in them in the form of asphalt-tar compounds, carbon deposits, and varnishes. To prevent precipitation of the above compounds in the oil, detergent-dispersing additives from the class of surface-active substances (surfactants) are introduced into the oil, which keeps the oxidation products of the motor oil in a colloidal state. When the additives in the free form are practically exhausted, oxidation products precipitate, causing engine wear.

During operation in engines, petroleum oils come into contact with metals. They are exposed to various environmental factors: temperature, pressure, electric field, light and other factors, under the influence of which the properties of the oil change over time: oxidation, polymerization, condensation of hydrocarbons, carbonization (incomplete combustion), contamination with mechanical impurities and waterlogging. As a result, asphalt-resinous compounds, colloidal particles, coke and soot, various salts, acids, metal shavings and dust, fibrous substances and water accumulate in the oil. This whole complex process of changing the physical and chemical properties of the oil is called it's aging [5].

Used oil submitted for regeneration must be pre-analyzed (using standard methods) under the defined norms according to its classification.

The analysis of operating conditions determined the most typical pollution:

- water is dissolved or in the form of an emulsion;
- products of thermal decomposition;
- primary and secondary oxidation products;
- mechanical impurities;
- dilution of oil with fuel.

Water penetrates the oil from the environment, from fuel combustion products, or due to leaks in the seals of the engine cooling channels. It is found in oil in a dissolved state and the form of emulsions; depending on temperature conditions, water can partially change from one state to another.

As a result of oil contact with heated engine parts, thermal decomposition (cracking) takes place, resulting in the formation of volatile and heavy products. In addition, oils are subject to significant local overheating and sometimes partially burn. Some metals (copper, zinc and others), which have a catalytic effect, significantly reduce the decomposition of hydrocarbons.

Diluting the oil with fuel causes a decrease in the viscosity of the working oil and the need to use oil with a sufficient reserve of viscosity. The content in gasoline oil is permissible within the limits of up to 10%, and in aviation oils—up to 3%. Depending on the fuel content, the flash point changes: the higher the flash point, the longer the oil retains its initial properties. Therefore, for the process of oil regeneration at modern installations, the combustible components that dilute the oil are almost entirely removed. The stage of fuel distillation is especially relevant for motor oils. Separation is possible by both one-time and gradual evaporation, and watered oils are regenerated according to the method, which consists in restoring the initial properties and qualities and obtaining the base oil. It is possible to prepare special technical conditions for permissible deviations of quality indicators for regenerated oils [6].

The presence of additives is primarily reflected in the methods of spent engine oils regeneration. Detergent additives, after short-term use of oil in the engine, cause it to darken due to the fact that they disperse, forming impurities in the oil that settle on the surfaces of the parts. Used motor oils drained from engines are practically not cleaned in sumps even for a long time at a temperature of 80 °C. Therefore, such used oils are classified as "non-filterable" and are difficult to regenerate.

2 Measuring Errors in Distribution of Integrated Heat Flux in the Thermal Conductivity Study

Methods of Disposal of Spent Engine Oils

The rational and economical use of lubricants and the problem of environmental protection provided for the secondary use of spent engine oils.

The main methods of rational disposal are as follows:

- combustion to obtain an additional source of energy;
- use for various technological needs;
- carrying out thermal decomposition, as a result of which light fractions are obtained—components of gasoline and diesel fuel, as well as bituminous materials used for arranging road surfaces;
- cleaning, regeneration and recycling.

One of the most promising ways of disposal of spent engine oils is their regeneration for reuse. Oil regeneration is an economically justified technology that allows reducing the ecological burden on the environment due to the reduction of the amount of oil that needs to be disposed of. From an economic and environmental point of view, the regeneration of oil is a more promising method than the utilization of oils by thermal decomposition. The regeneration process allows you to save valuable oil raw materials for obtaining oils, and the negative impact of the process on the environment is less than in the case of thermal cracking [7].

We will highlight two main areas of regeneration:

- restoration of original properties and qualities;
- production of base oils.

The first direction provides for the restoration of indicators to the established (standard), and it is possible to prepare special technical conditions for permissible deviations of quality indicators for regenerated oils. The second option is reduced to cleaning from impurities by removing additives.

Regeneration methods can be divided into the following groups [8]:

- Physical methods: settling, filtering, fuel distillation, rectification, washing with water;
- Physical and chemical methods: coagulation, adsorption. Using coagulants contributes to the increase and precipitation of asphalt-resinous substances, which are in the oil in a dispersed state, close to colloid. Adsorption cleaning methods are based on the ability of selective absorption of organic and inorganic substances found in petroleum. This method can remove asphalt-resinous and acidic substances, emulsified and dissolved water from the oil;

- chemical methods: sulfuric acid cleaning, alkaline cleaning. The use of this method allows you to clean the oil from asphalt-resinous, acidic, and some heterogenic substances, as well as from water, but at the same time, waste is formed that isn't easy to dispose of;
- combined methods.

Among the industrial methods of secondary processing, the following main forms of oil purification from products obtained during operation should be highlighted:

- vitriolic;
- adsorption;
- hydro cleaning;
- extractive;
- thin film evaporation;
- "PROP"—using a chemical method with demetallization of used oils;
- "Recycled"—use of dispersed metallic sodium.

In most countries, it is recognized as the most reasonable to collect used oils separately by brand, which ensures more qualified regeneration and processing with the production of high-quality products and less waste. The first place in the world regarding the number of installations and the volume of purification of raw materials belongs to the sulfuric acid method. If the world volume of secondary processing of used oils exceeds 1.5 million tons/year, then sulfuric acid treatment accounts for 1.2–1.3 million tons/year [8, 9].

The world volume of spent engine oils processing using sulfuric acid is about 80%. The disadvantage of this method is the formation of the most dangerous waste—acid tars, which are not subject to further use in the production sphere. Thus its accumulation creates an ecological threat to the environment.

The main methods of this type of regeneration are:

- acid contact cleaning;
- acid-contact cleaning with atmospheric-vacuum distillation;
- the "French Institute of Petroleum" (IFP) process;
- process of "Mattus/Garap" firms (France);
- operation with the stage of heat treatment of raw materials;
- process of the company "Meinken" (Germany).

The second place in the volume of industrial applications is occupied by processes using adsorption cleaning [9]. US companies most often use this technology. Distillation of water and fuel fractions is envisaged, followed by contact method cleaning. Activated clays are often used as sorbents since their raw material base in the USA is large enough.

Alternatives to adsorption purification are hydrogenation processes, but in this case, sorbents are necessary to protect hydro-purification catalysts from premature poisoning by tarry compounds and heavy metals. The hydrotreating process is the separation of molecules of unwanted sulphur-, nitrogen-, acid- and metal-containing radicals from hydrocarbons and the addition of atomic hydrogen in their place, which takes place at temperatures of 380–400 °C and pressure of 50–70 kg/cm^2 in the presence of aluminium-cobalt catalysts. This is a relatively complex and dangerous production process, requiring a high level of training, appropriate qualifications and education for service personnel [10].

Thin-film evaporation is a reasonably good process for the secondary purification of oils. The most common rotary thin-film evaporators are Luwa (Switzerland) and Enviroupur (USA). These devices allow you to distil up to 90% of used oil with minimal energy consumption. Ageing products (up to 10%) turn into bitumen, later used as a roofing or road material for construction [11].

Therefore, analyzing the existing methods at present, it is difficult to unambiguously choose the optimal and effective way of secondary processing since each has both advantages and disadvantages. Therefore, in each specific case, it is necessary to investigate the types of pollution, and their amount, and analyze the most effective and newest cleaning methods for these pollutants.

Statistical reporting, which existed until 1998 in Ukraine (was cancelled), allowed us to assess the main directions of the use of spent engine oils as follows: most of it, namely up to 30%, was regenerated at large enterprises with the aim of their further recycling, up to 15% was burned there as a boiler or furnace fuel, and other enterprises used 55%.

Physical–Chemical Properties of Used Oil

Depending on the intended purpose, three groups of used oils are established: used motor oils, used industrial lubricants, and mixed petroleum products [7].

The most important properties and qualitative characteristics of oils are viscosity, density, flash point, freezing point, ash content, presence of water, presence of mechanical impurities, and coking are presented in Table 1.

Table 1 Requirements for used motor oils submitted for regeneration

No	Indicators	Norm
1	Conditional viscosity at 20 °C, p	Above 40
2	Kinematic viscosity at 50 °C, mm^2/s (CST)	Above 35
3	The flash point, which is determined in an open crucible, °C, is not lower	100
4	The mass fraction of mechanical impurities, %, no more	1
5	Mass fraction of water, %, no more	2
6	The content of impurities	Missing
7	Solidification temperature of fractions, which boil above 340 °C, °C, not higher	−10
8	Density at 20 °C, kg/m^3, no more	905

Determination of density

The density was determined by the pycnometric method according to the method described in common standard formula determined the density of the studied petroleum product:

$$\rho = \frac{m_3 - m_1}{m} \tag{1}$$

where: m_3—mass of the pycnometer with oil product in g; m_1—the mass of the empty pycnometer in g; m—water number of the pycnometer in g.

The difference between parallel experiments did not exceed 0.0004.

Study of the viscosity of the spent engine oils emulsion

The viscosity of oil products can be influenced by two factors—temperature and the addition of a substance that is mutually soluble with the dispersion medium and has a lower viscosity. However, it turned out to be impossible to directly measure the kinematic viscosity of the spent engine oils emulsion since the product is highly dispersed, and even under conditions of dilution with solvents and high temperatures, none of the level marks was visible in the viscometers used to measure the viscosity. Therefore, it was decided to measure the relative viscosity for the studied mixtures, and according to the formula for converting the conditional viscosity into kinematic viscosity, there is a dependence, which is expressed as a dependence $of\ V_t = 7.41 \cdot BV_t$, we will calculate the kinematic viscosity (Fig. 1).

The method of determining the toxicity of oil

We burn the porcelain crucible for 2 h and cool it for 1 h in a desiccator, after which we weigh it with an error of no more than 0.0002 g. we place it in the outer one, on the bottom of which sand is poured. We cover both steel crucibles with lids. In

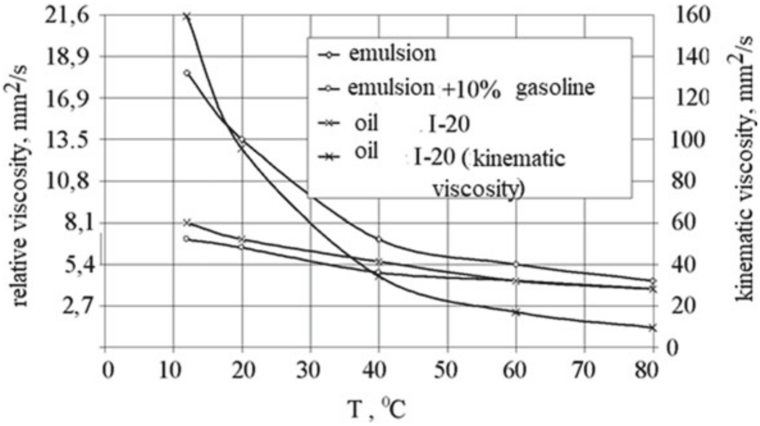


Fig. 1 Dependence of conditional and kinematic viscosity of petroleum products on temperature

the outer crucible, the top should not be tightly closed to ensure easy evaporation of steam. We put the entire system of crucibles inside the muffle. We put the whole device under the hood.

We put a burner under the bottom of the crucible and heat it for 13 min until smoke appears. The burning period is complete when no blue smoke is visible above the cap. Roast the crucible for another 7 min. Then set aside and cool for 20–40 min in a desiccator. We weigh the crucible with the experimental oil to the nearest 0.0002 g.

Coxivity (*Cox*) in percent, calculated by the formula:

$$Cox = \frac{G_k \times 100}{G}, \tag{2}$$

where *Gk*—mass of coke, g; *G*—weight of the crucible with oil, g.

Methodology for determination of ash content

A de-ashed paper filter is placed in a crucible, brought to a constant mass and weighed with an accuracy of 0.01 g. We weigh 25 g of the tested oil and pour it into the crucible. Then the weight is melted. The second filter, twisted in the form of a cone, is lowered with the base of the cone into the oil, covering its surface. We use a paper filter as a wick during oil burning.

We place the crucible on the electric stove, and next to it, we place the second crucible with dehydrated oil, in which a thermometer is immersed to control the temperature of the oil. We heat it to a temperature of 100–120 °C and hold it for a few minutes until the foam disappears. When the paper filter is saturated with oil, it is ignited, and the burning is observed until a carbon residue is formed. Next, the crucible is transferred to a muffle and calcined at a temperature of 650 °C for 2 h, then to a constant mass.

The formula calculates the ash content (A_c) in percent:

$$A_C = \frac{G_1 - G_2 - G_3}{G} \times 100, \tag{3}$$

where G_1—mass of the crucible with ash, g; G_2—mass of the crucible, g; G_3—mass of ash of paper filters, g; G—mass of the tested oil, g.

Determination of the content of mechanical impurities

A smooth paper ashless filter of the “Red Ribbon” brand with a diameter of 10–11 mm was placed in a weighing glass and dried to a constant weight in a thermostat at a temperature of 105–110 °C.

The lid of the glass was half open during the drying process. The filter, dried and cooled in a desiccator, was weighed together with a weighing glass with a closed lid on an analytical balance with an accuracy of 0.0002 g.

Drying and weighing were carried out until the difference between two consecutive weightings was no more than 0.0004 g. Repeated drying was carried out for 30 min.

Filters for analyses in which alcohol is used as a solvent were pre-treated in a filter funnel with 50 ml of hot alcohol.

The sample of the studied petroleum product was thoroughly mixed for 5 min and weighed into a tall beaker with a spout or a conical flask with a wide neck with a capacity of 500–800 ml on technical and chemical scales (with an accuracy of 0.1 g) 100 g of the product if its viscosity is 100 °C did not exceed 20 cSt, and 25 g for higher viscosity.

For the determination of mechanical impurities, toluene was used as a solvent, which is used for further washing. An alcohol-toluene mixture (1:4) was used to form a precipitate insoluble in toluene.

The mixture of the product and the solvent was thoroughly mixed and filtered. To determine the content of mechanical impurities in slowly filtered products, the solution was filtered under a vacuum.

If the studied product contained water, which made filtering difficult, then after dissolving the sample, the solution was allowed to stand for 20–30 min, after which it was filtered, carefully draining it. Settled water with residual toluene was diluted with 6–10 times the alcohol-ether mixture (4:1) passed through a filter. The residue in the flask was washed onto the filter with an alcohol-ether mixture. The filter was washed with the same mixture and hot toluene. After washing, the filter in a similar weighing glass was dried in a thermostat with a temperature of 105–10 °C to a constant mass. Before each weighing, the beaker with the filter was cooled in a desiccator to room temperature and tightly covered with a lid. The weighing accuracy was 0.0002 g.

The mass of the bux expressed the mass content of mechanical impurities in 100 g of the studied product. If the weight of the oil was less than or more than 100 g, the percentage of impurities Im was calculated according to the formula:

$$\mathrm{Im} = 100\frac{a}{A}, \tag{4}$$

where a—mass of mechanical impurities, g; A—weight of the product, g.

The content of mechanical impurities was determined as the arithmetic mean of the results of two parallel experiments.

Determination of water content in oil emulsion

There are many methods for determining the content of the dispersion phase in emulsions. However, the most straightforward and sufficiently accurate is the Dean-Stark method, which was used in the dissertation research; its essence consists of the simultaneous distillation of oil from a weight of water and a solvent. Straight-run gasoline (TU 38.401-67-108-92) is used as a solvent.

The water content in the spent engine oils was calculated according to the formula:

$$W = \frac{V \cdot \rho\ddot{a}}{C} \cdot 100 \tag{5}$$

Table 2 Physico-chemical properties of used oil

No	Indicators	Value
1	Conditional viscosity at 20 °C, p	13
2	Density at 20 °C, kg/m^3, no more	925
3	Kinematic viscosity at 50 °C, mm^2/s (CST)	22
4	Ash content, %	0.29
5	The mass fraction of mechanical impurities, %, no more	2.7
6	Mass fraction of water, %,	15.6
7	Colour on the CNT colourimeter, CNT units, no more	6.0

where W—water content, mass %; V—volume of water in the catcher, ml; $\rho_{ä}$—density of dispersed phase, g/ml; C—weight of oil taken for determination, g.

We have established that due to non-compliance with the conditions of collection, storage and transportation of spent engine oils, its quality indicators do not meet the established standards of Ukraine, namely GOST 21,046-86. Since the water content exceeds the normalised indicators, it was impossible to research such indicators as the solidification temperature and flash point. The Table 2 shows the indicators of the studied spent engine oils. According to the given physicochemical properties, the spent engine oils studied by us does not meet the standard indicators; the mass fraction of water is 15.6%, the content of mechanical impurities is 2.7%, and the density and ash content exceeds the collection norm. Therefore, it is almost impossible to choose a method of regeneration of the spent engine oils according to known methods.

Development of a Set of Measures for the Introduction of the Spent Engine Oils Collection System

The conducted environmental protection calculation showed that if only 10% of all spent engine oils, annually formed in Ukraine, get into the soil and pollute 100 ha of land with these spent engine oils, the environment will be damaged, the compensation of which requires UAH 5.8 million.

To reduce the damage caused to the environment by a large amount of used oils, it is necessary to dispose of them, but currently, there is no plant or factory for the disposal of oils in Ukraine. This measure can ensure the annual production of about 500,000 tons of the target product and significantly reduce emissions of harmful substances into the environment.

Environmentally friendly processes of processing used lubricants must also be economically profitable, which is connected with many factors, including the cost of raw materials and measures of state support (subsidies and subsidies), since ensuring the ecological safety of the environment is a social problem that must be solved at the state level.

To ensure the functioning of an effective system of protection of the natural environment from spent engine oils, it is necessary to solve three tasks [1, 2]:

- Create an effective spent engine oils classification and collection system.
- To develop a complex technology for the purification of spent engine oils, which would consider wide fluctuations in the concentrations of spent engine oils pollutants (water content varies from 0.8 to 20%).
- Create many installations that would provide the necessary processing volume of the collected spent engine oils.

A significant part of these dissertation studies [8] is devoted to developing a complex technology that would allow the processing of spent engine oils with different water content and various pollutants.

The first priority should still be the introduction of the spent engine oils collection system. And the collected valuable raw materials, provided there are no processing facilities, can be initially sold to foreign countries, where these production facilities function successfully and many of which are not working at full capacity. Since such activity is economically beneficial, many Ukrainian spent engine oils processors will appear in a short time. Then it is necessary to take many legislative measures to protect the domestic producer, which will allow the organising a system of spent engine oils processing in Ukraine.

It should be noted that despite the presence of a perfect legislative framework in Ukraine, which allows for establishing the functioning of the spent engine oils collection system, there are no legally approved norms for the collection of spent engine oils. Therefore, there is no fundamental primary accounting of spent engine oils by regional environmental protection departments. Development and approval of such standards is the first necessary measure.

The second necessary measure is creating a permit system for handling spent engine oils as hazardous waste. In our opinion, every enterprise that will receive more than 100 L of spent engine oils per year should be registered with the regional Department of Environmental Protection as a producer of highly toxic waste and obtain a permit for handling this waste (a similar mechanism is adopted in most European countries).

The third necessary measure is the creation of a system of economic stimulation of activity in the field of collecting spent engine oils. A fee should be established for the removal and identification of spent engine oils, which should be collected from the organisation of the storage of spent engine oils.

The fourth necessary measure is the creation and operation of a system of fines for violating the norms of handling spent engine oils as hazardous waste and wide publicity in the mass media of examples of the application of this system to specific violators.

3 Patterns of Adsorption Processes on Synthesized Sorbents Based on TPP Fly Ash. Characteristics of Synthetic Zeolite Based on Fly Ash of the Dobrotvirska Heat Power Plant

The surface morphology and chemical composition of the obtained samples were studied by electron microscopic analysis according to the method presented in Sect. 2. The diameter of the electron beam was 1 μm, and the acceleration potential was 15 kV. The elemental analysis of the zeolite surface was performed for different sections of samples with an area of 100 μm^2 [11] by scanning with an electronic probe. Data on the chemical composition of the synthesized samples were derived from the averaged results. The adsorbents obtained by the method of sintering (fusing) TPP fly ash with sodium hydroxide and the hydrothermal method according to the methodology presented in Sect. 2 contained zeolites X, Na-P1 and fayalite in the crystal structure.

The image of the surface of the particles of the original material (ash) and the synthesized zeolites is presented in Fig. 2. The images were obtained using a scanning electron microscope in the secondary electron mode, which ensures the appropriate resolution and informativeness of the results.

Points marked with numbers corresponding to spectrum numbers. The mass fractions of samples (Fig. 2) are given in the Table 3.

The spectrumn presented at Fig. 3 shows the presence of iron and manganese atoms in the sample, which allows these samples to be used for catalysis.

The chemical composition of this sample (Fig. 4) is typical for zeolites. It contains a significant amount of aluminium, which is typical for ion exchangers.

The spectruun presented at Fig. 5 shows the lack of calcium athoms atoms in the sample.

In Fig. 6, carbon atoms were identified. The chemical composition of the zeolite at this point provides for the possibility of ion exchange due to the presence of sodium

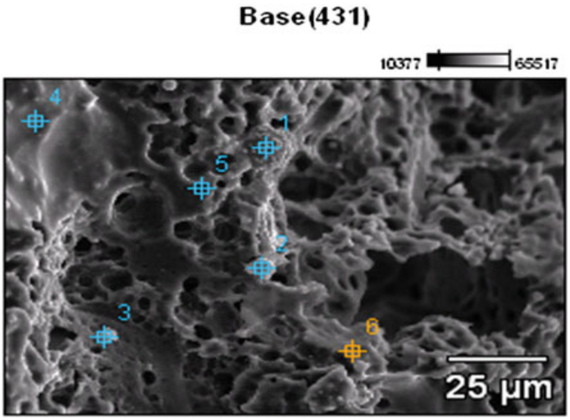


Fig. 2 Image of the surface of the synthesised samples obtained using SEM

Table 3 Mass fractions of components, mass %

Spectrum No	C	O	Na	Mg	Al	Si	P	S	K	Mn	Fe
1	27.8	34.3		1.06	4.20	1.54				0.95	29.7
2	38.6	39.7	0.43	0.33	7.55	10.4	0.05	0.12	1.35		1.63
3	35.5	43.0	0.53	0.31	6.86	9.77			1.50		2.02
4	88.2	9.63	0.15	0.11	0.27	0.30		0.42			0.35
5	99.8							0.19			
6	95.6	3.79		0.08	0.10	0.13		0.15			

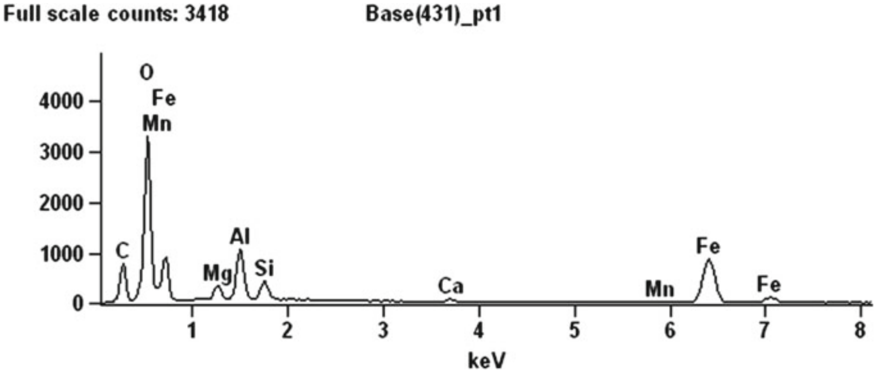


Fig. 3 The spectrum of the sample (Fig. 2) at point 1

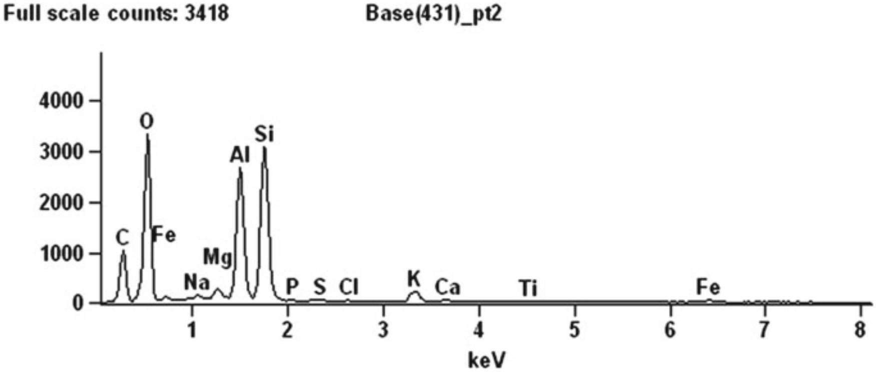


Fig. 4 The spectrum of the sample (Fig. 2) at point 2

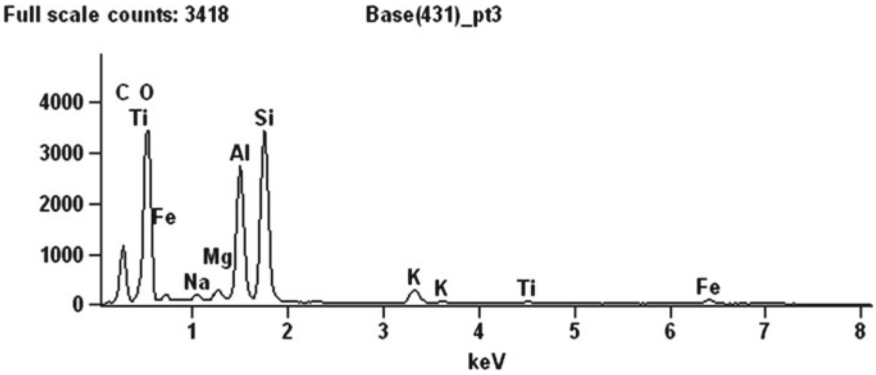


Fig. 5 The spectrum of the sample (Fig. 2) at point 3

and magnesium atoms and the adsorption of non-polar substances due to the presence of carbon atoms in the zeolite structure.

In Fig. 7, sulfur and carbon atoms are identified. This is explained by the inhomogeneity of the ash composition, which is a product of burning hard coal, and unburned particles can be found in it. Carbon atoms make it possible to adsorb such non-polar substances as petroleum products.

In Fig. 8. we can observe a high concentration of carbon atoms and trace concentrations of aluminium, magnesium, silicon, sulphur and calcium atoms, presumably in the form of oxides.

The data of Figs. 3, 4, 5, 6, 7 and 8 regarding the chemical composition of the synthesized zeolites are presented in the Table 4. As can be seen from the results, the chemical composition of the zeolite differs in the studied points, which can be explained by the heterogeneous chemical composition of fly ash, which is the raw material for this zeolite. However, the acceptable aluminium content in the studied

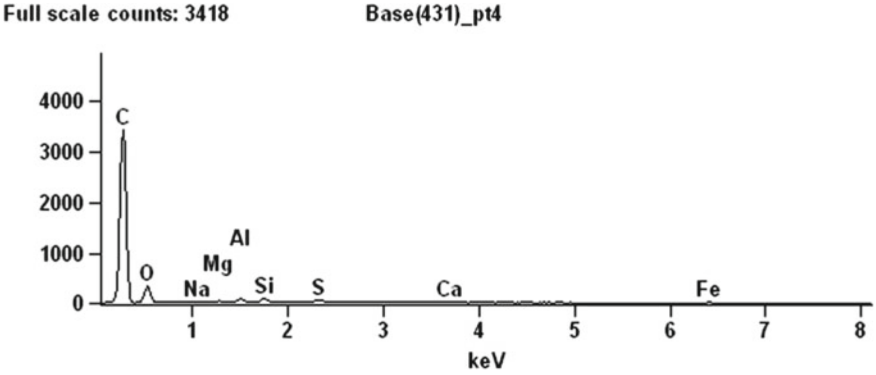


Fig. 6 The spectrum of the sample (Fig. 2) at point 4

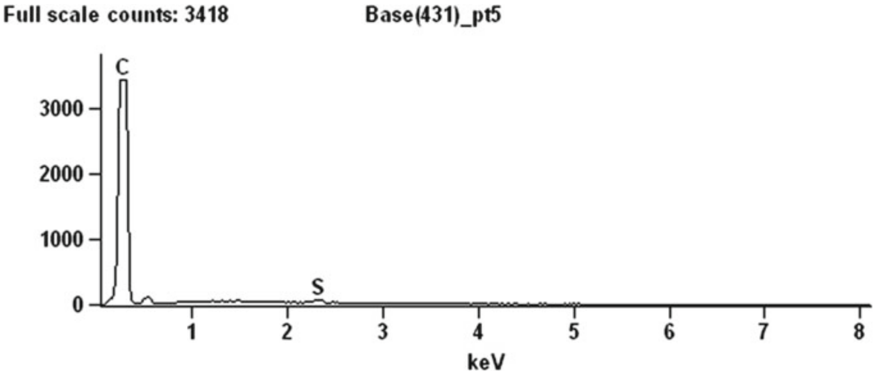


Fig. 7 The spectrum of the sample (Fig. 2) at point 5

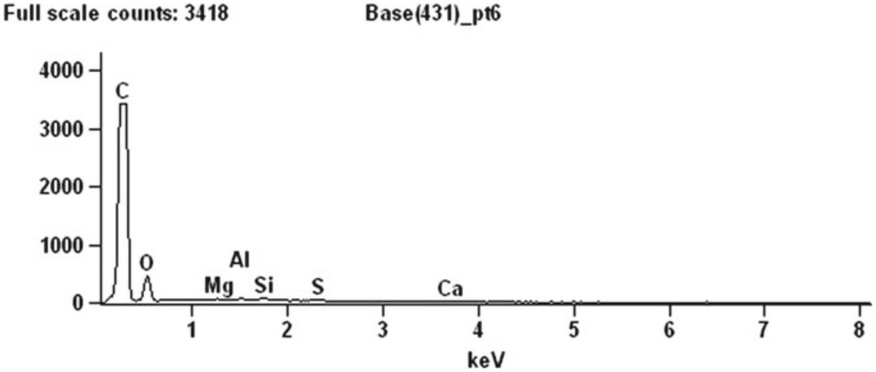


Fig. 8 The spectrum of the sample (Fig. 2) at point 6

samples should be noted. The ratio of aluminium to silicon was from 5:3 to 2:3 against the recommended 1:4.

Table 4 Concentration of atoms, at, %

Spectrum no	C	O	Na	Mg	Al	Si	P	S	K	Fe
1	43.91	40.69	–	0.83	2.95	1.04	–	–	–	10.09
2	49.44	38.79	0.29	0.21	4.37	5.58	0.02	0.06	0.54	0.45
3	46.44	42.23	0.36	0.20	3.99	5.46	–	–	0.60	0.57
4	91.67	7.51	0.08	0.06	0.12	0.13	–	0.16	–	0.08
5	99.93	–	–	–	–	–	–	0.07	–	–
6	96.90	2.88	–	0.04	0.04	0.06	–	0.06	–	–

The obtained synthetic adsorbent proved to be an effective sorbent for organic and inorganic substances.

Static activity a^* belongs to one of the essential characteristics of adsorbents. It is represented by the adsorption isotherm and is a function of the concentration C or the partial pressure of the component in the gas mixture P:

$$a^* = f(C, P). \tag{6}$$

Taking into account the different mechanisms of adsorption and, accordingly, other forms of isotherms, various mathematical models of isotherms have been proposed [12].

Sorption of Petroleum Products on Synthesised Zeolites

Synthetic zeolites based on TPP fly ash contain carbon in their composition. This makes it possible to use them for the adsorption of organic compounds, particularly oil products.

The sorption isotherm of diesel fuel with ash modified by the sintering method is typical for microporous sorbents, and the sorption isotherm for ash modified by the hydrothermal method is specific for mesoporous sorbents (Fig. 9). According to the Giles classification [1, 13], these isotherms belong to the L-type.

For example, isotherms of diesel fuel adsorption on synthesised sorbents, the basis of which is fly ash (Fig. 9), which can be described by the Langmuir isotherm and the Freundlich isotherm [14]. Sorption isotherms from Fig. 9 for fly ash, ash modified by

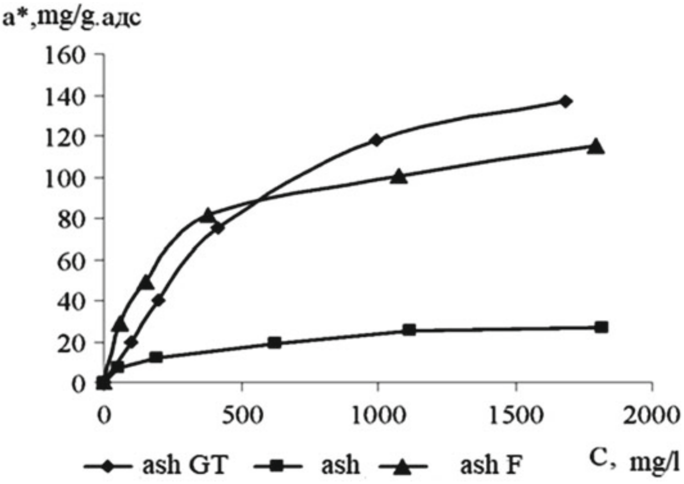


Fig. 9 Sorption isotherms of diesel fuel by modified sorbents

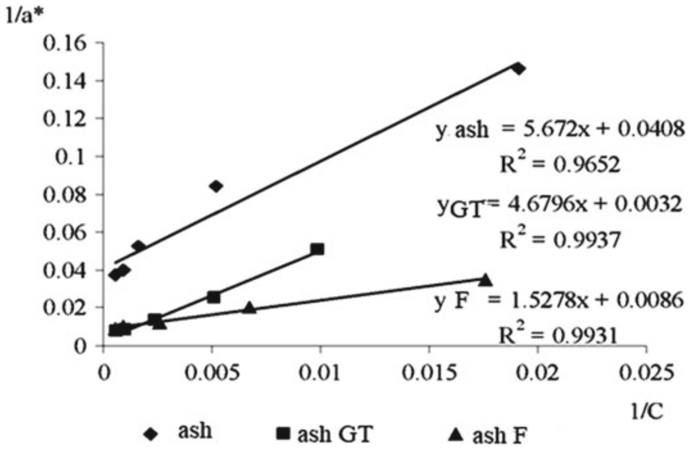


Fig. 10 Linearized Langmuir isotherm for the adsorption of diesel fuel by synthesised zeolites based on fly ash

the sintering method and the hydrothermal method [15], processed by the Langmuir model, are presented in Fig. 10.

Langmuir isotherm for ash:

$$a^* = 24.5\frac{0.007C}{1 + 0.007C}. \tag{7}$$

Langmuir isotherm for ash modified by the hydrothermal method:

$$a^* = 312.5\frac{6.84 \cdot 10^{-4}C}{1 + 6.84 \cdot 10^{-4}C}. \tag{8}$$

Langmuir isotherm for ash modified by the sintering method:

$$a^* = 116.28\frac{0.0056C}{1 + 0.0056C}. \tag{9}$$

Sorption isotherms for fly ash, ash modified by the sintering method and the hydrothermal method (Fig. 9), processed by the Freundlich model, are presented in Fig. 11.

The graphical dependence according to Fig. 11 can be represented by the following equations:

Freundlich isotherm for ash:

$$a^* = 5.67C^{1/0.9}. \tag{10}$$

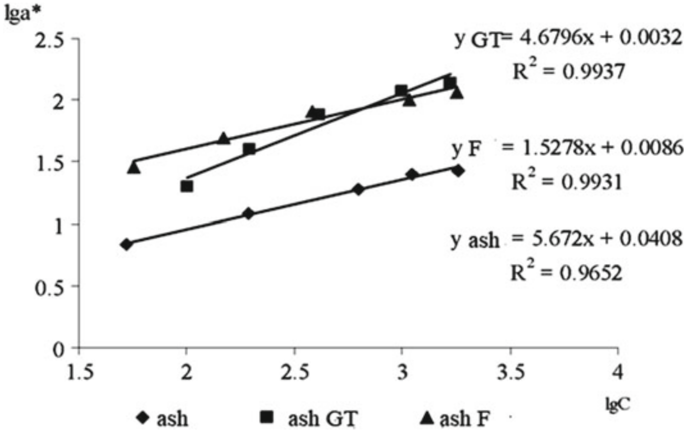


Fig. 11 Linearized Freundlich isotherm for the adsorption of diesel fuel by synthesised fly ash-based zeolites

Freundlich isotherm for ash modified by the hydrothermal method:

$$a^* = 4.68C^{1/0.99}. \quad (11)$$

Freundlich isotherm for ash modified by the sintering method:

$$a^* = 1.53C^{1/0.96}. \quad (12)$$

The value of the correlation coefficients indicates that in the given range of concentrations, both isotherms describe the adsorption statics well.

The use of zeolites for adsorption made it possible to establish that not only physical adsorption takes place but also ion exchange because the structure of the zeolite contains Na^+, K^+, Ca^{2+}, Mg^{2+} ions, which are able to exchange for cations that are in solution (e.g., heavy metal ions).

Technological Aspects of Regeneration of Used MOTOR *Oils and Their Application*

Based on the data analysis of the conducted experiments, we have proposed a block diagram of the complex process of spent engine oils regeneration, which allows you to implement renewal for spent engine oils with different initial water content, as well as under the conditions of the range of additives. Complex treatment of spent engine oils includes the selection and processing of all waste or environmentally hazardous substances that are recommended for use in other industries.

The scheme proposed by us includes the following stages:

1. coagulation;
2. adsorption cleaning;
3. advocacy;
4. centrifugation;
5. fuel diversion.

For the coagulation process, we use the most effective demulsifier Sot for this oil. The solvent is used to reduce the viscosity of spent engine oils, as well as to reduce the heating temperature, which significantly speeds up the dehydration process and also reduces energy costs.

The first stage of purification includes: coagulation, centrifugation and settling. As a result, we will get a purified spent engine oils with a water content of 0.8%. The second stage of regeneration includes adsorptive cleaning, where the spent engine oils is simultaneously purified from water up to 0.1%, as well as mechanical impurities, resins and asphaltenes.

The stage of adsorption purification is mandatory for the regeneration of all types of spent engine oils. The use of adsorption purification is proposed to increase the yield of high-quality oil, and from the point of view of ecology, the purity of the process.

For spent engine oils with a water content of 0.8%, regeneration begins with the second stage, which includes adsorption cleaning, where water is removed and cleaned from asphaltenes and, resins, mechanical impurities. The spent engine oils centrifugation process includes cleaning from mechanical impurities that got into them during operation, as well as from the adsorbent, which is still in the spent engine oils at this time. The residual amount of water adsorbed on bentonite and mechanical impurities is also removed.

After centrifugation, the spent sorbent separated from the spent engine oils is sent for disposal. At the final stage of the regeneration process, we use the distillation of fuel fractions. The rectification column provides for the distillation of fuel from regenerated motor oil: in this case, we obtain a gasoline fraction that boils in the range of 50–215 °C and a diesel fraction at a temperature of 180–350 °C. This method makes it possible to obtain a better quality of regenerated oil. So, using the block diagram proposed, we will get regenerated oil for which the technical requirements of TU U 23.2-22340203-044:2011 have been developed. As a result of the conducted experimental studies on used motor oil, taking into account the proposed complex technological scheme, the following parameters of regenerated oil were obtained, which are presented in Table 5.

Table 5 Parameters of regenerated oil

No	Name	Indicators
1	Density at 20 °C, kg/m^3, no more	900
2	Kinematic viscosity at 40 °C, mm^2/s Kinematic viscosity at 100 °C, mm^2/s	36.06 5.6
3	The flash point is determined in an open crucible, not lower than °C	180
4	Colour on the CNT colourimeter, CNT units, no more	3
5	Mass fraction of water, %, no more	0.1
6	Viscosity index	90
7	Acid number, mg of KOH per 1 g, no more	0.05
8	Ash content, mass %	0.05
9	Optical density	0.24
10	The mass fraction of mechanical impurities, %, no more	0.009

4 Conclusions

A complex of legal, organisational and technological measures has been developed to prevent pollution of the natural environment by using motor oils. The estimated damage caused to the environment under conditions of 10% of all spent engine oilss that are annually formed in Ukraine enters the soil. The pollution of 100 ha of land and the environment by these spent engine oilss causes damage, which requires 5.8 million hryvnias for compensation. A complex of organisational measures for the collection of spent engine oils has been developed. The results of experimental studies of the statics of oil product adsorption by zeolite are presented, and their adsorption capacity is established. The process of static patterns of sorption on a synthesised sorbent based on fly ash, which is formed during the burning of hard coal at thermal power stations, was studied. The sorption isotherms for the hydrothermal and thermal modification methods were determined. A complex technology for the regeneration of fuel oil has been developed, which includes the stages of dehydration, adsorption purification, centrifugation and distillation of fuel and allows the regeneration of fuel oil with different initial water content. The regenerated crude, according to the studied parameters, can be reused in machines and mechanisms of industrial equipment as a component of base oil for the manufacture of motor and industrial oils.

References

1. Sun, X., Shi, K., Mo, S., Mei, J., Rong, J., Wang, S., Li, Z.: A sustainable reinforced-concrete-structured sponge for highly-recyclable oil adsorption. Sep. Purif. Technol. **305**, 122483 (2023). https://doi.org/10.1016/j.seppur.2022.122483
2. Shamanskyi, S., Boichenko, S., Khrutba, V., Barabash, O., Shkilniuk, I., Yakovlieva, A., Topilnyckyi, P., Pavliukh, L.: Improving the photobioreactor operation efficiency in the technological

scheme of wastewater treatment. East.-Eur. J. Enterp. Technol. **6**(10(114), 6–15 (2021). https://doi.org/10.15587/1729-4061.2021.248746

3. Lashkhi, V.L., Zakharova, N.N.: Role of surface phenomena in chemmotology of oils. Chem. Technol. Fuels Oils **27**(12), 655–665 (1991). https://doi.org/10.1007/BF00725710
4. Nahursky, O., Krylova, H., Vasiichuk, V., Kachan, S., Nahursky, A., Paraniak, N., Malovanyy, M.: Utilization of household plastic waste in technologies with final biodegradation. Ecol. Eng. Environ. Technol. **23** (2022). https://doi.org/10.12912/27197050/150234.
5. Sabadash, V., Omelianova, S.: Mathematical prediction of the scale of migration of heavy metals in the soil profile. In: 15th International Conference Monitoring of Geological Processes and Ecological Condition of the Environment, vol. 2021, No. 1, pp. 1–5. EAGE Publications BV (2021). https://doi.org/10.3997/2214-4609.20215K2048.
6. Zhang, T., Ding, M., Zhang, H., Tao, N., Wang, X., Zhong, J.: Fish oil-loaded emulsions stabilized by synergetic or competitive adsorption of gelatin and surfactants on oil/water interfaces. Food Chem. **308**, 125597 (2020). https://doi.org/10.1016/j.foodchem.2019.125597
7. Porteous, J.D.: Design with people: the quality of the urban environment. Environ. Behav. **3**, 155–177 (1971). https://doi.org/10.1177/001391657100300204
8. Ostrikov, V.V., Sazonov, S.N., Orobinskii, V.I., Afonichev, D.N.: Determination of dispersing-stabilizing properties of motor oils and their dirtiness in performance conditions. Chem. Technol. Fuels Oils **55**, 577–583 (2019). https://doi.org/10.1007/s10553-019-01069-7
9. Boichenko, S., Yakovlieva, A., Kale, U., Nagy, A.: Analysis of technological potential for utilization of waste aviation lubricating materials. Technol. Audit. Prod. Reserv. **2**(1), 58 (2021). https://doi.org/10.15587/2706-5448.2021.229673
10. Gumnitsky, J., Sabadash, V., Matsuska, O., Lyuta, O., Hyvlud, A., Venger, L.: Dynamics of adsorption of copper ions in fixed-bed column and mathematical interpretation of the first stage of the process. Chem. Chem. Technol. **2**(16), 267–273 (2022). https://doi.org/10.23939/chcht16.02.267
11. Adamchuk-Chala, N., Ponomarenko, S., Yankiv-Vitkovska, L., Chala, Y.: Technologies for restoring soil from oil pollution. In: Chemmotological Aspects of Sustainable Development of Transport, pp. 153–165. Cham: Springer International Publishing (2022). https://doi.org/10.1007/978-3-031-06577-4_8
12. Konovalov, S., Zubenko, S., Patrylak, L., Yakovenko, A., Povazhnyi, V., Burlachenko, K.: Revisiting the synthesis of fatty acid alkyl esters of lower monohydric alcohols by homogeneous base-catalyzed transesterification of vegetable oils. In: Chemmotological Aspects of Sustainable Development of Transport, pp. 49–80. Cham: Springer International Publishing (2022). https://doi.org/10.1007/978-3-031-06577-4_4
13. Yakovleva, A., Boichenko, S., Lejda, K., et al.: Antiwear properties of plant—mineral-based fuels for airbreathing jet engines. Chem. Technol. Fuels Oils **53**, 1–9 (2017). https://doi.org/10.1007/s10553-017-0774-x
14. Symak, D., Sabadash, V., Gumnitsky, J., Hnativ, Z.: Kinetic regularities and mathematical modelling of potassium chloride dissolution. Chem. Chem. Technol. **15**(1), 148–152 (2021). https://doi.org/10.23939/chcht15.01.148
15. Sydorchuk, O.V., Matsuska, O.V., Sabadash, V.V., Humnytsʹkyy, Y.A.M. (2014). Parallel-serial adsorption of phosphate ions by natural sorbents. East.-Eur. J. Enterp. Technol. **6**(6), 56–60. https://doi.org/10.15587/1729-4061.2014.30874

Removal of Contaminants from an Aqueous Solution by a Magnetic Field Using the Effect of Focusing Ionic Impurities

Oleh Terentiev, Anatoliy Kryuchkov, Mykola Sergienko, Viktor Rozen, and Artur Jaworski

1 Introduction

The relevance of the problem of water purification is noted in the UN materials "Management of water resources in conditions of uncertainty and risk". As a result, the High Level Panel on Water (HLPW) was convened in April 2016 to ensure availability and sustainable water consumption for all countries. In relation to Ukraine, the relevance is confirmed by the Law of Ukraine "On the Nationwide Program" "Drinking Water of Ukraine for 2016–2030" dated March 3, 2015 No. 2455-IV. Water shortage is associated with population growth and rapid urbanization of human activities. Therefore, water purification and processing was, is and will be an urgent problem all over the world.

The use of traditional chemical and mechanical methods is associated with the use of expensive reagents and complex equipment, moreover, they are not always effective and safe. Therefore, more and more emphasis is placed on physical cleaning methods.

Physical methods of water purification are more effective and cheaper. Water purification by physical methods is carried out by external force fields, without

---

O. Terentiev · A. Kryuchkov · M. Sergienko (✉) · V. Rozen
National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute", Kyiv, Ukraine
e-mail: ux0un@ukr.net

V. Rozen
General Energy Institute of NAS of Ukraine, Kyiv, Ukraine

A. Jaworski
Rzeszow University of Technology, Rzeszow, Poland

S. Boichenko et al. (eds.), *Modern Technologies in Energy and Transport*, Studies in Systems, Decision and Control 510, https://doi.org/10.1007/978-3-031-44351-0_8

adding chemicals to the working volume. Therefore, such studies should be considered relevant, aimed at further improvement and development of water reuse technology. However, in this direction of research, the conditions for the influence of the electromagnetic field on the impurities contaminating the liquid are insufficiently substantiated.

2 Analysis of Literary Studies and Statement of the Problem

In work [1], a review and analysis of wastewater disinfection was carried out. Known methods of wastewater disinfection, such as combining with domestic wastewater, recycling, aerobic and anaerobic processes have both advantages and disadvantages. Disadvantages include frequent cleaning of the filters themselves, and the need to have a reserve of special reagents for their restoration, coagulation, formation of lumps, chemical precipitation, adsorption, dismantling of ammonium, chemical oxidation, ion exchange. The advantages include the simplicity of the design, the availability of replaceable filters that can be quickly replaced, and the formation of sediment on the filter elements, and not on the working surfaces of the device. Modern technologies: membrane filtration, microfiltration, ultrafiltration, nanofiltration and reverse osmosis are science-intensive and expensive.

Research has established that the mentioned possibilities of increasing the efficiency of membrane methods by electromagnetic influences on impurities are becoming more and more widespread. In works [2–10], the effect of electromagnetic field (EMF) on the control of membrane fouling and scale formation is studied. Due to the installation of reverse osmosis (RO reverse osmosis), desalination of brackish groundwater was achieved. EMF reduced membrane scaling and improved RO performance by 38.3%. Despite all the advantages of reverse osmosis installations, they also have disadvantages—the structural complexity of manufacturing filter elements with nano-sized cells, high cost, etc.

Scale and biofouling are two main problems in the operation of reverse osmosis (RO) membranes [11]. This is a fairly new technology. From literature it is clear that the scientific basis of its supposed effectiveness has not yet been established. Systematic scientific research is needed to confirm the application and commercialization of EMF technologies. The application of EMF is a pretreatment for fouling control in RO membrane systems.

The investigated [11] determined the quantitative value of the electrical properties of RO membranes during the processes of pollution and cleaning using electrical impedance spectroscopy. “Process condition” monitoring is particularly useful for pollution control in the RO industry. Monitoring of the fouling process of single and binary pollutants on the RO membrane was carried out. Different forms of the Nyquist graph were obtained for different types of pollution. However, it should be noted that this paper does not provide quantitative values of the electrical properties of RO membranes. The growth of a layer of pollution on the surface of the membrane is also considered a disadvantage.

Ultrasonic treatment was introduced into the membrane distillation process [12, 13] and the effect of ultrasonic irradiation on the control of silica fouling was investigated. A hollow fiber membrane can retain its mechanical properties and initial pore size distribution in the presence of ultrasonic irradiation. The disadvantage is that increasing the concentration factor had almost no effect on the liquid flow. A large amount of silica settled on the surface of the membrane. To overcome this problem in operation, the surface of the membrane should be kept clean. Under ultrasonic irradiation, the permeate flow remained stable and increased by approximately 43%. Ultrasonic irradiation can effectively control silica fouling during membrane distillation.

Good results were achieved when using water purification with direct and reverse osmosis [14]. Engineers of the University of California in Riverside (USA) have developed a new method of restoring drinking water from highly concentrated salt solutions with almost 100% yield. In the work, considerable attention is paid to the modes of recovery of drinking water from highly concentrated salt solutions. It is not entirely clear how and under what conditions almost 100% yield was achieved. In our opinion, additional research in this direction is necessary.

Modern studies [3] are focused on a review of the rapid growth in the use of magnetized water in various fields of science. The work illuminates the circulation of water for 24 h. in electromagnetic fields of intensity 500, 1000, 1500 and 2000 G. The advantages of magnetization and the use of magnetized water are the improvement of the geotechnical properties of the soil due to the precipitation of calcite. It increases the bond between soil particles and subsequently the strength of the soil. But improving the geotechnical properties of the soil due to the precipitation of calcite is not always beneficial for the natural environment.

The operation of vacuum-plasma and power electronics devices is based on the use of electromagnetic control of the shape and direction of the electron flow of charges [4]. The magnetic field in induction devices is created using HF inductors. This technology improves the vaporization of materials with subsequent ionization.

In the study [5], the efficiency of $CaCO_3$ crystallization caused by a different combination of treatment with an alternating electromagnetic field (AEMF alternating electromagnetic field) and ultrasonic (ultrasonic (US) treatment).

The disadvantage is that the results improve only with the correct addition of Mg^{2+} ions. A combination with AEMF+US or US+AEMF can significantly improve the physical effectiveness of anti-scaling. But the work does not define the concept of correct addition of Mg^{2+} ions. This can cause difficulties associated with the choice of modes of operation of the alternating electromagnetic field and processing of the flow with ultrasound.

Experiments conducted in order to assess the impact of sediment before and after treatment of the working surfaces of the equipment with an electromagnetic field were conducted in work [6]. The scale of the brine consisted mainly of calcium bicarbonate ions. The reported results were obtained using a Dynamic Scale Loop system with brine exposed to a magnetic field generated by a 6480 Gauss class N45SH magnet in a diametrical orientation for 2.5 s. The disadvantage of such a solution is the complexity of managing the magnetic treatment of the working surface. This circumstance is related to the fact that the scale of brine is not placed evenly on the work surface. This significantly changes the stability and uniformity of the treatment of the working surfaces of the equipment by the electromagnetic field.

Various methods are used for water purification, such as ultraviolet irradiation, heat treatment, addition of disinfectants, such as chlorine, etc. Using these methods of water purification reduces turbidity, improves taste and removes microbes. Studies [7] evaluated water purification using Phyllanthus embolic wood. As a result, color, aroma, turbidity, conductivity, solids, alkalinity, calcium, iron, chloride and nitrate levels are increased in the test container. The following were reduced: pH, total hardness, sulfate and magnesium levels. The level of Escherichia coli, total coliforms and fecal coliforms was reduced. Despite the practical significance of such results, water purification using Phyllanthus embolic wood is not sufficiently considered in the paper.

The study [8] provides information on the positive aspects of magnetism and magnetic materials for water purification. These cleaning methods can ensure that the water complies with the standards. Magnetic separation is one of these cleaning methods. It is used in the mining and oil industry. It provides not only water purification, but also cleaning of pipes from the sticking of impurities on the inner wall. Under the influence of a magnetic field, the energy of the ion state of impurities in the liquid increases. This leads to the ionization of impurities, which increases the efficiency of the electromagnetic system. Due to the difference in the concentration of cations and anions in the liquid, electric fields arise, caused by the electric charge of the total volume of ions. The effect of the magnetic field on the liquid affects the trajectory of the charged particle. Overcoming the problem of managing the trajectory of particle movement is associated with the difficulty of determining the necessary factors for optimal indicators of the cleaning process. In [9], a new membrane electrocoagulation reactor (electrocoagulation membrane reactor ECMR) is given, in which ultrafiltration (UF) membrane modules are placed between the electrodes. Its use improves the quality of wastewater and reduces membrane fouling. Higher current density and slightly acidic pH in EMCR promoted faster formation of large follicles. The disadvantage is structural complexity, contamination and blocking of membrane pores, the formation of a polarized cake layer was controlled by current density and voltage.

The influence of the electromagnetic field during salt and water transport and carbonate recovery was investigated [13, 14]. The deposition of salts during reverse osmosis desalination is interesting. The electromagnetic field was created by an alternating current. Current flows through a solenoid wound around the membrane separation module. Current strength and frequency were 25 A and 50 Hz, respectively. Experiments were carried out using $CaCO_3$ solution at a concentration of 5.5 mmol/l. For comparison, membrane desalination was carried out in the presence and absence of an electromagnetic field. Powder-like elements were formed under the influence of an electromagnetic field. They had a lower density than precipitation formed in the case of non-use of an electromagnetic field. Powder-like elements almost did not react to the electromagnetic field. This is due to the difficulty of determining the operating parameters for choosing their cleaning modes.

Mathematical models of ocean eddies (whirlpool) are presented in [15]. Attention is drawn to the mathematical model of oceanic eddies [16]—the complexity of the processes operating in eddies requires complex mathematical apparatus for their description [17]. The given models do not allow to describe complex processes in eddies.

The studies analyzed definitely have positive results. Therefore, such research should be considered relevant, aimed at further improvement and development of water purification technology for its reuse [18, 19].

However, in the considered studies, the conditions and results of the influence of the electromagnetic field on the trajectory of impurities contaminating the liquid are insufficiently substantiated. Also, there are undiscovered possibilities of accumulation of impurities due to the action of Lorentz forces in the paraboloid of rotation, and the possibility of separating purified water from impurities that contaminate it during the creation of a vortex in the working focusing chamber [20, 21].

Thus, there are reasons to assert:

- about the possibility of controlling the trajectory of the movement of impurities;
- and the Lorentz forces contribute to the focusing of the paraboloid of rotation;
- directional regulation of the processes of focusing of impurities by the magnetic influence unit in the working focusing chamber.

This determines the need for more in-depth research in this direction. The analysis of water purification methods made it possible to formulate the following research idea.

In the flow of water contaminated with ionic impurities, it is necessary to form a magnetic field with a structure that should ensure focusing in the cross section of the liquid flow the maximum concentration of ionic impurities, which will lead to the distribution in space and time of the total contamination of the flow into two flows:

- purified main flow by volume with a low concentration of impurities;
- the second axial flow with a much smaller volume and with a high concentration of ionic impurities, which makes it quite easy to remove it from the volume of the purified flow.

3 The Purpose of the Study

To develop a method and a means of removing ionic impurities from an aqueous solution by a magnetic field using the effect of focusing ions into a paraboloid of rotation with a small flow volume and a high concentration of ionic impurities, which greatly facilitates the spatial distribution of purified and contaminated flows and the effective removal of the flow with impurities from the environment to the tank of purified water.

To achieve the set goal, the following tasks were solved:

1. Investigate on a physical and mathematical model the process of focusing ionic impurities into a paraboloid of rotation under the action of a magnetic field during the purification of a flow of a contaminated aqueous solution.
2. To develop and investigate the principle scheme of the research stand in accordance with the physical–mathematical model of focusing the flow of ionic impurities into a paraboloid of rotation.
3. To justify the mathematical model of the formation of the necessary structure of the magnetic field for focusing the flow of ionic impurities into the paraboloid of rotation and to simulate the process on the created virtual device using the Lab VIEW software environment.
4. To conduct a comprehensive study of the operating parameters of the process of cleaning an aqueous solution from ionic impurities by a structured magnetic field with the combined use of:
   - a physical-mathematical model of the process of focusing ionic impurities into a paraboloid of rotation under the action of a magnetic field;
   - a virtual device using the Lab VIEW software environment;
   - an experimental laboratory stand for researching the possibilities of controlling real trajectories of ion movement under the influence of a magnetic field.

4 Physico-Mathematical Model of Focusing of Ionic Impurities by an Electromagnetic Field in a Liquid Flow

Many substances that get into water are ionized. Therefore, in water we have a mixture of metal ions, acid residues and other substances that for one reason or another must be removed from the solution. A number of technologies using an electromagnetic field have been developed to purify water from ionic impurities.

The Lorentz force acts on a particle of mass m and charge q in a contaminated aqueous solution from the side of the electromagnetic field.

$$\overrightarrow{F} = q\overrightarrow{E} + q(\overrightarrow{V} \times \overrightarrow{B}), \tag{1}$$

where: $\overrightarrow{E}$—electric field strength, $\overrightarrow{B}$—magnetic field induction, $\overrightarrow{V}$—velocity of a particle with a charge q.

The force $\overrightarrow{F} = q \cdot \overrightarrow{E}$ is the force acting on the charge from the side of the electric component of the field, and can have an arbitrary direction relative to the speed of the particle of matter. The work of this electric force can be positive, negative and zero depending on the angle between the direction of velocity $\overrightarrow{V}$ and the intensity of the electric field $\overrightarrow{E}$.

The second force acting on the charged particle is the magnetic force and is directed perpendicular to the velocity of the particle $\overrightarrow{F}m = q(\overrightarrow{V} \times \overrightarrow{\mathrm{B}})$, this force does no work. The magnetic force does not change the kinetic energy of a particle with a charge (q), does not change the velocity module $\left|\overrightarrow{V}\right|$ and only changes the direction of the velocity.

When considering the motion of a particle with mass m and charge q in a magnetic field, the velocity of the particle can be written as the sum of the velocity parallel to the magnetic field $\overrightarrow{V}_{\parallel}$ and perpendicular to it $\overrightarrow{V}_{\perp}$:

$$\overrightarrow{V} = (\overrightarrow{V}_{\parallel} + \overrightarrow{V}_{\perp}). \tag{2}$$

In this case, the Lorentz force acting on the charge of the particle will be equal to:

$$\overrightarrow{F} = e\overrightarrow{V}_{\perp} \cdot \overrightarrow{B}, \tag{3}$$

where e—electron charge.

The component of the Lorentz forces along the magnetic field is zero. Then the equations of motion for the parallel and perpendicular components of velocity have the form:

$$m(d\overrightarrow{V}_{\parallel}/dt) = 0; \tag{4}$$

$$m(d\overrightarrow{V}_{\perp}/dt) = e\overrightarrow{V}_{\perp} \times \overrightarrow{B}. \tag{5}$$

The modules of the vectors $\overrightarrow{V}_{\perp}$ and $\overrightarrow{B}$ do not change. The force in the right-hand side of expression (5) is perpendicular to the velocity and is constant in magnitude. This equation describes the motion of a particle with a constant acceleration directed all the time perpendicular to the velocity, i.e., we have motion in a circle. The left part of Eq. (5) is the product of the mass by the centripetal acceleration $\overrightarrow{V}_{\perp}/$ r, so it can be written:

$$mv^2/r = |q|/(v_{\perp} \cdot B), \tag{6}$$

where r—radius of the circle.

This equation fully characterizes the movement of a charged particle in a circle in a plane that is perpendicular to a uniform magnetic field. The direction of rotation depends on the sign of the charge q and is set by the rules of left or right screws.

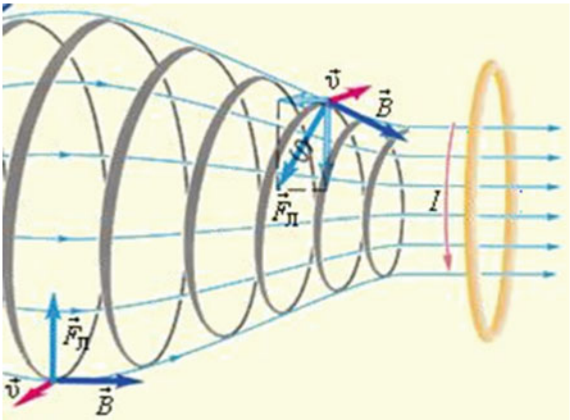
From Eq. (6), we can find expressions for the angular frequency of rotation in a circle

$$\omega = v_{\perp}/r = \left|\overrightarrow{q}\right|B/m, \tag{7}$$

as well as for the radius of the orbit

$$r = v_{\perp}/\omega = mv_{\perp}/|q|B. \tag{8}$$

Fig. 1 Lorentz force generation by a current-carrying coil



The complete movement of a charged particle of a contaminated substance in a homogeneous, constant magnetic field consists of uniform movement along the field and rotation in a plane perpendicular to the field. That is, the particle moves in a spiral with a step:

$$l = v_{\parallel} \cdot 2\pi/\omega. \tag{9}$$

Consider a magnetic field whose induction lines are parallel to each other, and the magnitude of the field varies in the direction perpendicular to the field (Fig. 1). If the field is uniform, then the charged particle moves in a circle [17]. However, taking into account the heterogeneity of the field, the radius of curvature of the trajectory changes during movement: where the field is larger, the radius is smaller and vice versa. That is, in fact, the particle behaves as in a transverse electromagnetic field, but the radius of curvature of the trajectory changes not due to energy, but due to the magnitude of the magnetic field in different points of space.

In this case, particle drift occurs due to the inhomogeneity of the magnetic field in a direction that is perpendicular both to the magnetic field itself and to the direction in which the magnetic field is inhomogeneous.

The system of equations in this case has the form:

$$m\left(\frac{d^2x}{dt^2}\right) = 0; \tag{10}$$

$$m\left(\frac{d^2y}{dt^2}\right) = qv_zB; \tag{11}$$

$$m\left(\frac{d^2z}{dt^2}\right) = -qv_\mathrm{y}B. \tag{12}$$

The analysis and solution of this system of equations, taking into account the fact that v_y is much smaller than v_z under appropriate initial conditions, showed that Eq. (11) for the y coordinate can be written in the form:

$$\frac{d^2y}{dz^2} = \frac{q}{mv}B(\mathrm{z}), \tag{13}$$

that is, taking into account the change in magnetic induction in the direction of the (Z) coordinate, the solution of Eq. (13) has the form:

$$y = \left[\frac{q}{mv}\right]b, \tag{14}$$

where $b = \int_0^{z_0}(Z_0 - \eta)\mathrm{B}(\eta)d_\eta$ is a constant that depends on the configuration of the electromagnetic field and is found by calculation or experimentally (η) is the integration variable.

The exact analytical solution of this problem is rather complicated, so the drift speed can be set with some approximation [2] in the form:

$$v_d = \left(\frac{mv^2}{qB^2}\right) \cdot \frac{dB}{dy}. \tag{15}$$

In this case, the drift is perpendicular to the magnetic induction vector $\overrightarrow{B}$ and to the direction of maximum change of the magnetic induction module. In vector form, Eq. (15) has the form:

$$v_d = mv^2/2qB^2[[\overrightarrow{b} \times grad\left|\overrightarrow{B}\right|] \tag{16}$$

where $\overrightarrow{b} = \overrightarrow{B}$/B—unit vector along the magnetic field; grad $\left|\overrightarrow{B}\right|$—vector which is directed to the maximum growth of the modulus of the vector $\overrightarrow{B}$

In nature, in general, the induction lines of a non-uniform magnetic field are not straight. They are curved lines, at each point of which it is possible to indicate their curvature. At the same time, the charged particle rotates around the conducting center, which is located on the line and moves along it. The trajectory of the particle. There is a spiral that winds up on the line of magnetic induction. In the coordinate system associated with the conducting center, the particle is acted upon by the centrifugal force of inertia $\overrightarrow{F}_{cf}$, equivalent to the action of the electric field with the intensity $\overrightarrow{E}_{cf} = \overrightarrow{F}_{cf}/q$. Thus, the particle moves under conditions equivalent to a transverse electromagnetic field. The particle will drift in a direction perpendicular to both the magnetic induction $\overrightarrow{B}$ of the field and the force $\overrightarrow{F}_{cf}$ perpendicular to the plane. In this case, the movement in a circle relative to the center is carried out with the drift speed $\overrightarrow{V}_d$. To find it, you need to write down the equation of motion:

$$m\left(\frac{d\overrightarrow{V}}{dt}\right) = q\overrightarrow{E} + q\overrightarrow{V} \times \overrightarrow{B}, \tag{17}$$

and find its solution in the form [1],

$$v_d = B^{-2}(\overrightarrow{E}_{cf} \times \overrightarrow{B}) = E_{cf}/B, \tag{18}$$

or the expression for the drift speed caused by the curvature of the magnetic force line in the form:

$$v_d = mv_{\|}^2/qBR, \tag{19}$$

where $v_{\|}$—projection of the particle velocity onto the direction of the magnetic field.

For the general picture, this drift is added to the drift associated with the inhomogeneity of the magnetic field (16).

The conducted analysis showed that the movement of a charged particle with mass m and charge q has three components:

- rotation of the particle around the line of force of the magnetic field;
- movement of the conducting center along the magnetic line of force;
- the drift of the conducting center in the direction perpendicular to the vector $\overrightarrow{B}$ of the magnetic field and the gradient of the magnetic induction module.

To further clarify the geometric, kinematic, force and energy parameters of the focusing volume of ionic impurities, it is necessary to introduce the concept of magnetic moment into the analysis. In many practical cases, the magnetic field changes little over a distance of the order of the radius of the trajectory of the charged particle. By analogy with the magnetic orbital moment of elementary particles, we can talk about the magnetic moment of a macro particle moving in a magnetic field. The feasibility of introducing such a concept makes sense in the fact that in slowly changing magnetic fields this magnetic moment retains its value and its use greatly simplifies the analysis of the movement of a charged particle under the action of a magnetic field. In this case, the magnetic moment of the charged particle during circular motion along the trajectory will be written in the form:

$$p_m = SI, \tag{20}$$

where S—the area covered by the electric current; I $=\frac{\overrightarrow{q}}{T}$—electric circuit current; T is the period of rotation along a circular path.

Taking into account the size and shape of the movement trajectory, we obtain:

$$p_m = \left(\frac{\overrightarrow{q}}{\mathrm{T}}\right)\pi R^2 = \frac{1}{2}mv^2/B. \tag{21}$$

When introducing the concept of magnetic moment during the movement of a charged particle under the action of an electromagnetic field, it is also appropriate to introduce the concept of an adiabatic invariant of magnetic moment. Adiabatic invariance of the magnetic moment means its conservation in electromagnetic fields that change slowly in space or time. It is shown [3] that when the magnetic field changes in time $dp_m/dt = 0$, then the magnetic moment also does not change, $p_m = const$ [3].

Thus, we assume that the magnetic moment p_m (19) does not change during the movement of a charged particle in the case of slow changes in the electromagnetic field in space and time.

And this, in turn, means that charged particles move along the surface of a magnetic tube, that is, a tube whose surface is created by lines of force of magnetic induction. This statement follows from the fact that the magnetic flux through the cross-section of the tube does not change along it. Then the magnetic flux through the cross section of the tube can be written as:

$$\phi = \pi R^2 B = \frac{2\overrightarrow{V}m}{q^e} \cdot p_m = const \cdot p_m. \tag{22}$$

It can be seen from this expression that the preservation of the magnetic flux along the magnetic tube is equivalent to the preservation of the magnetic moment of a particle that moves along a trajectory located on the surface of the tube, that is, it is really seen that the particle moves along the surface of the power tube.

To fully characterize the movement of a particle, it is necessary to take into account its drift (16) and (19). As a result of its drift, the particle moves from one power tube to another in such a way that the magnetic flux contained in these tubes is the same.

5 Mathematical Model of the Formation of the Structure of the Electromagnetic Field to Control the Trajectory of the Movement of Ionic Impurities in the Volume of the Working Chamber

Given that charged particles move in a hydraulic flow under the action of a non-uniform magnetic field along the surface of a magnetic tube, which is created in three-dimensional space by the lines of force of magnetic induction $\overrightarrow{B}$, for the mathematical description of this surface a conical helical surface is chosen, which, in accordance with the physics of the process, allows to simulate the movement charge q with mass m in the three-dimensional space of the working magnetic chamber.

In this regard, the Ulysses Dini equation [17] was used to describe the ion focusing process.

$$x = a \cdot \cos(u) \cdot \sin(v);$$

$$y = a \cdot \sin(\mathrm{u}) \cdot \sin(\mathrm{v}); \tag{23}$$

$$z = b \cdot u + a \cdot \left(\cos(v) + \log\left(\tan\left(\frac{v}{2}\right)\right)\right).$$

The range of changing the parameters of the equation: $0 < = \mathrm{u} < = 4\pi$; $0.01 < = \mathrm{v} < = 1$; $\mathrm{a} = 1, \mathrm{b} = 0.2$

In the general conical form, this equation has the form:

$$\frac{(x - x_0)^2}{a^2} + \frac{(y - y_0)^2}{b^2} - \frac{(z - z_0)^2}{c^2} = 0, \tag{24}$$

where the constants *a* and *c* are determined by the ratios *c*/*a*.

Thus, the lateral surface of a right circular cone (conical surface) is a second-order surface. The transition of the particle trajectory due to drift from one surface of the magnetic field to another is taken into account. In parametric notation, it has the form of a conical helix:

$$X = C \cdot e^{mt} \cos t;$$

$$Y = C \cdot e^{mt} \sin t; \tag{25}$$

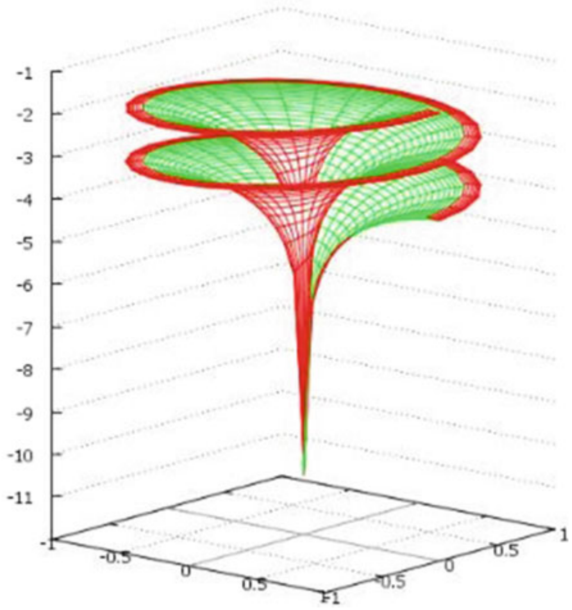
$$Z = C \cdot e^{mt} \mathrm{ctg}\alpha,$$

where t—arc length of the curved trajectory; α—angle between the axis of the cone and its origin; φ—angle between the tangent to the helical line and the generating cone; *m*—sin α/tg φ.

A virtual device has been developed to simulate the focusing modes of impurities polluting the fluid flow. The simulation results confirm the shape and dimensions of the conical helix of the charged particle trajectory in an inhomogeneous magnetic field of the corresponding configuration. The projection of a conical helix on a plane perpendicular to the axis of the cone is a logarithmic spiral with a pole in the projection of the cone apex (Fig. 2) [17].

The simulation results confirm the shape and dimensions of the conical helical line of the trajectory of the charged particle in a non-uniform magnetic field of the corresponding configuration.

Fig. 2 Ulysses Dini cone surface model



6 Laboratory Stand for Cleaning an Aqueous Solution with a Non-uniform Magnetic Field Using the Effect of Focusing Ionic Impurities

The hydraulic scheme of the stand for electromagnetic focusing of liquid contamination (Fig. 3) has a tank 1 of contaminated liquid, an initial pipeline with a coarse filter 2. The filter used is an Irritec disc filter with a connection diameter of 1 inch.

Pump 3 JEX500 has electrical power from a two-phase motor with a voltage of 220 V and a frequency of 50 Hz. The working fluid through the hydraulic line through the tee is directed into the line with the safety valve 4. In the event of excess pressure in the hydraulic system of the stand, thanks to the safety valve 4, there will be no emergency pressure increase in the system due to the pumping of part of the working fluid back to the tank 1.

Further, the working fluid through the working condition regulator 5 is directed to the focus input of the working chamber 6 of impurities (WCF). Several (from 2 to 4) “snail” inlet channels are placed at the entrance of the WCF for the initial mechanical spiral twisting of the contaminated liquid. On the outer wall of the WCF, several coils are placed in series with an interval of 7. Moreover, each subsequent coil has a larger number of turns of wire (n1….n5), which provides a Larmor which ensures the Larmor precession of the movement of impurity particles, an increase in electromagnetic induction and a decrease in the radius of rotation of pollution particles.

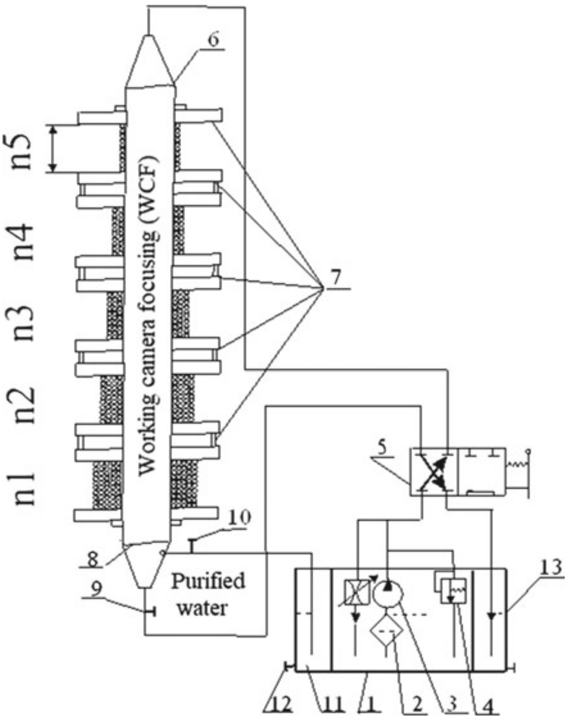


Fig. 3 Scheme of the stand for electromagnetic focusing of liquid contaminants

Thus, in the WCF, under the action of the Lorentz force in a magnetic field, impurities are focused around the WCF axis into a paraboloid of spiral rotation. Its top is directed to the central hole of the insert. To remove impurities from the WCF, a special insert is installed in its final part (Fig. 4).

Insert 8 (Fig. 4) in the end part of the WCF for separating the liquid flow has one central hole 1 to remove impurities from the contamination of the liquid flow, through the sampling valve 9, into the tank 13 of the liquid with impurities and, for

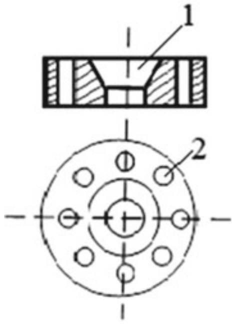


Fig. 4 Insert 8 at the end of the WCF to remove focused impurities from the fluid flow: 1—central hole for removing contaminants; 2—holes for removing the purified liquid

example, 8 peripheral holes 2 to remove the purified liquids. liquid, through the valve 12 sampling, into the tank 11—purified liquid.

7 Research Program and Results

For planning and conducting the research, the ranges of changes of the main factors are established, by changing which it is possible to regulate the process of ion focusing both in space and in time (Table 1).

The main parameter of the focusing magnetic system, as well as the entire installation as a whole, is the value of the magnetic induction $\overrightarrow{B}$ and the structure of the magnetic field. From a constructive point of view, the main geometric parameter is the Larmor parameter the radius of the particle trajectory in the magnetic field:

$$R = mU_{\perp}l/(|q|\mu_0\mu In), \tag{26}$$

where m—mass of the charged particle; q—particle charge; $U_{\perp}$—velocity of the particle perpendicular to the magnetic field lines; l—length of the focusing coil; μ_0—magnetic constant; μ—magnetic permeability; I—current of the magnetization loop; n—number of coil turns.

It is possible to regulate the cleaning process by changing three parameters: the rate of the fraction $V_{\perp}$; magnetizing circuit current I; the total length of the focus coils l. This is done by regulating the current I (Fig. 5), while changing the magnetic induction B, within the established limits (Table 2).

The magnetic field can be changed due to the total length of the magnetization coils l (Fig. 6), as well as by changing the number of turns n of the wire on the WCF coils.

Checking the results of modeling the trajectories of charged particles in an aqueous solution on a laboratory bench confirmed the possibility of using a method for cleaning a polluted water flow from ionic impurities magnetic field using the focusing effect (Table 2).

Such a dual approach in modeling the process of focusing of ionic impurities in a stream of polluted water under the action of a non-uniform magnetic field, as well as experiments conducted on a laboratory bench, allow:

Table 1 Factor regulation ranges

Factor	Levels			Variation interval
	Lower	Average	Upper	
Q—fluid flow, × 10^{-2}, м^3/sec	1.40	2.75	4.10	1.35
$\overrightarrow{B}$—magnetic field induction, × 10^{-5}, T_l	2.244	4.488	6.732	2.244
Number of coils	1	2	3	1

Fig. 5 Influence of the magnetization current on the Larmor radius: **a**—idle mode; **b**—mode of operation

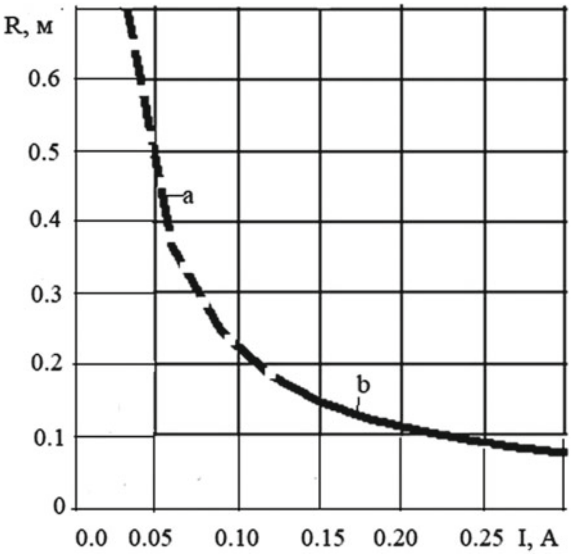


Table 2 Maximum and minimum focusing radii of ions at a current in the focusing coils of 1.0 A and 8.0 A, respectively

Pollutants ion impurities	Coil current, I_{min}, A	Radius larmor, R_{max}, m	Coil current, I_{max}, A	Radius larmor, R_{min}, m
Anions				
Sulfate, SO_4^2	1	0.0978	8	0.0123
Hydrocarbonate, HCO_3	1	0.0318	8	0.0048
Chloride, Cl	1	0.0221	8	0.0028
Cations				
Iron, Fe^{3+}	1	0.0348	8	0.0044
Calcium, Ca^{2+}	1	0.0255	8	0.0032
Potassium, K^+	1	0.0224	8	0.0030
Magnesium, Mg^{2+}	1	0.0152	8	0.0019
Sodium, Na^+	1	0.0143	8	0.0018
Ammonium, NH_4^+	1	0.0109	8	0.0014

- to confirm the shape of the trajectory of ion movement in a magnetic field, which is adequately modeled by a curvilinear conical surface using the equation Ulissa Dani;
- to establish a connection between the parameters of the trajectory of the ions during focusing with the working dimensions of the magnetic chamber and the experimental laboratory stand;

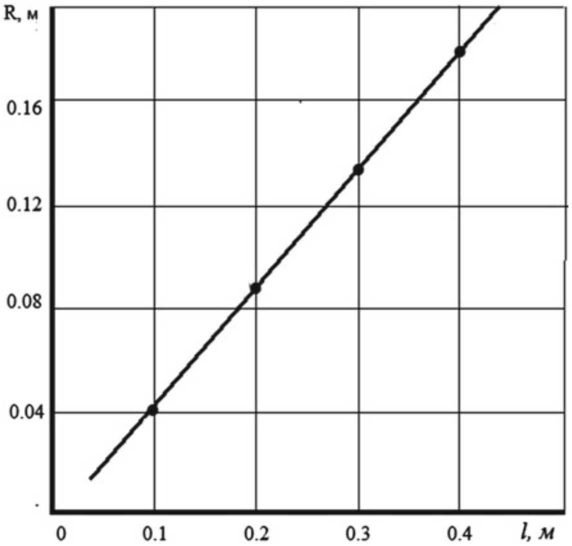


Fig. 6 Dependence of the radius (R) of impurities on the length of the focusing coils

– to set the parameters of the focusing process, which allow you to control its course both in the three-dimensional space of the working magnetic camera and in time.

8 Discussion of the Results of the Study of the Effect of a Non-uniform Magnetic Field on the Purification of an Aqueous Solution Using the Effect of Focusing by Ionic Impurities

The study of the process of interaction of pollution ions with a magnetic field using a physical and mathematical model basically confirmed the idea of the possibility of focusing ionic impurities in a water stream under the influence of a non-uniform magnetic field. The relationship between the intensity of the magnetic field and the geometric and kinematic constructive ones is established parameters of the magnetic camera.

Model laboratory stand using a virtual environment allowed us to choose a conical spiral line according to the Ulysses Dini equation as the trajectory of the movement of a charged particle in a water stream under the influence of a non-uniform magnetic field, as a three-dimensional geographical image of the particle's movement in space. When modeling the process of cleaning the water flow using the LabVIEW package, the mass of particles, their charges, speed, as well as the hydrodynamic resistance of the liquid and the design features of the magnetic coils, which are associated with giving the field the necessary structure, are taken into account.

This approach greatly simplified both the development of the hydraulic scheme of the stand (Fig. 3) and the design and manufacture of the research laboratory stand.

In accordance with the developed methodology and research program, the laws of the effect on charged impurities in the water flow of a non-uniform magnetic field were established on the laboratory bench, which led to the focusing of ions in the volume of the paraboloid of rotation. and the formation of an internal flow with a high concentration of impurities and reduced to a given cross section of the Larmor radius.

It was established that the process of formation of an internal axial flow with a high concentration of impurities should be regulated by changing three parameters:

- total length l of magnetic coils (due to the length of each coil l_i and the number of turns of wire on each coil ni);
- velocity of charged particles $V_\perp$ in the flow of polluted water (due to regulation of the total flow of liquid through the working focusing chamber);
- the magnitude of the magnetic induction $\overrightarrow{B}$ along the trajectory of the particle in space (due to the change in the current I in the working focusing coils).

It was established that the size of the Larmor radius R at the beginning of the trajectory is mainly influenced by the value of the current I (and through it the value of the initial magnetic induction $\overrightarrow{B}1$ and the size of the internal flux R_2 at the exit from the magnetic coils is significantly influenced by the value of the magnetic field itself $\overrightarrow{B}2$ so and its gradient $\frac{\partial B2}{\partial y}$.

The obtained dependence of the Larmor radius on the current of the magnetic coils $R = f(I)$, (Fig. 5). It was found that for current values $I < 0.125$ A, the focusing mode is not set. The operating mode starts at a current of $I \geq 0.25$ A, which corresponds to a trajectory with a radius of curvature $R \leq 0.075$ m.

Thus, it is confirmed that the effective influence on the trajectory of the movement of impurities is possible not only due to an increase in the magnitude of the magnetic induction field $\overrightarrow{B}$, but also due to the gradient of the field in the axial direction in accordance with expression (16) when changing the number of turns n and the total length of the magnetic coils l (Fig. 6).

In general, at a given maximum concentration of impurities in the purified stream, the most effective purification mode is established with simultaneous adjustment of at least three parameters (I, $U_\perp$, l) both with manual and automated control.

9 Conclusions

1. The proven idea of using the effect of focusing by an inhomogeneous magnetic field of ionic impurities in a stream of polluted water is based on the fundamental laws of Ampere, Lorentz, and Larmor. The essence of the idea is the ability to realize the trajectory of the movement of ionic impurities in the liquid flow with a non-uniform magnetic field due to a purposeful dynamic change in its structure.

2. The process of focusing charged particles by a non-uniform magnetic field using an analytical physical–mathematical model of the field, the constructive shape and dimensions of the magnetic chamber is substantiated dimensions and working focusing camera.
3. Simulation modeling of the magnetic field using a working impurity focusing camera and a trajectory model in virtual space confirmed the previous results of analytical modeling and made it possible to specify the shape and parameters of the impurity trajectory using the Ulysses Dini equation, as a three-dimensional geometric representation of the trajectory in the form of a conical spiral line. Based on the simulation results, a hydraulic scheme of the cleaning system and a schematic diagram of the experimental laboratory stand were developed.
4. The development and use of an experimental laboratory stand made it possible to confirm in practice the possibility of regulating the real trajectory of the movement of charged particles in a water stream under the action of a non-uniform magnetic field and to make the necessary corrections in the mathematical models of the liquid purification process.
5. The conducted set of theoretical and experimental studies showed the reality and effectiveness of the method of cleaning a polluted water flow with a non-uniform magnetic field using the effect of focusing ionic impurities with their subsequent removal from the cleaned flow.

References

1. Abbas, A.H.A., Jingsong, G., Ping, L.Z., Ya, P.Y., Al-Rekabi, W.S.: Review on land leachate treatments. Am. J. Appl. Sci. **6**(4), 672–684 (2009)
2. Jiang, W., et al.: A pilot study of an electromagnetic field for control of reverse osmosis membrane fouling and scaling during brackish groundwater desalination. Water **11**, 1015 (2019)
3. Shamanskyi, S., Boichenko, S., Pavliukh, L.: Estimated efficiency of biogenic elements removal from waste water in the ideal displacement photobioreactor. In: Zaporozhets, A., Artemchuk, V. (eds.) Systems, Decision and Control in Energy II. Studies in Systems, Decision and Control, vol. 346. Springer, Cham (2021). https://doi.org/10.1007/978-3-030-69189-9_21
4. Karkush, M.O., Ahmed, M.D., Al-Ani, S.M.: Effects of magnetic fields on the properties of water treated by reversed osmosis. Preprint (2019)
5. Han, Y., et al.: Effect of alternating electromagnetic field and ultrasonic on $CaCO_3$ scale inhibitory performance of EDTMPS. J. Taiwan Inst. Chem. Eng. **99**, 104–112 (2019)
6. Han, Y., et al.: Influence of alternating electromagnetic field and ultrasonic on calcium carbonate crystallization in the presence of magnesium ions. J. Cryst. Growth **499**, 67–76 (2018)
7. Al Helal, A., Soames, A., Gubner, R., Iglauer, S., Barifcani, A.: Influence of magnetic fields on calcium carbonate scaling in aqueous solutions at 150 °C and 1 bar. J. Colloid Interf. Sci. **509**, 472–484 (2018)
8. Selvaganesa Pandian, S., Amuthan, A.: Effect of soaking of phyllanthus embolica wood in drinking-water for purification. Int. J. Pharmacol. Clin. Sci. **1**(1), 19–27 (2012)
9. Ambashta, R.D., Sillanpää, M.: Water purification using magnetic assistance. J. Hazard. Mater. **180**(1–3), 38–49 (2010)
10. Sun, J., et al.: Performance and mechanisms of ultrafiltration membrane fouling mitigation by coupling coagulation and applied electric field in a novel electrocoagulation membrane reactor. Environ. Sci. Technol. **51**, 8544–8551 (2017)

11. Tselischev, O.B., Kudryavtsev, S.O., Loriya, M.G., Leonenko, S.V., Tselishcheva, M.A.: Modification of motor gasoline with bioethanol in the cavitation field. Voprosy Khimii i Khimicheskoi Tekhnologii **6**, 171–178 (2020)
12. Piyadasa, C., et al.: The application of electromagnetic fields to the control of the scaling and biofouling of reverse osmosis membranes—a review. Desalination **418**, 19–34 (2017)
13. Sim, L.N., Gu, J., Coster, H.G.L., Fane, A.G.: Quantitative determination of the electrical properties of RO membranes during fouling and cleaning processes using electrical impedance spectroscopy. Desalination **379**, 126–136 (2016)
14. Tselishchev, A., Loriya, M., Boychenko, S., Kudryavtsev, S., Laneckij, V.: Research of change in fraction composition of vehicle gasoline in the modification of its biodethanol in the cavitation field EUREKA. Phys. Eng. **2020**(5), 12–20 (2020)
15. Hou, D., Zhang, L., Fan, H., Wang, J., Huang, H.: Ultrasonic irradiation control of silica fouling during membrane distillation process. Desalination **386**, 48–57 (2016)
16. Rouina, M., Kariminia, H.-R., Mousavi, S.A., Shahryari, E.: Effect of electromagnetic field on membrane fouling in reverse osmosis process. Desalination **395**, 41–45 (2016)
17. Kudzina, D.V., Kotsar, O.M.: Effectiveness of household wastewater treatment using natural mineral sorbents. Probl. Water Supply, Drain. Hydraul. **27** (2016)
18. Khmelnik, S.I.: The equation of whirlpool. Pap. Indep. Authors **43**(111), 1–15 (2018)
19. Bernn-Vera, F.J., Wang, Y., Olascoaga, M.J., Goni, G.J., Haller, G.: Objective detection of oceanic eddies and the agulhas leakage. J. Phys. Oceanogr. **43**, 1426–1438 (2013)
20. Dini, U.: Sopra un problema che si presenta nella teoria generale delle reppresentazioni geografica di una superficie su un'altra. Ann. di Math., Ser. **2**(3), 269–293 (1869). See also: [arXiv.org/abs/1301.2492 Alexey V. Bolsinov, Vladimir S. Matveev. Local normal forms for geodesically equivalent pseudo-Riemannian metrics]
21. Khizyrov, Y.S.: Tides and low tides are the result of the precession of eddies. Reports of Independent Authors **33** (2015)

Removal of Biogenic Compounds from Sewage Water in a Culture of Euglena Gracilis (EUGLENOPHYTA)

Inna Nezbrytska, Sergii Shamanskyi, Lesia Pavliukh, Zoya Gorbunova, Olena Horbachova, and Viktor Repeta

1 Introduction

It is truism nowadays to recognize that pollution associated problems are a major concern of society. Environmental laws are given general applicability and their enforcement has been increasingly stricter. So, in terms of health, environment and economy, the fight against pollution has become a major issue. Today, although the strategic importance of fresh water is universally recognized more than ever before, and although issues concerning sustainable water management can be found almost in every scientific, social, or political agenda all over the world, water resources seem to face severe quantitative and qualitative threats. The pollution increase, industrialization and rapid economic development, impose severe risks to availability and quality of water resources, in many areas worldwide [1].

A major report by the World Health Organization (WHO) has recently been released, according to which a polluted environment is one of the leading causes of high mortality in the world. According to the organization, almost a quarter of the world's population dies due to poor environmental conditions: environmental risks cause more than 100 of the most dangerous diseases, and every year they kill 12.6 million people, which is 23% of all deaths in the World [2].

I. Nezbrytska · Z. Gorbunova
Institute of Hydrobiology of NAS of Ukraine, Kyiv, Ukraine

S. Shamanskyi (✉)
Kyiv National University of Construction and Architecture, Kyiv, Ukraine
e-mail: shamanskiy_s_i@ukr.net

L. Pavliukh · O. Horbachova · V. Repeta
National Aviation University, Kyiv, Ukraine

S. Boichenko et al. (eds.), *Modern Technologies in Energy and Transport*, Studies in Systems, Decision and Control 510, https://doi.org/10.1007/978-3-031-44351-0_9

2 Analysis of Literature Data and Problem Statement

Water resources of any country are a source of drinking water for the population, and therefore require their rational use and protection from pollution. One of the biggest problems of river pollution is the poor quality of wastewater treatment. In many regions there is no complete set of treatment facilities and sanitary protection zones at all.

Due to the high rate of urban development there is an increase in wastewater. This situation leads to the fact that existing treatment systems become inefficient, and the quality of treated wastewater often does not meet the required standards [3]. Discharge of insufficiently treated wastewater from nutrients into water bodies is one of the most common causes of eutrophication. Aquatic ecosystems respond to nutrient enrichment primarily by the intensive development of cyanobacteria. Their rapid reproduction causes "blooming" of water, which leads to oxygen deficiency and mass death of fish and other aquatic organisms. Favorable conditions are created for the development of pathogenic microflora and pathogens [4]. This problem is especially relevant for small rivers and lakes. "Water blooming", makes impossible to use water for recreation, fishing and domestic needs. The phytoplankton toxins can cause health problems through exposure to the human body after contact with the skin or the use of contaminated water for drinking. Therefore, there is a problem of more efficient wastewater treatment from nutrients because these compounds are removed in low amounts which usually do not exceed 10% [5].

The main goal of this paper is to study the metabolism of Euglena gracilis in relation to nitrogen and phosphorus compounds that enter wastewater due to human activity.

The supply of nutrients to surface waters occurs as due to natural factors (leaching from the layer of soil, precipitation, intra-reservoir processes), and also because of anthropogenic (receipts from industrial and economic domestic wastewater, agricultural land runoff and animal complexes). The most surface water bodies in Ukraine are classified as polluted or much polluted. This condition significantly increases environmental risks. It is the use of water that does not meet quality requirements that causes and spreads many infectious and non-infectious diseases [6]. The consequences of water pollution by nutrients are regularly described in national reports on drinking water quality in Ukraine. Watercourses receive pollution from many different sources, which vary both in strength and volume. As known the main sources of water pollution are: wastewater, farms, oil spills, solid municipal waste, agriculture, atmospheric precipitations etc. The composition of wastewater is a reflection of the life styles and technologies practiced in the producing society. It is a complex mixture of natural organic and inorganic materials as well as man-made compounds. Three quarters of organic carbon in sewage are present as carbohydrates, fats, proteins, amino acids, and volatile acids. The inorganic constituents include large concentrations of sodium, calcium, potassium, magnesium, chlorine, sulphur, phosphate, nitrates, bicarbonate, ammonium salts and heavy metals [7].

Total nitrogen represents the sum of organic and inorganic nitrogen compounds. For wastewater Kjeldahl-nitrogen is generally applied as a measure. The Total Kjeldahl Nitrogen value (TKN) represents a total nitrogen concentration, which is the sum of organic nitrogen compounds and ammonium nitrogen ($TKN = org–N + NH^{4-}N$ [mg/L]). Nitrogen mainly occurs in wastewater in this form. After biological wastewater treatment, it mainly occurs as oxidized nitrite [8].

Municipal wastewaters may contain from 5 to 20 mg/L of total phosphorous, of which 1–5 mg/l is organic and the rest in inorganic. The individual contribution tends to increase, because phosphorous is one of the main constituent of synthetic detergents. The individual phosphorous contribution varies between 0.65 and 4.80 g/inhabitant per day with an average of about 2.18 g. The usual forms of phosphorous found in aqueous solutions include:

- Orthophosphates: available for biological metabolism without further breakdown.
- Polyphosphates: molecules with 2 or more phosphorous atoms, oxygen and in some cases hydrogen atoms combine in a complex molecule. Usually polyphosphates undergo hydrolysis and revert to the orthophosphate forms. This process is usually quite slow.

Normally secondary treatment can only remove 1–2 mg/L, so a large excess of phosphorous is discharged in the final effluent, causing eutrophication in surface waters. New legislation requires a maximum concentration of P discharges into sensitive water of 2 mg/L [9]. Figure 1 demonstrates phosphorous compounds presented in wastewater.

Diehard wastewater engineers understand the value of wastewater, which they view as an asset rather than a waste. That's why some of them call it "used water" instead, and refer to what most people call wastewater treatment plants as water resource recovery facilities.

In fact, wastewater can contain more than three times the amount of energy needed to treat it. One simple and mature technique for recovering part of this energy is anaerobic digestion, a natural process in which microorganisms feed on grease and other organic materials in wastewater and produce biogas, just as yeast can eat up barley and spit out beer. Biogas contains roughly 50% methane, which can be used as a renewable fuel for boilers, furnaces and heating systems or to turn turbines and generate electricity [10].

More advanced techniques, such as hydrothermal processes, take sewage sludge—the solids removed from wastewater during treatment—and convert it into biobased

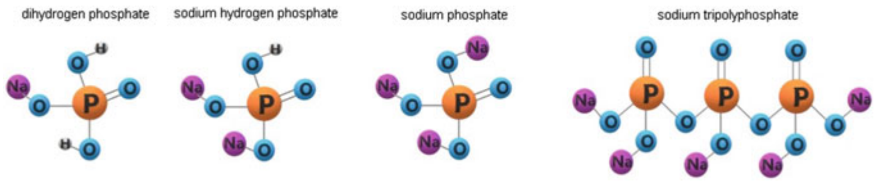

dihydrogen phosphate sodium hydrogen phosphate sodium phosphate sodium tripolyphosphate

Fig. 1 The main phosphate compounds in wastewater fuels that can be used to replace gasoline and diesel fuel. This process is currently at the demonstration stage.

In additional to sewage sludge, many researchers—including us—are very interested in microalgae. Microalgae are promising feedstock for biofuels, and some of them can grow in wastewater.

Researches of scientists in many countries of the world are focused on the problems of wastewater treatment. There are many methods and technologies to purify waste water. Biological wastewater treatment, with application of microalgae, originating from a variety of industries has been regarded as an economically and technologically justified process.

Microalgae constitute a diversified group of eukaryotic photosynthetic microorganisms which colonize both the marine and freshwater environments. Microalgae are among the fastest developing photosynthetic organisms. Their photosynthetic mechanism is similar to that of terrestrial plants. Microalgae do not compete for cultivated land. With access to water, carbon dioxide and biogenic compounds such as nitrogen and phosphorus, offer higher biomass yields than terrestrial plants. Algae have the ability to produce 50 times more biomass than higher plants [11, 12]. Different varieties of algae are able to develop in a wide variety of environments, even in degraded or contaminated areas [13]. Such cultures bring a positive effect to the natural environment because algae may be produced using communal, agricultural or industrial waste-water containing carbon dioxide which is required for their growth CO_2 [14]. The molar ratio of the algae biomass main components proposed by Grobbelaar [15] is as follows: CO–0.48; H–1.83; N–0.11; P–0.01. In the course of microalgae population development, four following phases can be distinguished: adaptation phase, growth phase, stationary phase and decline phase [16, 17]. The importance and interest in algae has been increasing with time.

Thus, the scientists from Uttaranchal University (India), have developed a method for purifying wastewater using microalgae and successfully tested it on the waters of the Indian Bindal River [18]. As part of the first phase of the experiment, scientists used several tens of liters of contaminated water by placing microalgae in it. The result was a significant reduction in total bacteria and E. coli (by 90%), organic and inorganic compounds (by 90%) and total organic carbon, as well as a decrease in alkalinity and water hardness (by 70%). The content of heavy metals in water also significantly decreased: for example, the content of zinc, lead, copper, iron, nickel and other metals decreased by about 90%. Biodiesel was obtained from algal biomass used to purify polluted water.

It is not the first year that there have been discussions around the topic of banning the use of phosphates in detergents. And at a time when the countries of the world legally limited or completely banned the use of phosphates in detergents back in the 80s and 90s of the last century, outdated technical regulations continue to operate in Ukraine.

But so far we have disappointing statistics regarding phosphate discharges into surface water bodies with wastewater. For example, the analysis of data from the state water use accounting for 2019 shows that last year almost 6 thousand tons of phosphates were dumped into the water bodies of Ukraine. The largest polluter of water bodies is the housing and communal economy—5354 tons [19].

In order to solve this global world problem, in the 1970s, under the auspices of the UN, an international agreement on the protection of the world's oceans and freshwater resources was concluded. It defines the main areas of activity to reduce pollution. And the first of them is the reduction and complete cessation of pollution of water resources by biogenic substances, especially phosphorus. However, experiments conducted in some countries have shown that phosphate fertilizers are slow-moving compounds and remain in the soil for up to 5–8 years. The share of contamination of water bodies with mineral phosphate fertilizers is from 10 to 30% of the total input of phosphorus. More than 60% of phosphates enter water bodies due to the use of phosphate washing powders.

In the early 1970s, some US states began to restrict and ban the use of phosphates in laundry detergents. In 1994, they were banned throughout the country. In July 2010, 17 states also banned the use of phosphates in dishwasher detergents. In 1976, the use of phosphates in washing powders was stopped in Japan. In 2011, the European Parliament banned phosphates in laundry detergents from June 2013 and in dishwasher detergents from January 2017. Manufacturers of washing powders began to replace phosphates with substances that are biodegradable. At the same time, in many countries of the world, the construction of special treatment facilities for the removal of phosphorus and nitrogen from wastewater began. As scientists explain, the optimal concentration of phosphates in washing powder should not exceed five percent. In this case, the use of detergent is not harmful to humans. Moreover, at such a concentration, phosphates are completely rinsed from the fabric with water [20].

After washing with dirty water, tripolyphosphate directly enters the soil, and from there into rivers and lakes. Its quantity accumulates, and then it begins to act as a fertilizer. That is, the water system of rivers and lakes is being increasingly fed with harmful discharges from cities and industrial waste. Such feeding of water first causes rapid flowering, and then the inevitable aging of the reservoir. In places where the dangerous substance accumulates on the surface of the water, a "harvest" of blue-green algae is observed, which has the ability to reproduce with terrible force: 1 g of sodium tripolyphosphate stimulates the formation of 5–10 kg of algae, which, when decomposed, poison water and fish. More than 220.000 tons of washing powders are sold in Ukraine every year, most of which contain sodium tripolyphosphate. Thus, more than 25 thousand tons of this dangerous compound are dumped into the water, which can lead to a large-scale environmental disaster. Phosphates are not only produced by algae. Plankton is also actively growing. And the more any kind of suspension is in the water, the less opportunity there is to use rivers and reservoirs as sources of drinking water. But since we have no other water, we have to use this poisoned water. The circle closed. We began to poison the environment in which we live with phosphates—we get back through food and drink all that we poisoned ourselves. An excess of phosphorus initiates the following chain: rapid growth of plants—death of plants—decay—impoverishment of water bodies with oxygen—deterioration of the life of organisms [21].

There is a hypothesis that the main supplier of phosphates into the environment is the use of household chemicals. Studies of leading brands of detergents have shown that the vast majority of them contain a large amount of phosphates. We present the research data in Table 1.

An excessive number of microorganisms poisons the water with waste products, higher animals (fish, crayfish, etc.) begin to die due to a lack of oxygen in the water. In addition, blue-green algae not only reduce the level of oxygen in the water but also accumulate toxic substances. When they decompose, these accumulations enter the environment.

Together with water, phosphates enter the human body. A person comes into contact with all the toxic components of washing powders through the skin because it is almost impossible to rinse them from linen and clothes.

Phosphates contribute to increased degreasing of the skin, active destruction of cell membranes, sharply reduce the barrier function of the skin, and can also cause manifestations of various types of allergic reactions.

An excess of sodium phosphate can be perceived by the body as a laxative, and an excess of potassium phosphate can cause a disturbance of the intestinal microflora. In addition, phosphates can lead to the development of allergies, negatively affect the work of the kidneys and liver [23].

The association 'Ukrvodokanalekologia' has submitted a petition to the President of Ukraine to submit to the Verkhovna Rada for consideration a draft law on a complete ban on the production, import, sale and use of phosphate-containing detergents in Ukraine. Phosphates entering water bodies due to the use of synthetic detergents are one of the main sources of their pollution and the development of such negative processes as water bloom (eutrophication).

According to the data of the state record of water use, in the last four years, the total content of phosphates in waste water of water supply and sewerage and, to a lesser extent, other enterprises of the Mykolaiv region has increased 3 times.

As stated in the petition, the problem of removing phosphorus compounds from wastewater does not have an optimal solution. Since the existing biological methods do not allow to achieve the necessary degree of purification of waste water from phosphorus compounds, and physical and chemical methods require significant costs and additionally create the problem of the need to treat sediments formed during reagent treatment.

Table 1 Content of PO_4^{3-} in powders [22]

The name of the powder	Optical density	Content of PO_4^{3-} (mg/100 g of powder)	Phosphate content (mg/L of water at laundry)
Persil	0.3	387	34
Tide	0.29	374	32.9
Ariel	0.29	374	32.9
Gala	0.19	245	21.56
Amway	0.15	193	16.99

Most of the world's countries have long since abandoned the use of phosphate-based detergents in order not to pollute their water bodies with them. The European Union has adopted a number of legislative acts on reducing the negative impact of detergents on human health and the environment [24].

Foam separation, chemical precipitation in the form of sparingly soluble compounds and destructive destruction are used to reduce the concentration of surfactants, and ion exchange and sorption are used to further purify water. The processing of information on methods of purification of wastewater from surfactants and phosphates makes it possible to highlight a number of the latest methods of purification.

In recent years, data on the issue of reduction of nitrogen and phosphorus in wastewater discharged into open water. These publications mainly advertise the own developments of private firms, but the theoretical foundations and mechanism of biological processes of nitrification–denitrification and dephosphorization of wastewater remain unresolved. So far, there are no reliable and theoretically sound methods of technological calculations of aeration tanks, which carry out anaerobic and aerobic processes of deep wastewater treatment from nitrogen and phosphorus. Researches of authors [25, 26] indicate that the growth of microhydrogen rates is a superior and effective biological method for purifying waste water from nitrogen and phosphorus. As a matter of fact, micro-hydrophilic growths are used to regulate their metabolism, to reduce their concentration in water [25]. Besides, micro-hydrophilic growth is a byproduct of photosynthesis, which can be used as aerobic bacteria for biological distribution of organic bacteria present in cold waters. The purification of waste water from the microwells is recognized ecologically without baking, and there are no examples of secondary flows, such as the use of an active mule, which requires disposal [1]. Most often for the purification of sewage waters, nitrogen and phosphorus are used to produce green micro-growth, sprouts are representatives of the genus Chlorella, Scenedesmus and Chlamydomonas. Protein, it appears [27].

Scientific references [28] provide many examples of algae-based systems in wastewater treatment used algae cultures of Botryococcus braunii species as the third phase of wastewater treatment in closed systems. Such a technological solution allowed for efficient removal of both nitrogen and phosphorus from communal wastewater discharged from activated sludge reservoirs. The use of wastewater resulted in algae biomass production with a high concentration of carbohydrates. Authors [27] presented data and a detailed description of the application of varied waste-water in Chlorella sp. algae culture. They distinguish three main wastewater sources: communal, agricultural and industrial, containing a wide variety of components. Researchers indicate that nutrients such as nitrogen and phosphorus contained in wastewater may successfully be used as a culture medium for an intensive biomass culture.

Wastewater rich in organic carbon, nitrogen and phosphorus may serve as a convenient source of carbon and nutrients for a year-long microalgae production [29].

Scientific reports indicate that some single-cell microalgae such as Chlorella and Scenedesmus are highly tolerant to wastewater environments and efficiently remove biogenic compounds [30].

It follows from the literature that to deepen the wastewater from nitrogen and phosphorus in existing treatment plants must primarily use biological agents and techniques, rather than chemicals, which greatly impair operating costs and may create additional difficulties with the disposal of sewage sludge.

3 Research Methodology

Strain Euglena gracilis Klebs HPDP-114 was obtained from the collection of microalgae cultures of the Institute of Hydrobiology of the National Academy of Sciences of Ukraine. Euglena are characterized by an elongated cell (15–500 μm [1 μm = 10−6 m], or 0.0006–0.02 inch) with one nucleus, numerous chlorophyll-containing chloroplasts (cell organelles that are the site of photosynthesis), a contractile vacuole (organelle that regulates the cytoplasm), an eyespot, and one or two flagella. Unlike plant cells, Euglena lacks a rigid cellulose wall and has a flexible pellicle (envelope) that allows them to change shape. Though they are photosynthetic, most species can also feed heterotrophically (on other organisms) and absorb food directly through the cell surface via phagocytosis (in which the cell membrane entraps food particles in a vacuole for digestion). Food is often stored as a specialized complex carbohydrate known as paramylon, which enables the organisms to survive in low-light conditions. Euglena reproduces asexually by means of longitudinal cell division, in which they divide down their length, and several species produce dormant cysts that can withstand drying.

The experiments used synthetic domestic wastewater, which was prepared by adding to the culture medium different concentrations of ammonium nitrogen ($N–NH4^+$) and phosphorus phosphates ($P–PO_4{}^{3-}$) (Table 2). NH_4Cl was used as a source of $N–NH^{4+}$, KH_2PO^{4-} as a source of $P–PO_4{}^{3-}$. Algae were kept at a temperature of 24 ± 2 °C and illumination of 3500 lx (with alternating light and dark periods 16:8). The duration of cultivation of Euglena gracilis in wastewater was 7 days. Materials for analysis were selected on 0 and 7 days of the experiment.

The concentration of ammonium nitrogen and phosphorus phosphates in wastewater was investigated by conventional methods in hydrochemistry.

Table 2 Composition of domestic wastewaters

No of the experiment	Concentration, mg L^{-1}	
	$N–NH^{4+}$	$P–PO_4{}^{3-}$
1	30.00 ± 1.12	7.00 ± 0.18
2	50.00 ± 2.25	14.00 ± 0.56
3	90.00 ± 2.68	26.00 ± 0.67

Dry mass of the culture was determined by weight [31, 32]. The algal cell suspension was filtered through a pre-dried and weighed membrane filter (pore diameter 0.45 μm). Filters with precipitated algae were dried in a thermostat at a temperature of 105 °C to constant weight.

Biomass productivity was calculated by the formula:

$$BP = \frac{N - N_0}{T} \quad (1)$$

where N—the dry matter content at the end of cultivation, (mg L^{-1} day^{-1}); N_0—dry matter content at the beginning of cultivation, (mg L^{-1} day^{-1}); T—duration of cultivation (7 days).

The content of chlorophyll a and the sum of carotenoids was determined by extract-spectrophotometric method [31]. For extraction, the algae filter was placed in a porcelain mortar and thoroughly ground with the addition of quartz sand and 90% acetone. The obtained extract was separated by centrifugation during 15 min at 5000 thousand rpm. Spectrophotometry was performed at wavelengths of 664, 647 and 480 nm, corresponding to the maxima of light absorption in 90% acetone, respectively, chlorophyll a, b and carotenoids. Non-specific absorption of the light extract at a wavelength of 750 nm was also measured.

The chlorophyll a content was calculated by the formula [33, 34]:

$$\text{Chlorophylla} = (11.93E644 - 1.93E647) \cdot \frac{V_1}{V_2}, \quad (2)$$

where V_1—extract volume, cm^3; V_2—the volume of the filtered sample, dm^3; E 664 and E 647—experimentally determined the optical densities of the extract at wavelengths 664 and 647 nm.

The total carotenoid content was calculated by the formula [34, 35]:

$$\text{Cartenoids} = 10 \cdot (E480 - 3E750) \cdot \frac{V_1}{V_2} \cdot 1 \quad (3)$$

where V_1—extract volume, cm^3; V_2—the volume of the filtered sample, dm^3; 1—the thickness of the spectrophotometric cell, sm; and E 480 and E 750—optical densities of the extract at wavelengths 480 and 750 nm.

The content of photosynthetic pigments was expressed in terms of dry weight of algae.

All measurements were performed in triplicate. Statistical processing of the results was performed using IBM SPSS Statistics Base v.22.

4 Results and Disscusion

Typical forms of phosphorus in munitipal sewage waters are the next.

- Orthophosphates—salts of phosphoric acids, in particular orthophosphoric acid H_3PO_4, with one phosphorus atom, for example sodium orthophosphate Na_3PO_4. They are simple molecules that are suitable for using in biological metabolism without prior decomposition.
- Polyphosphates—polymethyl phosphates with the general formula $M–O–[P(OM)(O)–O]_n–M$, where M is any metal. Their chains pass between other chemical groups, for example, sodium-3-phosphate $(Na_5P_3O_{10})_n$. They are complex molecules with two or more phosphorus atoms, which before assimilation by organisms require preliminary hydrolysis with decomposition into orthophosphates. It takes a long time;
- Organic phosphates—orthophosphoric acid esters with the general formula $(RO)_nP(O)(OH)_{3\text{-}n}$, where RO is a hydrocarbon radical, for example, methyl phosphate (methylphosphoric acid $(CH_3O)P(O)(OH)_2$).

According to [36], municipal sewage waters can contain from 5 to 20 mg/dm^3 of total phosphorus (in terms of phosphates for PO_4, it is from 15.7 to 62.7 mg/dm^3). Organic compounds make up from 1 to 5 mg/dm^3 (3.1 … 15.7 mg/dm^3) out of it. All the rest are inorganic compounds. The individual contribution of phosphorus to the sewage network from one inhabitant of a residential area is estimated from 0.65 to 4.80 g/day. The average value is 2.18 g/day. This contribution tends to increase due to the increased use of detergents.

According to [37], municipal sewage waters can contain from 4 to 16 mg/dm^3 of total phosphorus (12.5–50.1 g/m^3 of phosphates). According to [38], these waters may contain 10 mg/dm^3 of total phosphorus (31.3 g/m^3 of phosphates).

Secondary (biological) treatment of sewage waters, as a rule, reduces the content of phosphates by 1 … 2 g/m^3. It's not enough.

According to the data from the Bortnytska Aeration Station [39], the content of phosphates in the sewage waters of Kyiv city is 26 g/m^3 at the standard level of 8 g/m^3. That is, there is an excess of more than three times. In terms of total phosphorus, this value can be 8.48 g/m^3. With a phosphorus removal efficiency of 0.2 at traditional sewage treatment plants, its residual concentration in treated sewage waters is 6.78 g/m^3. The plant discharges about 0.6×106 m^3 of treated sewage into the Dnipro river. Under such conditions, 4,068 tons of phosphorus is supplied to the Dnipro with municipal sewage waters. It is known that each gram of phosphate compounds, under the remaining favorable conditions, causes an increase of 5 … 10 kg of cyanobacteria in the water body.

The typical forms of nitrogen in municipal sewage waters are the next.

- Nitrogen nitrites—salts of nitric acid (HNO_2), for example, $NaNO_2$.
- Ammonium nitrogen (general formula NH_4^+).
- Nitrogen nitrates—salts of nitric acid (HNO_3), for example, $2NaNO_3$.
- Nitrogen in organic compounds.

The most toxic among these compounds are nitrites, and the least toxic are nitrates. Ammonium nitrogen occupies an intermediate position.

According to the results of the studies, Euglena gracilis for 7 days almost completely removes ammonium nitrogen and phosphorus phosphates from the studied wastewater (Table 3). It has been shown [25] that the ability of microalgae to remove nitrogen and phosphorus compounds from the aquatic environment is determined primarily by the physiological characteristics of species, including metabolic rate and the need for nutrients to maintain their viability. In the process of bioremediation of microalgae, a large amount of nitrogen and phosphorus is used for the synthesis of proteins, nucleic acids, phospholipids and other important organic compounds.

The growth intensity of Euglena gracilis was assessed by the accumulation of dry mass (Table 4). At concentrations of $N–NH_4^+$ 30 mg L^{-1} and $P–PO_4^{3-}$ 7 mg L^{-1} the increase in biomass was 120 mg L^{-1} day^{-1}, at concentrations of ammonium nitrogen 50–90 mg L^{-1} and phosphorus phosphate 14–26 mg L^{-1} it was 151–156 mg L^{-1} day^{-1}, which indicates a positive dynamics of dry mass accumulation during the experiment. Researches [26] obtained similar results on Euglena sp. During short-term cultivation of this alga in domestic wastewater, 98% removal of $N–NH_4^+$ (initial concentration 25 mg L^{-1}) and 85% removal $P–PO_4^{3-}$ (initial concentration 16 mg L^{-1}) was achieved, the biomass productivity index was 132 mg L^{-1} day^{-1}.

The photosynthetic activity of Euglena gracilis under the conditions of the experiment was evaluated by the change in the content of pigments—chlorophyll and the sum of carotenoids (Table 5). During the cultivation of Euglena gracilis in wastewater with a concentration of $N–NH_4^+$ and $P–PO_4^{3-}$ 30 and 7 mg L^{-1}, respectively, the content of chlorophyll in the biomass doubled. At the concentration of ammonium nitrogen 50–90 mg L^{-1} and phosphorus phosphate 14–26 mg L^{-1} at the end of the experiment, the content of basic photosynthetic was 2.5 times higher than the initial values. A similar trend was observed in the case of carotenoids, their

Table 3 Changes in the concentration of nutrients in wastewater, M ± m, n = 3

No of the experiment	Initial concentration (0 days), mg L^{-1}		Final concentration (7 days), mg L^{-1}	
	$N–NH_4^+$	$P–PO_4^{3-}$	$N–NH_4^+$	$P–PO_4^{3-}$
1	30.00 ± 1.12	7.00 ± 0.18	Traces	Traces
2	50.00 ± 2.25	14.00 ± 0.56	Traces	Traces
3	90.00 ± 2.68	26.00 ± 0.67	0.44 ± 0.01	0.05 ± 0.02

Table 4 Dry weight of Euglena gracilis (mg L^{-1}), M ± m, n = 3

No of the experiment	0 days	7 days
1	70.00 ± 3.56	909.00 ± 32.68
2	70.00 ± 3.56	1127.00 ± 51.25
3	70.00 ± 3.56	1162.00 ± 51.90

Table 5 Changes in the content of photosynthetic pigments in Euglena gracilis, M ± m, n = 3

No of the experiment	Chlorophyll a, mg/g DW		Carotenoids, mg/g DW	
	0 days	7 days	0 days	7 days
1	3.84 ± 0.14	8.12 ± 0.36	0.89 ± 0.03	2.15 ± 0.06
2	3.84 ± 0.14	9.53 ± 0.44	0.89 ± 0.03	2.47 ± 0.11
3	3.84 ± 0.14	9.69 ± 0.60	0.89 ± 0.03	2.53 ± 0.15

content increased more than 2 times, indicating high photosynthetic activity of algae. However, it should be noted that the dry weight changed to a greater extent than the content of photosynthetic pigments. During seven days of cultivation, the dry weight increased 13–16 times. According to [26], an important feature that allows Euglena algae to develop intensively in wastewater is the ability to mixotrophic type of food.

Biomass Euglena gracilis is considered a promising raw material for biofuel production, as it is characterized by a high content of lipids [40]. Cultivation of Euglena gracilis in domestic wastewater can provide not only an environmentally friendly way to extract nutrients from them, but also a cost-effective way to obtain biomass of microalgae for biodiesel production.

5 Conclusions

The efficiency of microalgae application in the processes of contaminated wastewater treatment is analyzed. It is established that the use of microalgae is a reliable and effective biological method of wastewater treatment from nitrogen and phosphorus compounds. It is known that microalgae absorb these substances to maintain their metabolism, thereby reducing their concentration in water. In addition, microalgae produce oxygen as a by-product of photosynthesis that can be used by aerobic bacteria to biodegrade organic pollutants present in wastewater.

Wastewater treatment using microalgae is recognized as environmentally friendly because it does not generate secondary waste, such as spent activated sludge, which requires disposal. Eugene algae is most often used to treat wastewater from nitrogen and phosphorus compounds.

The peculiarities of Euglena gracilis metabolism, which are characterized by resistance to high concentrations of nitrogen and phosphorus, have been studied.

Experimental studies have been performed and the ability of Euglena gracilis to reduce the concentration of nutrients in wastewater has been established. Due to experimental sessions we can conclude that after 7 days ammonium nitrogen and phosphorus phosphates from the studied wastewater was almost completely removed.

It is shown that the ability of microalgae to remove nitrogen and phosphorus compounds from the aquatic environment is determined primarily by the physiological characteristics of the species, in particular the intensity of metabolism and the need for nutrients to maintain their vital functions. In the process of bioremediation of microalgae, a large amount of nitrogen and phosphorus is used for the synthesis of proteins, nucleic acids, phospholipids and other important organic compounds.

It is established that the biomass of Euglena gracilis is considered a promising raw material for biofuel production, as it is characterized by a high content of lipids. Cultivation of Euglena gracilis in domestic wastewater can provide not only an environmentally friendly method of extracting nutrients from them, but also a cost-effective way to obtain biomass of microalgae for biodiesel production.

References

1. Abdel-Raouf, N., Al-Homaidan, A.A., Ibraheem, I.B.M.: Microalgae and wastewater treatment. Saudi J. Biol. Sci. **19**(3), 257–275 (2012). https://doi.org/10.1016/j.sjbs.2012.04.005
2. 2016. https://www.unian.ua/ecology/1304769-vbivcha-priroda-yak-zabrudnennya-navkolishnogo-seredovischa-vplivae-na-zdorovya.html
3. Shamanskyi, S.I., Boichenko, S.V.: Energy efficient and environmentally friendly technology of stabilizing airline enterprises' wastewater sludges. East.-Eur. J. Enterp. Technol. **5**(8(77), 39–45 (2015). https://doi.org/10.15587/1729-4061.2015.52264
4. Shamanskyi, S., Boichenko, S., Pavliukh, L.: Estimated efficiency of biogenic elements removal from waste water in the ideal displacement photobioreactor. In: Zaporozhets, A., Artemchuk, V. (eds.) Systems, Decision and Control in Energy II. Studies in Systems, Decision and Control, vol. 346. Springer, Cham (2021). https://doi.org/10.1007/978-3-030-69189-9_21
5. Jędrzejewska-Cicińska, M., Krzemieniewski, M.: Effect of corrosion of steel elements on the treatment of dairy wastewater in a UASB reactor. Environ. Technol. **31**(6), 585–589 (2010). https://doi.org/10.1080/09593331003616821
6. Pavliukh, L., Shamanskyi, S., Boichenko, S., Jaworski, A.: Evaluation of the potential of commercial use of microalgae in the world and in Ukraine. Aircr. Eng. Aerosp. Technol. ahead-of-print No. ahead-of-print (2020). https://doi.org/10.1108/AEAT-08-2020-0181
7. Lim, S., Chu, W., Phang, S.: Use of Chlorella vulgaris for bioremediation of textile wastewater. J. Bioresour. Technol. **101**, 7314–7322 (2010)
8. Nezbrytska, I., Shamanskyi, S., Pavliukh, L., Kharchenko, G.: Assessment of inorganic nitrogen and phosphorus compounds removal efficiency from different types of wastewater using microalgae cultures. Ocean. Hydrobiol. Stud. **51**(1), 45–52 (2022). https://doi.org/10.26881/oahs.2022.1.05
9. Shamanskyi, S., Boichenko, S.: Development of environmentally safe technological water disposal scheme of aviation enterprise. East.-Eur. J. Enterp. Technol. **6**(10(84)), 49–57 (2016). https://doi.org/10.15587/1729-4061.2016.86053
10. https://theconversation.com/wastewater-is-an-asset-it-contains-nutrients-energy-and-precious-metals-and-scientists-are-learning-how-to-recover-them-113264
11. Li, Y., Horsman, M., Wu, N., Dubois-C, L.C.Q., Alero, N.: Biofuels from microalgae. Biotechnol. Prog. **24**(4), 815–820 (2008)
12. Apt, K.E., Behrens, P.W.: Commercial developments in microalgae biotechnology. J. Phycol. **35**(2), 215–226 (2002). https://doi.org/10.1046/j.1529-8817.1999.3520215
13. Mata, T.M., Martins, A.A., Caetano, N.S.: Microalgae for biodiesel production and other applications: a review. Renew. Sust. Energ. Rev. **14**, 217–232 (2010). https://doi.org/10.1016/j.rser.2009.07.020
14. Chisti, Y.: Biodiesel from microalgae. Biotechnol. Adv. **25**(3), 294–306 (2007). https://doi.org/10.1016/j.biotechadv.2007.02.001
15. Grobbelaar, J.U.: Algal Nutrition—Mineral Nutrition (2003).https://doi.org/10.1002/9780470995280.ch6

16. Barsanti, L., Gualtieri, P.: Algal Culturing. Algae: Anatomy, Biochemistry and Biotechnology. CRC Press, Boca Ranton, pp. 209–250 (2006)
17. Singh, B., Guldhe, A., Rawat, I., Bux, F.: Towards a sustainable approach for development of biodiesel from plant and microalgae. Renew. Sust. Energ. Rev. **29**, 216–245 (2014). https://doi.org/10.1016/j.rser.2013.08.067. https://www.rfbr.ru/rffi/ru/press_about/o_2106600
18. Solovchenko, A.E., Lukjjanov, A.A., Vasylj'eva S.G. y dr.: Vozmozhnosty byotekhnologhycheskoj pererabotky seljskokhozjajstvennыkh otkhodov s yspoljzovanyem mykrovodoroslej. Vestnyk Mosk. un-ta. Ser. 16. Byol. No. 1, pp. 38–49 (2014)
19. Shamanskyi, S., Boichenko, S., Khrutba, V., Topilnyckyi, P., Pavliukh, L.: Improving the photobioreactor operation efficiency in the technological scheme of wastewater treatment. East.-Eur. J. Enterp. Technol. **6**(10–114), 6–15 (2021)
20. http://journals.nubip.edu.ua/index.php/Energiya/article/viewFile/3660/3581
21. The negative impact of household chemicals and harmful substances on humans indoors. http://ukrref.com.ua/?id=MjQxMg%3D%3D
22. https://vspu.edu.ua/faculty/geogr/chemistry/art25_03/3_1.pdf
23. https://hmarochos.kiev.ua/2020/09/30/chym-shkidlyvi-fosfaty-i-chomu-yih-varto-zaboronyty-v-pralnyh-poroshkah/
24. Shamanskyi, S., Boichenko, S.: Environment-Friendly Technology of Airport's Sewerage. In: Karakoç, T., Colpan, C., Şöhret, Y. (eds.) Advances in Sustainable Aviation. Springer, Cham (2018). https://doi.org/10.1007/978-3-319-67134-5_11.
25. Madkour, A.G., Rasheedy, S.H., Dar, M.A., et al.: The differential efficiency of Chlorella vulgaris and Oscillatoria sp. to treat the municipal wastewater. J. Biol. Agric. Healthcare **7**(22), 83–94 (2017)
26. Mahapatra, D.M., Chanakya, H.N., Ramachandra, T.V.: Euglena sp. as a suitable source of lipids for potential use as biofuel and sustainable wastewater treatment. J. Appl. Phycol. **25**(3), 855–865 (2013). https://doi.org/10.1007/s10811-013-9979-5
27. Sawayama, S., Inoue, S., Dote, Y., Yokoyama, S.Y.: CO_2 fixation and oil production through microalgae. Energy Convers. Manag. **36**(69), 729–731 (1995). https://doi.org/10.1016/0196-8904(95)00108
28. Schenk, P.M., Thomas-Hall, S.R., Stephens, E., Marx, U.C., Mussgnug, J.H., Posten, C., Hankamer, B.: Second generation biofuels: high-efficiency microalgae for biodiesel production. Bioenerg. Res. **1**(1), 20–43 (2008). https://doi.org/10.1007/s12155-008-9008-8
29. Nezbrytskaya, I.N., Kureyshevich, A.V., Yarovoy, A.A., et al.: Peculiarities of the influence of high concentrations of ammonium on the functioning of some species of cyanoprokaryota, chlorophyta, and euglenophyta. Hydrobiol. J. **55**(2), 69–82 (2019)
30. Chiu, S.Y., Kao, C.Y., Chen, T.Y., Chang, Y.B., Kuo, C.M., Lin, C.S.: Cultivation of microalgal Chlorella for biomass and lipid production using wastewater as nutrient resource. Bioresour. Technol. **184**, 179–189 (2015). https://doi.org/10.1016/j.biortech.2014.11.080
31. Ruiz-Marin, A., Mendoza-Espinosa, L.G., Stephenson, T.: Growth and nutrient removal in free and immobilized green algae in batch and semi-continuous cultures treating real wastewater. Bioresour. Technol. **101**(1), 58–64 (2010). https://doi.org/10.1016/j.biortech.2009.02.076
32. Shkilniuk, I., Boichenko, S.: Biological risk of aviation fuel supply. In: Babak, V., Isaienko, V., Zaporozhets, A., (eds.) Systems, Decision and Control in Energy I. Studies in Systems, Decision and Control. Springer, Cham, Switzerland, vol. 298, pp. 179–199 (2020)
33. Nezbrytskaya, I.N., Kureyshevich, A.V.: Changes in the content of photosynthetic pigments in representatives of chlorophyta and cyanoprokaryota at a high temperature. Hydrobiol. J. **51**(4), 46–56 (2015)
34. Jeffrey, S.W., Humphrey, F.H.: New spectrophotometric equations for determining chlorophyll a, b, c1 and c2 in higher plants, algae and natural phytoplankton. Biochem. Physiol. Pflanz. **167**, 171–194 (1975)
35. Parsons, T.R., Strickland, J.D.H.: Discussion of spectrophotometric determination of marine-plant pigments and carotinoids. J. Marine. Res. **21**, 155 –163 (1963)
36. Lenntech. Phosphorous removal from wastewater (2017). https://www.lenntech.com/phosphorous-removal.htm

37. Tchobanoqlous, G., Burton, F.L., Stensel, H.D.: Wastewater Engineering: Treatment and Reuse. 4th edn. Metcalf&Eddy Inc., 1819 p. (2003)
38. Kroiss, H.: Betrieb von Klaeranlagen, vol. 202. Technische Universitat Wien, Wien, Band, 626 p. (2007)
39. 2017. http://old.menr.gov.ua/press-center/news/150-news28/2631-kyivvodokanal-b-ie-na-spolokh-protiahom-travnia-vmist-fosfativ-u-stichnykh-vodakh-iaki-nadkhodiat-na-ochystku-vtrychi-perevyshchuie-hranychnodopustymu-kontsentratsiiu
40. Toyama, T., Hanaoka, T., Yamada, K., et al.: Enhanced production of biomass and lipids by Euglena gracilis via co-culturing with a microalgae growth-promoting bacterium, Emticicia sp. EG3. Biotechnol. Biofuels 12, pp. 205 (2019). https://doi.org/10.1186/s13068-019-1544-2

Advance in Alternative Motor Fuels Technology

The Use of Biocomponents and Additives to Improve the Quality and Safety of Diesel Fuels

Maria Michela Dell'Anna, Valentyna Tkachuk, Oxana Rechun, and Galina Golodyuk

1 Introduction

In recent years there was information that European countries, such as Italy, Denmark, Spain, the United Kingdom had annual productions of waste cooking oil (WCO) between 0.1 Mt and 0.5 Mt [1]. The other EU countries annually produced below 0.1 Mt. Analyzing the same data on a per capita basis, Several EU countries, Portugal for example are major producers (up to 6.5 kg/capita/year) [2]. Environmental and sustainability experts agree: The world needs to take quick action on climate change and accelerate our transition to clean energy. And with rising costs and fuel shortages, in part driven by the war in Ukraine, the urgency around securing a reliable, affordable energy source is of the utmost importance to all planet now.

2 Methodology

Achievements of the tasks outlined in the article are realized with the use of standard, generally accepted in the oil refining industry, as well as special physical, physicochemical and other methods. Standard methods are based on current national standards (DSTU), harmonized with international (ISO) and European (EN). The basis of experimental studies of performance indicators is based on known standardized techniques using modern devices.

M. M. Dell'Anna
DICATECH, Politecnico Di Bari (POLIBA), Bari, Italy

V. Tkachuk (✉) · O. Rechun · G. Golodyuk
Lutsk National Technical University, Lutsk, Ukraine
e-mail: v.tkachuk@lntu.edu.ua

S. Boichenko et al. (eds.), *Modern Technologies in Energy and Transport*, Studies in Systems, Decision and Control 510, https://doi.org/10.1007/978-3-031-44351-0_10

3 Literature Overview

As there is a large amount of produced WCO, it is crucial to recycle this waste and transform it into a economically valuable "new product". One of the ways to recycle this waste is to transform it into biofuel [3–5].

Since biodiesel can be synthetized from fresh vegetable oils (rapeseed, sunflower, soybean oil) as well as from used cooking oils, the global production of biodiesel fuel is expected to definitely grow. However, there are certain problems with the use of biodiesel, such as increased viscosity and insufficient purification from by-products of transesterification [6].

In addition, a high-quality biodiesel should contain monounsaturated fatty acid methyl ester as the main component. On the whole, the biodiesel produced by the most common method of transesterification contains a large amount of polyunsaturated fatty acids methyl ether (FAMEs). This way of production harms product quality [7]. Therefore, the use of additives to biodiesel fuel, optimization of its composition is an crucial task for further research.

Comparing to diesel biodiesel has exceptional environmental advantages. The study performed by the United States National Biodiesel Council admits that burning biodiesel emits, on average, 48% less carbon monoxide, 47% less particulate matter, and 67% less hydrocarbon comparing to diesel from petroleum [8].

Therefore, research into the properties of various types of biodiesel continues to be relevant.

Diesel biofuels have become progressively widespread abroad in the latest years. A number of Western European countries are experiencing an increase in production of diesel fuel from vegetable raw materials. It is observed in Germany, France, as well as in the United States, Brazil, and Malaysia [9]. The European countries focus on production of diesel biofuels from rapeseed oil, encompassing from rapeseed grown in Ukraine. In the United States and Brazil the production of biodiesel from soybean oil is promoted. The Southeast Asian countries prefer production from palm oil [10].

A mixture of complex methyl esters obtained from rapeseed oil (MERO) is used as 100% diesel fuel in tractors operating in Austria. In France, they used a mixture of diesel fuel with 5% MERO. The soybean oil-based methyl esters are used as a 100% non-fuel or as a 20% addition to petroleum fuel in the USA. Regtettably, this problem is more theoretical in nature in Ukraine because of the absence of data about results of a study of the mass use of bio-components for diesel fuel.

In our previous research, we optimized the composition of mixed fuel based on petroleum diesel fuel, as well as biocomponents such as isobutyl ester and methyl ester of rapeseed oil, and we also analyzed their indicators of performance properties [11] The advantages of using such mixed fuels with respect to fossil fuel were:

1. raise of cetane number (when this indicator is higher, the level of noise and smoke during engine operation is lower);
2. possibility of tuning values of density and viscosity, while ensuring the pumping of fuel through the car's fuel system and its anti-wear properties;

3. improvement of lubricating features of the fuel, thus preserving car engine from consumption;
4. decreasing of the sulfur content in the obtained fuels with biocomponents, therefore improving their environmental properties;
5. modifying the flash point. in a closed crucible, lowering the limit temperature of filterability.

Another advantage of fuel modification of adding rape oil methyl and isopropyl esters is the improvement of the value indicator of washing ability.

In another work [12], the properties of biodiesel fuel based on sunflower and soybean oil, their chemical composition, have been investigated. In addition, vegetable oil based-biodiesel such as sunflower and soybean oil has better fluidity in cold temperature regions comparing to animal fat-based biodiesel. This may be the result of the high amount of polyunsaturated FAMEs compositions in feedstock.

A number of research works [13, 14] are devoted to the improvement of oxidative stability and cold fluidity by the partial hydrogenation of biodiesel method. In addition, hydrogenation can lead to an increase in cetane number. It is a crucial fuel property corresponding to the ignition quality. After moderate hydrogenation of unsaturated FAMEs, we can raise the ignition performance of fuel to a more satisfactory level.

A recent review paper summarizes the improvements in terms of the production, cold flow properties, oxidation stability as well as catalytic material for the hydrogenation process, and feedstock for the production concerning the ways to reduce trans-isomers in hydrogenated biodiesel [15].

Some investigations have been devoted to the inspection of the technologies and biofuel types produced [16, 17]. Current state of execution shows a predominance of studies for biodiesel production through transesterification.

After all, some studies make use of different technologies with other types of biofuels produced through the valorization of WCO. These technologies are as following the production of hydrogen-rich syngas in gasification and bio-oils through various types of pyrolysis as well as biokerosene.

4 Materials and Methods of the Study

Evaluation of parameters of operational properties for fuels is made using standard methods of investigation of physical and chemical properties of fuels. These methods are standard for both oil and alternative fuels.

Density, kinematic viscosity, cetane number, solidification temperature, sulphur content, heat of combustion were resolved in biodiesel fuel that was used for research. All the indicators were figured by standard methods according to EN 14214.

Gas chromatography analyses was performed using an HP 6890 instrument equipped with a flame ionization detector (FID) and an HP-1 (Cross linked Methyl Siloxane) and capillary column (60.0 m × 0.25 mm × 1.0 μm). All research objects were taken from commercial sources and operated as such. Received Soybean oil and WCO were got from the food market and consumer spending. FAMEs were prepared from SO and WCO through a transesterification reaction according to the procedure described in [18]. First, 50 g of vegetable oil was heated at 60 °C. Then, a solution of methanol (16.9 g) and potassium hydroxide (0.5 g) in a MeOH/oil molar ratio equal to 9:1 was added to the heated oil. It was left under stirring at 600 rpm for 2 hundred refluxing conditions.

After that the mixture was poured into a separating funnel and left standing overnight. That was made to separate the FAMEs from the glycerol. Once separated, the FAMEs phase was washed several times with distilled water at 60 °C and dried over Na2SO4. The average molar weights of the SO and WCO FAMEs mixtures were calculated basing on their composition.

5 Results and Discussion

The consumption of fossil petroleum products in the EU is gradually mixing, if in 2000 it amounted to 396.72 million tons, then in 2020–310.31 million tons (Fig. 1).

In 2020, the final consumption of oil and petroleum products for energy and non-energy purposes in the EU Member States fell 8.9% to 384.0 (Mtoe) In almost one year it reached the lowest level ever recorded in the 31-year time series. It definitely showed the effects of the COVID restrictions for most EU Member States that started in the first few months of 2020.

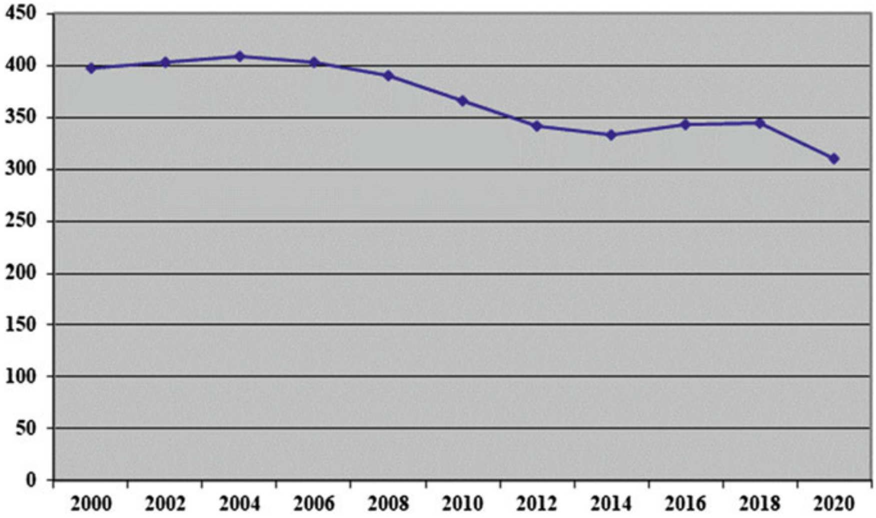


Fig. 1 Consumption of oil and oil products in EU, million tons

The consumption declined from the peak of 2001 (499 Mtoe) to a low point in 2014 (409 Mtoe). Before the shock of the pandemic restrictions it was increasing.

In 2020, the disruption of the pandemic-related restrictive measures had influence on the consumption in the Member States to different degrees affected the most Luxemburg (−21.4%), Malta (−15.7%) and Greece, Spain, Sweden, Slovenia and Italy (all between −14 and −15%) (Table 1).

Member States have different energy and non-energy consumption patterns of oil and petroleum products. It is affected by the size and structure of countries' economies. In 2020, Germany continued to lead with a 22.5% share of the total final

Table 1 Consumtion of oil and petroleum products in 2020 (equivalent of million tons of oil)

Country	2020	Change from 2019 (%)	2020 share (%)
Germany	88.54	−5.48	22.53
France	59.79	−12.15	15.57
Italy	37.77	−14.10	9.83
Spain	37.19	−14.72	9.68
Poland	27.82	−4.46	7.25
Netherlands	22.96	−0.84	5.98
Belgium	17.70	−7.62	4.61
Austria	10.17	−9.26	2.65
Romania	9.01	−2.43	2.35
Czech Republic	8.44	−8.72	2.20
Sweden	7.56	−14.65	1.97
Greece	7.49	−14.82	1.95
Portugal	7.44	−11.37	1.94
Finland	7.02	0.44	1.83
Hungary	6.97	−6.87	1.81
Ireland	5.66	−8.28	1.47
Denmark	5.04	−7.16	1.31
Bulgaria	3.74	−3.43	0.97
Slovakia	3.36	0.37	0.88
Croatia	2.59	−10.50	0.67
Lithuania	2.39	−1.88	0.62
Slovenia	1.99	−14.64	0.52
Luxembourg	1.85	−21.38	0.48
Latvia	1.36	−1.27	0.35
Estonia	1.02	−2.01	0.26
Cyprus	0.92	−9.21	0.24
Malta	0.27	−15.70	0.07

EU consumption. It was followed by France (15.6%), Italy (9.8%) and Spain (9.7%) [19].

Over the past three years, exports of spent raw materials to European oil companies have grown by 40%, and demand is forecast to triple by 2030.

Due to a large amount of produced WCO, it is important to recycle this waste to transform it into an economically valuable "new product". One of the methods to recycle this waste is to transform it into biofuel.

That's why samples of biodiesel fuel based on soybean oil and waste cooking oil were selected as objects of research in this article.

The main physical and chemical parameters are listed in Table 2. As we can see, the cetane number needs to be increased, the density decreased, and the solidification temperature decreased.

Figure 2 reports the analyses of Commercial soybean oil (SO) and waste cooking oil (WCO) after their transesterification in methanol. As well the resulting FAMEs compositions are presented there.

SO and WCO have a similar FAMEs composition (Fig. 2). They are rich in polyunsaturated methyl esters, such as C18:2 (methyl linoleate, 48.2–46.9%) and C18:3 (methyl linolenate, 4.8–5.8%). These esters should be converted into the more valuable monounsaturated C18:1 product. The further formation of C18:0 methyl stearate which is present in raw SO and WCO FAMEs in a low amount (5.8–6.8%)

Table 2 Physical and chemical parameters of biodiesel samples

Indicator	Soybean biodiesel (SO)	Waste cooking oil (WCO)
Saturated fatty acid, %	15.900	18.000
Mono unsaturated fatty acid, 17.70%	−7.6230.100	29.300
Poly unsaturated fatty acid, %	54.000	52.700
Degree of unsaturation	138.100	134.700
Saponification value, mg/g	200.958	201.132
Iodine value	130.249	126.249
Cetane number	44.124	45.030
Long chain saturated factor	4.180	4.790
Cold filter plugging point, ºC	−3.345	−1.428
Cloud point, ºC	0.163	0.741
Pour point, ºC	−6.644	−6.016
Allylic equivalent	138.100	134.700
Bis-Allylic position equivalent	60.400	58.100
Oxidation stability	4.774	4.828
Higher heating value	39.450	39.454
Kinematic viscosity, mm^2/s	3.649	3.670
Density. g/cm^3	0.881	0.880

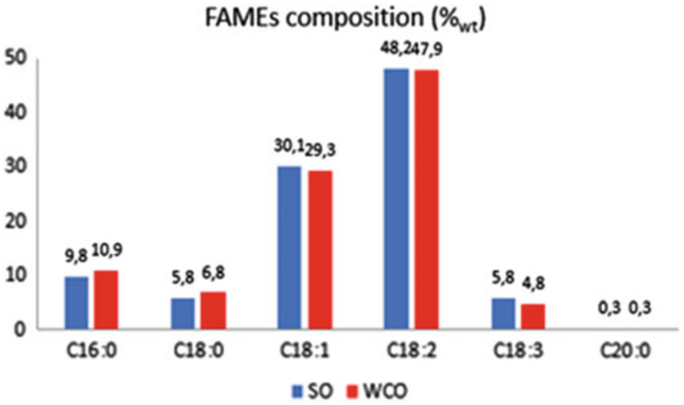


Fig. 2 SO and WCO FAMEs composition (%$_{wt}$)

should be avoided with exception of methyl palmitate (C16:0, 9.8–10.9%) and a negligible quantity of methyl arachidate (C20:0, 0.3%).

The biodiesel upgrading focuses on converting C18:3 and C18:2 starting esters into C18:1 methyl oleate (cis configuration), preventing the formation of methyl elaidate (C18:1, trans configuration), which has a melting point higher than its cis isomer, having detrimental effects on the cold flow properties of the whole mixture. Though, enriched with the trans-C18:1 biodiesel isomer demonstrated better lubricity features than FAMEs mixture containing C18:1 species in only a cis configuration [19].

As an outcome of the research, biodiesel fuel is obtained from waste oil, which has a low cetane number, increased viscosity and a somewhat high solidification temperature. Improvement of these indicators of operational properties is possible with the use of applications, biocomponents and additives.

Optimizing the composition of such mixed fuel will allow to produce it taking into account the desired quality indicators and economic efficiency.

Considering the situation with the import dependence of most countries on oil fuel, serious geopolitical changes and war in Central Europe, climate change, constant environmental pollution due to the increase in the car fleet in the world, the production of biodiesel fuel from waste, namely used cooking oil, is extremely necessary. Optimizing the composition of such fuel with the provision of high operational properties is a huge potential for replacing fossil fuel, reducing the significant share of its use.

In Ukraine, temperatures are quite low for 3–4 months, so the problem of improving the low-temperature properties of diesel fuels is relevant and economically important. For quite a long time, the solidification temperature of diesel fuels was reduced by reducing the boiling point. This direction turned out to be economically unjustified, since some of the valuable fractions of diesel fuel were converted to fuel oil, the price of which was significantly lower. Another direction for improving the low-temperature properties of diesel fuel is catalytic processes.

At a temperature of 350–400 °C, hydroisomerization of n-alkanes occurs on the catalyst in the presence of hydrogen-containing gas, while the maximum filterability temperature of the fuel decreases by 20–30 °C. The process requires significant capital expenditures, amounting to tens of millions of dollars.

The most economically justified and technologically simple is the use of depressor additives, when added in small quantities (0.05–0.1% by weight) a significant reduction in the solidification temperature and the maximum filterability temperature is achieved.

As the analysis showed, the most effective are ethylene copolymers with vinyl acetate, ethylene copolymers with alkyl methacrylates, polyolefins (branched polyethylene, ethylene copolymers with propylene, chlorinated polyethylene), alkyl methacrylate polymers, polymers of maleic and fumaric acid derivatives, as well as others.

In recent years, there has been a widespread trend towards the development of composite depressor additives, which consist of two or more components of the active substance, which are characterized by greater efficiency due to the synergy of the components.

However, the effectiveness of the same depressor can vary significantly depending on the chemical composition of diesel fuel and its fractional composition. For a particular diesel fuel, it is necessary to try out depressors from several manufacturers and choose the best one based on efficiency and price. A special feature of depressor applications is also their composition, which is a trade secret of manufacturers.

Three depressors of foreign companies were studied: Clariant, Basf and Diesel-u depressor, developed at the Petroleum Institute (Poland), since there is no production of depressor additives in Ukraine. Depressors have different effects on road accidents derived from different oils, at different plants, using different technologies, and when using biocomponents. Therefore, the determination of the optimal concentration of deperesoroids in DPA with bio components is relevant. Diesel fuel (sample 1) and diesel fuel with the addition of rapeseed oil ethyl ester (sample 2) were taken as raw materials for the research. The characteristics of depressors are shown in Table 3.

The chemical structure of the selected substances was studied by infrared spectroscopy, shown in Figs. 3, 4 and 5.

Table 3 Characteristics of depressors

Indicators	Depressors		
	Dodiflow clariant	Keroflux basf	Diesol-u oil institute poland
Density, kg/m3	890–920	875–915	870–900
Viscosity at 50 °C, mm^2/s	100–150	40–80	2–4
Flash point, °C	>50	>64	>45
Solidification temperature °C	< +25	< +25	< –30
Solidification temperature °C	Absent		

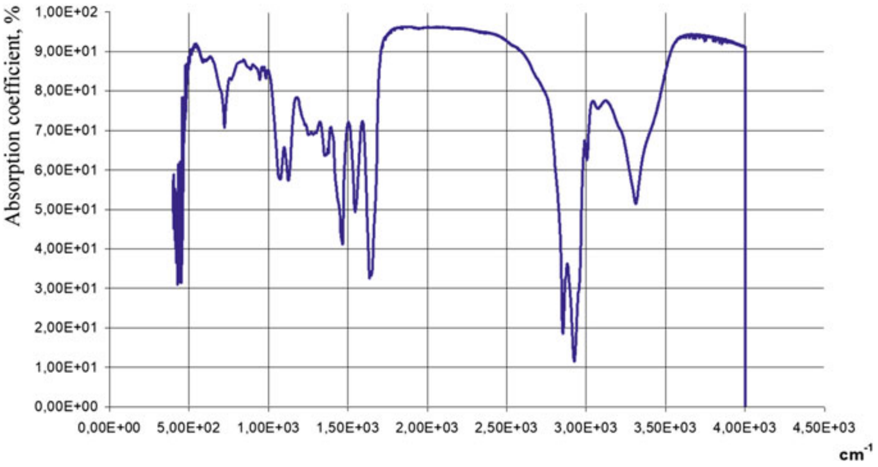


Fig. 3 IR spectrum dodiflow 4273 (clariant)

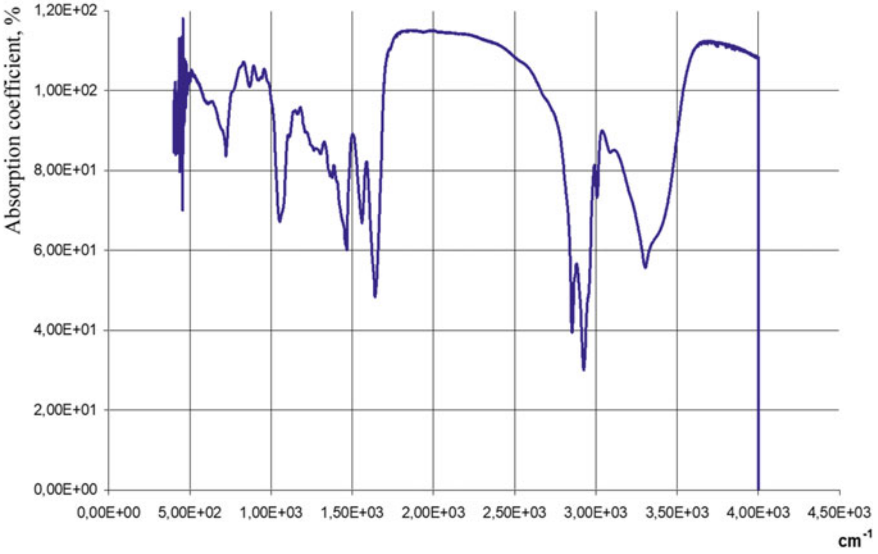


Fig. 4 IR spectrum keroflux 6312 basf

Analysis of the IR spectra of Dodiflow3905-2 (Clariant) confirms the presence of methyl groups in the frequency range: 1470, 2930 cm^{-1}, methylene groups in the Alkane and alkene chains in the frequency range 725 cm^{-1}, 1400 cm^{-1}, 1470, 2860, 2930 cm^{-1}, ethyl (–CH2–CH2–) groups in the frequency range 1060, 1470 cm^{-1}, carboxylic acid radicals in the frequency range: 1310, 1400, 2930 cm^{-1}, ethenylene groups in the frequency range 1310, 1640, 3010 cm^{-1}, h-propyl groups in the frequency range 1470 cm^{-1}, primary alcohol groups in the frequency range: 1310, 1400, 3310 cm^{-1}, secondary alcohol groups in the frequency range: 1310, 1400, 3310 cm^{-1}. Analysis of the IR spectra of Keroflux 6312 (Basf) confirms the presence of a methyl group in alkane chains in the frequency range: 1370, 1470, 2860 cm^{-1}, methylene groups in Alkane chains in the frequency range 725, 948, 2930, 3090 cm^{-1}, ethylene groups in alkenes in the frequency range: 608, 1650, 3010 cm^{-1}, primary alcohol groups in the frequency range: 1080, 1130, 1470, 3320 cm^{-1}, h-propyl group in the frequency range of 1470 cm^{-1}.

Analysis of the Diesol-u IR spectra of the Petroleum Institute (Poland) confirms the presence of methylene groups in the frequency range: 728, 1460, 2860, 2930 cm^{-1}, primary alcohol groups in the frequency range: 1080, 1130, 1470, 3320 cm^{-1}.

The distribution of functional groups is shown in Table 4. establishing the presence of certain functional groups in depressors makes it possible to explain the greater or lesser effect of different depressors.

The results of studies of the effect of depressor additives on the low-temperature property are shown in Table 5.

As can be seen from the table below, BASF products for both petroleum diesel fuel and fuel with bio-components showed the highest depressor effect with minimal consumption to achieve a filterability temperature of −20 °C.

The Polish-made Diesol-u depressor has the lowest price, however, to achieve a filterability temperature of −20 °C, its consumption is 150% higher [20].

Thus, the addition of a depressor additive will make it possible to obtain a winter grade of diesel fuel, which has a significant reduction in the solidification temperature

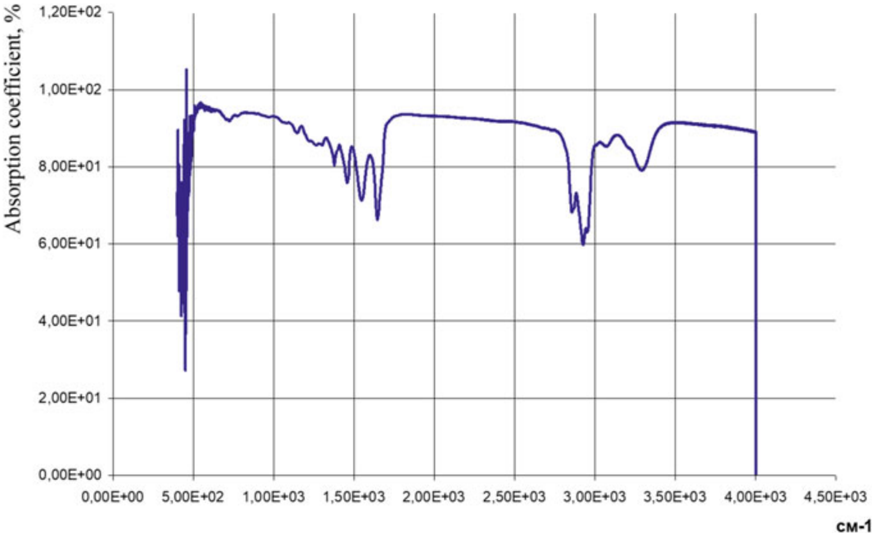


Fig. 5 IR spectrum diesol-u

Table 4 Functional groups of the studied substances and their absorption frequencies (cm^{-1})

Functional group	Absorption frequencies, cm $^{-1}$		
	Dodiflow 3905–2	Keroflux 6312	Diesol-u
Carboxylic acid radicals	1310, 1400, 2930	–	–
Methyl group	1470, 2930	1370, 1470, 2860	–
Methylene groups	725, 1400, 1470, 2860, 2930	725, 948, 2930, 3090	728, 1460, 2930, 2860
Ethyl groups	1060, 1470		
Ethenylene group	1310, 1640, 3010	608, 1650, 3010	
H-profile group	1470	1470	
Primary alcohol groups	1310, 1400, 3310	1080, 1130, 1470, 3320	1080, 1130, 1470, 3320
Secondary alcohol groups	1310, 1400, 3310	–	–

and the maximum filterability temperature of −20 °C, which allows it to be used in winter at very low ambient temperatures.

Since the cetane number determines the start of the engine, determines the rate of pressure growth, fuel consumption and smoke content of exhaust gases, then according to the norms of foreign countries, the cetane number should not be lower than 53. Therefore, for all imported passenger cars running on diesel fuels, it is desirable to increase the cetane number to the norms of European standards. Ignition promoters are used to improve the ignition of diesel fuels in the combustion chamber.

The principle of operation of ignition promoters is explained by the slight decay of their molecules (most often nitrates or peroxides) along O–O and O–N bonds with a low (about 150 kJ/mol) activation energy. The resulting free radicals initiate fuel ignition. Additives of this type act only at the initial stages of the combustion process, which is why they are called ignition promoters or cetane-boosting additives.

As previous studies have shown, the cetane number of basic diesel fuel and diesel fuel with esters meets the requirements of SSTU [21], but is lower than the requirements of the World Fuel Charter, which approved the cetane number indicator at the level of 53 [22].

The effect of the cetane-boosting additive Nitrocet-50, developed by the Petroleum Institute (Krakow, Poland), was studied. The characteristics of this additive are shown in Table 6.

The cetane-boosting additive Nitrocet-50 was introduced into diesel fuel as a 50% solution in a solvent.

The raw materials for the research were L-grade diesel fuel (sample 1) and diesel fuel with the addition of rapeseed oil ethyl ester (sample 2). The dependence of the cetane number on the additive content is shown in Fig. 6.

Analyzing Fig. 6, it can be argued that to increase the cetane number of diesel fuel of Petroleum Origin (sample 1) to 53 units, it is necessary to add the cetane boosting

Table 5 Results of studies of the effect of depressor additives to achieve the maximum filtration temperature −20 °C

Depressor	Depressor concentration, % by weight	Maximum filterability temperature, °C	
		Sample 1	Sample 2
1	2	3	4
Output diesel fuel	0	–7	–8
Dodiflow 4273 (4800 €/t)	0.005	–14	–13
	0.010	–17	–16
	0.020	–19	–18
	0.030	–21	–20
Dodiflow 3905–2 (4860 €/t)	0.005	–14	–12
	0.010	–18	–16
	0.020	–20	–19
	0.030	–22	–21
Dodiflow 5416 (4910 €/t)	0.005	–15	–14
	0.010	–19	–18
	0.020	–21	–20
	0.020	–22	–21
Keroflux ES 6100 (4720 €/t)	0.005	–15	–14
	0.010	–17	–16
	0.015	–19	–18
	0.020	–22	–20
	0.030	26	–23
Keroflux ES 6211 (4825 €/t)	0.005	–16	–15
	0.010	–18	–17
	0.015	–20	–19
	0.020	–23	–20
	0.030	–27	–23
Keroflux ES 6312 (4890 €/t)	0.005	–16	–15
	0.010	–18	–17
	0.010	–20	–18
	0.020	–24	–18
	0.020	–28	–22
Diesol-u (4100 €/t)	0.005	–12	–13
	0.010	–14	–15
	0.020	–17	–18
	0.030	–20	–20

Table 6 Quality indicators of cetane boosting additive Nitrocet-50

Indicator	Value
Density at 20 °C, kg / m3	900–920
Flash Point, °C	Higher 45
Freezing temperature, °C	Lower −35
Sulfur content, % by weight	Absence

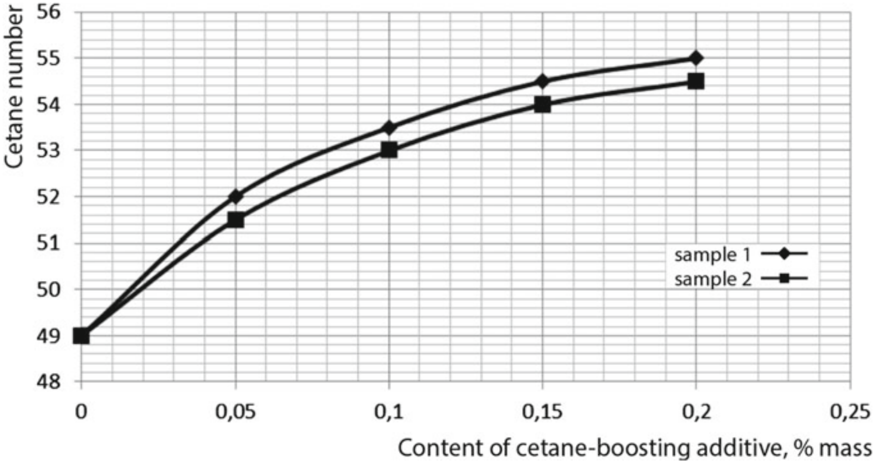


Fig. 6 Dependence of the cetane number of diesel fuel on the content of cetane boosting additive

additive Nitrocet-50 in the amount of 0.08% by weight, to increase the cetane number of diesel fuel with the addition of methyl ester of rapeseed oil (sample 2) to 53 units, it is necessary to add the cetane boosting additive Nitrocet-50 in the amount of 0.1% by weight.

The physical and chemical properties of fuel with the addition of 7% MERO and Cetane boosting additive Nitrocet-50 and conventional diesel fuel of the L Brand, which are shown in Table 7, were studied.

The data in this table show that when biocomponents and a cetane-boosting additive were added to petroleum fuel, the cetane number increased by 4 units.

The density and viscosity due to biocomponents have slightly increased. Studies have shown that in terms of physical and chemical parameters, biofuels meet the requirements of the regulatory document [21], in particular, they have a lower flash point in a closed Crucible by 4 °C, a lower sulfur content by 2.9 mg/kg.

In terms of sulfur content, ash content and mass fraction of polycyclic aromatic hydrocarbons, the new fuel has significantly better performance compared to petroleum, which improves its environmental properties. Another advantage is that fuel with the addition of rapeseed oil methyl esters has improved cleaning properties. The solidification temperature due to the use of depressors decreased to −20 °C. other indicators meet the requirements of DSTU 7688:2015.

Table 7 Physical and chemical parameters of diesel fuel with biocomponents

Indicator	Test methods	According to DSTU 7688:2015 for LG brand 3	Actual data	
			DF + 7% rapeseed oil methyl ester	DF brand L
Cetane number, not less than	DSTU ISO 5165	51	53	49
Density at t = 15 °C, kg/m^3, within	DSTU ENISO 3675	820–845	846	835
Mass fraction of polycyclic aromatic hydrocarbons, %, max	DSTU EN 12,916	8	7	7
Sulfur content, mg/kg, no more than	DSTU ENISO 20884	10	7,1	8
Flash point, °C, not lower than	DSTU ISO 2719	55	59	58
Ash content, % (weight), no more than	DSTU ENISO 6245	0.005	0.004	0.004
Lubricity: diameter of wear fields at t = 60 °C, microns, not more than	DSTU ISO 12156	460	430	450
Kinematic viscosity at t = 40 °C, mm^2/ s, within	DSTU GOST 33	2.00–4.50	3.9	3.7
Maximum filterability temperature, °C, not higher than	DSTU EN 116	–20	–20	–7

A complex of physical and chemical properties and quality parameters of diesel fuel of petroleum origin and fuel with the addition of rapeseed oil esters were studied. As a result, it is noted that the characteristics of biocomponents are somewhat different from those of petroleum diesel fuel, and a number of environmental indicators are better than those of fuel of petroleum origin.

When bio-components are added to petroleum diesel fuel in the amount of 7%, first of all, environmental indicators are improved: sulfur content, mass fraction of aromatic hydrocarbons, ash content. Also, when a cetane-boosting additive is added, the cetane number increases and the lubricity is significantly improved, which increases the service life of the car's engine. Depressor additives reduce the solidification temperature. In addition, biodiesel saves fuel costs because it is cheaper than petroleum diesel fuel.

The influence of multifunctional additives of European manufacturers on the physical–chemical parameters and reduction of harmful emissions of the developed diesel fuel using a biocomponent was tested and determined [21].

Keropur® Energy DP additives manufactured by Basf (Germany) and Chimec EP-D plus additives manufactured by Chimec (Italy) were used to improve the physical and chemical parameters (increase the environmental friendliness of fuels). The composition of keropur® Energy DP additive included: combustion modifiers—barium alkylphenolates and nitrogen—containing dispersing additive, detergent additive—surfactant and oxygen—containing solvent, demulsifier—copolymers of ethylene and propylene oxides, defoamer-polyorganosiloxanes, antioxidant-substances based on dialkyl-n-phenyldiamines.

Due to the conducted studies, the following indicators were determined: efficiency of maintaining the purity of detergent additives, corrosion inhibition, anti-foam efficiency, water separation efficiency test, stability to oxidation (Fig. 7).

When determining the effectiveness of additives in maintaining purity, the initial fuel without adding additives was first investigated. The obtained value of the flow restriction, which characterizes the tendency of diesel fuel to carbon formation on the nozzle, for the base fuel was 79.4%. This value is at the level of the results of typical fuels that comply with the European standard EN 590 [23].

When Keropur® DP ENERGY additive is added to fuel in the amount of 150 mg/kg after 10 h. the flow restriction test was 58.4% (Table 8). Reducing the flow limit by more than 20% means good efficiency of the additive in this fuel in maintaining the cleanliness of the injection system (Keep Clean effect).

A comparison of the results obtained and data for the most common diesel fuels on the European market shows that the developed fuel with Keropur® DP ENERGY additive in a dosage of 150 mg/kg can be attributed to the segment of branded brands of leading international companies, such as Esso, Shell, etc. When adding Chimec

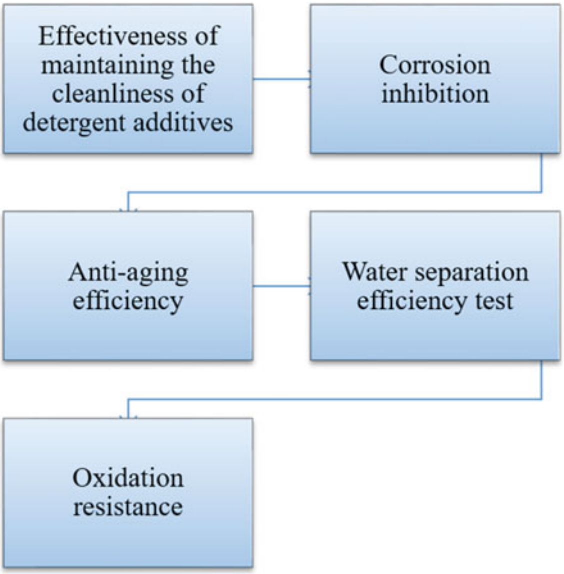


Fig. 7 Sequence of assessment of physical and chemical quality indicators of STS with biocomponents and additives Keropur ® Energy and Chimec EP-d plus

Table 8 Fuel efficiency with a bio component for maintaining cleanliness (Keep Clean) and cleaning (clean-up) injectors

Products	Dosage, ppm	0.1 mm nozzle needle lift				Average value
		F. 1	F. 2	F. 3	F. 4	Flow restriction, %
		Flow restriction, %				
DP	0	79,6	78,4	83,6	76,1	79,4
Keropur DP ENERGY	150	59,6	54,7	64,6	54,7	58,4
Keropur DP 4510	150	67,7	68,8	66,0	70,2	68,2
Chimec EP-D plus	190	–	–	–	–	52,0

with EPD plus e additive of 190 mg/kg after 10 h. the flow restriction test was 52%, which is also a high result.

Additionally, the effectiveness of the additive for cleaning was tested. At the same time, contaminated injectors are installed in the engine after running on basic diesel fuel and determining the flow limit without cleaning the resulting carbon deposits. Then the engine was run on a standard cycle already on the tested fuel with a keropur DP ENERGY additive package in a dosage of 150 mg/kg. In this case, the flow limit is reduced from 79.4% (basic diesel fuel) to 68.2%, i.e. more than half of the resulting deposits are removed in just one run within 10 h (Table 9). This result of this test is considered acceptable for European fuels.

When determining the corrosion effect of diesel fuel with the addition of additive packages, it was found that the base diesel fuel exhibits relatively high corrosion activity according to the ASTM D 665 a standard, and in variant B (with seawater) the corrosion area is more than 75%. Corrosion, however, can be completely inhibited by adding the Keropur® DP ENERGY multifunctional package at a dosage of 150 mg/kg (method A) to the fuel. In a much more rigid version of the study, there is a significant inhibition of corrosion processes. The addition of 190 ppm Chimec EP-D plus e additive also significantly reduces the corrosion effect of diesel fuel. The results are shown in Fig. 8.

The complete absence of steel corrosion in the ASTM D 665 a variant is considered generally accepted for the branded diesel fuel segment (with distilled water) and limited corrosion activity is allowed in variant B with seawater. Diesel fuel with the

Table 9 Results of the study of corrosion of diesel fuel with a bio component when adding additives

Additive	Dosage, mg/kg	Rating on the scale NACE
DP brand L (method A)	0	B
Keropur DP ENERGY (method A)	150	A
DP brand L (method B)	0	E
Keropur DP ENERGY (method B)	150	C
Chimec EPD plus (method B)	190	B++/A class

Table 10 Results of testing of diesel fuel with a bio component for the efficiency of water separation when adding additives

Additive	Quantity, mg/kg	Time, min	Phase separation limit, score	Diesel phase, point	Water phase, point	Water loss, l
DP	0	5	4	2	3	1
Keropur DP ENERGY	150	5	3	2	1	0
Diesel fuel	0	240	3	2	1	0
Keropur® DP ENERGY	150	240	2	1,5	1	0
Chimec EP-D plus	190	5	2	3	1	0
Chimec EP-D plus	190	240	1	2	1	0

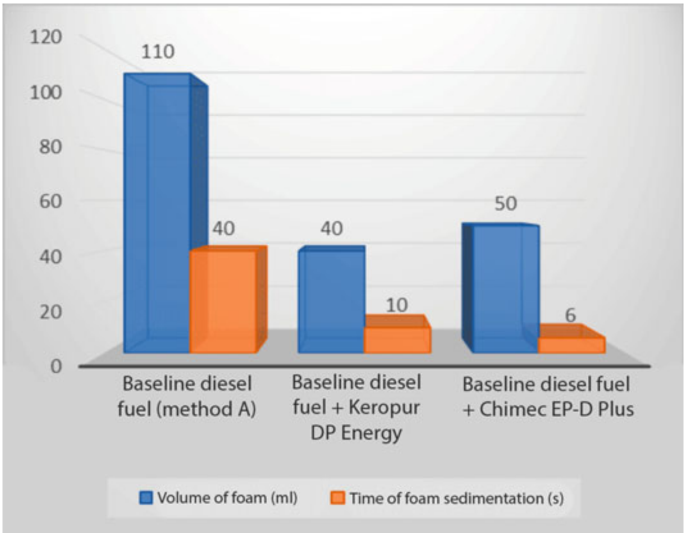


Fig. 8 Results of diesel fuel antigenicity tests using additives

Keropur ® DP ENERGY Package at a dosage of 150 mg/kg and Chimec with EPD plus at a dosage of 190 mg/kg fully meets these requirements.

Conducting tests to determine the anti-foam properties showed that the use of Keropur® DP ENERGY additive package in diesel fuel at a concentration of 150 mg/kg reduces the volume of foam formed by 64% from 110 to 40 ml and reduces the foam deposition time by 4 times from 40 to 10 s (Table 8). The use of the chemical EP-d plus additive package in diesel fuel at a dosage of 190 mg/kg reduces the volume of foam formed by 55% from 110 to 50 ml and reduces the foam deposition time by 6.7 times from 40 to 6 s.

Thus, according to these indicators, fuel with additives significantly exceeds the generally accepted recommendations of the World Fuel Charter.

During the study to determine the efficiency of water separation, it was found that the base fuel shows a noticeable emulsification of water in this study. The addition of 150 mg/kg of Keropur® EP ENERGY and chemical EP-d plus additives in a dosage of 190 mg/kg effectively improves the behavior of L-grade DP when separating water both after 5 min and after 4 h of exposure. Table 8 shows the experimental data obtained.

When determining oxidative stability, it was found that the base fuel has high oxidative stability with a significant margin compared to the normalized level. With the introduction of 150 mg/kg of Keropur® DP ENERGY or Chimec additive with EPD plus at an amount of 190 mg/kg, this indicator is further reduced by 44% (Table 10).

The use of multifunctional additive packages for diesel fuel allows you to maintain the cleanliness of the engine fuel injection system at the required technical level. Consequently, the optimal composition of the fuel–air mixture is ensured and the most complete and efficient combustion is guaranteed [24].

At the same time, the level of emissions of harmful substances in exhaust gases—soot (PM), unburned hydrocarbons (UH), carbon monoxide (CO) and nitrogen oxides (NO_x) is significantly reduced, as well as the consumption of diesel fuel and, accordingly, the release of carbon dioxide CO_2 ("greenhouse gas") is reduced by 2–5%. Statistical data from field tests to reduce the emission of harmful substances from cars are shown in Table 11.

The optimal consumption of keropur DP ENERGY and Chimec additives with EPD plus is 150 per 190 g/t, respectively. At the market price of Keropur® DP ENERGY additive 3200 €/t and chemical EP-d plus 3350€/t, the cost of diesel fuel will increase by 0.480 €/t when using Keropur® DP ENERGY additive and 0.637 €/t when using chemical EP-d plus additive. Thus, when purchasing additives from 2 different manufacturers, it is necessary to take into account, in addition to the cost of the additive, the delivery scheme, payment terms, the volume of one-time batches, and the technological ease of mixing diesel fuel with the additive.

Table 11 The influence of Keropur DP ENERGY and Chimes EP-D plus additives on the reduction of harmful emissions in diesel fuel with a biocomponent

Harmful substance	Emission reduction, %	
	Keropur® DP ENERGY	Chimec EP-D plus
Hydrocarbons that are not burned	15.0	20.0
CO	10.0	9.0
NO_x	2.0	10.7
PM	10.0	5.7
CO_2	4.0	1.8

So, the developed fuel with Keropur® DP ENERGY additive in a dosage of already 150 mg/kg can be attributed to the segment of branded brands of leading international companies, such as Esso, Shell, etc. the flow restriction test was 52%, which is a high result.

Generally accepted for the branded diesel fuel segment is the complete absence of steel corrosion in the ASTM D 665 a variant (with distilled water) and limited corrosion activity in the B variant with seawater. Diesel fuel with the Keropur® DP ENERGY package at a dosage of 150 mg/kg and Chimec EPD plus at a dosage of 190 mg/kg fully meets these requirements.

The use of the Chimec EP-D plus additive package in diesel fuel at a dosage of 190 mg/kg allows you to reduce the volume of foam formed by 55% from 110 to 50 ml and reduce the time of foam deposition by 6.7 times from 40 to 6 s. When determining the oxidative stability, it was established that the base fuel has a high oxidative stability with a significant margin compared to the standardized level. With the introduction of 150 mg/kg of Keropur® DP ENERGY or Chimes EP-D plus in the amount of 190 mg/kg, this indicator is additionally reduced by 44%.

6 Conclusions

The use of multifunctional additive packages for diesel fuel allows you to maintain the cleanliness of the engine fuel injection system at the required technical level. At the same time, the level of emissions of harmful substances in exhaust gases—soot, unburned hydrocarbons, carbon monoxide and nitrogen oxides is significantly reduced, as well as diesel fuel consumption and, accordingly, the release of carbon dioxide are reduced by 2–5%. According to the results of the conducted studies, the high efficiency of both additives was established.

References

1. Nascimento, L., Ribeiro, A., Ferreira, F., Valerio, N., Pinheiro, V., Araújo, J., Vilarinho, C., Carvalho, J.: Turning waste cooking oils into biofuels—valorization technologies: a review. Energies, **15** (2022).https://doi.org/10.3390/en15010116
2. Teixeira, M.R., Nogueira, R., Nunes, L.M.: Quantitative assessment of the valorisation of used cooking oils in 23 countries. Waste Manag. **78**, 611–620 (2018)
3. Foster, W., Azimov, U., Gauthier-Maradei, P., Molano, L.C., Combrinck, M., Munoz, J., Esteves, J.J., Patino, L.: Waste-to-energy conversion technologies in the UK: processes and barriers—a review. Renew. Sustain. Energy Rev. **135**, 110226 (2021)
4. Koul, B., Yakoob, M., Shah, M.P.: Agricultural waste management strategies for environmental sustainability. Environ. Res. 112285 (2021)
5. El-Araby, R., Abdelkader, E., El Diwani, G., Hawash, S.I.: Bio-aviation fuel via catalytic hydrocracking of waste cooking oils. Bull. Natl. Res. Cent. **44**, 177 (2020)
6. European Biomass Industry Association. https://www.eubia.org/. Accessed 1 Oct 2022

7. Lau, P.C., Kwong, T.L., Yung, K.F.: Effective heterogeneous transition metal glycerolates catalysts for one-step biodiesel production from low grade non-refined Jatropha oil and crude aqueous bioethanol. Sci. Rep. **6**, 23822 (2016). https://doi.org/10.1038/srep23822
8. Energy Efficiency & Renewable Energy, Biofuel Basics-Biofuel Basics Bioenergy Technologies Office. https://www.energy.gov/eere/bioenergy/biofuel-basics. Accessed 5 Oct 2022
9. Vipper, A.B., Yevdokimov, A.Y.: Diesel fuels based on vegetable raw materials abroad. Oil Refin. Petrochem. **6**, 11–14 (2004)
10. Iakovleva, A., Boichenko, S., Gay, A.: Cause-effect analysis of the modern state in production of jet fuels. Chem. Chem. Technol. **8**(1), 107–116 (2014). https://doi.org/10.23939/chcht08.01.107
11. Merezhko, N., Tkachuk, V., Komakha, V., Rechun, O., Kovalska, L.: Optimization of diesel fuel composition with bio-component and functional additives. Lect. Notes Mech. Eng. (2021). https://doi.org/10.1007/978-3-030-77823-1_35
12. Tang, H, Salley, S.O., Simon, N.K.Y.: Fuel properties and precipitate formation at low temperature in soy-, cottonseed-, and poultry fat-based biodiesel blends. Fuel **87**, 3006–3017 (2008).https://doi.org/10.1016/j.fuel.2008.04.030
13. Natthida, N., Nattapong, T., Apanee, L.: Partial hydrogenation of palm oil-derived biodiesel over Pd/C catalysts. Int. J. Adv. Sci. Eng. Tech. **4**, 195–200 (2016)
14. Iakovlieva, A., Vovk, O., Boichenko, S., Lejda, K., Kuszewski, H.: Physical-chemical properties of jet fuel blends with components derived from rapeseed oil. Chem. Chem. Technol. **10**(4), 485–492 (2016). https://doi.org/10.23939/chcht10.04.485
15. Derick, A., Meia, D., Zuoa, L., Zhanga, Q., Wangb, J.: A review on partial hydrogenation of biodiesel and its influence on fuel properties. Fuel **251** (2019). https://doi.org/10.1016/j.fuel.2019.04.036
16. Bezergianni, S., Voutetakis, S., Kalogianni, A.: Catalytic hydrocracking of fresh and used cooking oil. Ind. Eng. Chem. Res. **48**, 8402–8406 (2009)
17. Bezergianni, S., Kalogianni, A.: Hydrocracking of used cooking oil for biofuels production. Bioresour. Technol. **100**, 3927–3932 (2009)
18. Oil and petroleum products—a statistical overview. https://ec.europa.eu/eurostat/statisticsexplained/index.php?title=Oil_and_petroleum_products_-_a_statistical_overview. Accessed 5 Oct 2022
19. Fiore, A., Romanazzi, G., Leonelli, C., Mastrorilli, P., Dell'Anna, M.: Partial hydrogenation of soybean and waste cooking oil biodiesel over recyclable-polymer-supported Pd and Ni nanoparticles. Catalysts **12**, 506 (2022)
20. Tkachuk, V.: Study of operational properties of diesel fuel with bioadditives. Commod. Bull. **13**, 244–255 (2020)
21. Boichenko, S., Zubenko, S., Konovalov, S., Yakovlieva, A.: Synthesis of Camelina oil ethyl esters as components of jet fuels. East.-Eur. J. Enterp. Technol. **1**(6(103)), 42–49 (2020). https://doi.org/10.15587/1729-4061.2020.196947
22. Technical regulation on requirements for automobile gasoline, diesel, marine and boiler fuels. https://zakon.rada.gov.ua/laws/show/927-2013-%D0%BF. Accessed 10 Dec 2022
23. Merezhko, N., Tkachuk, V., Romanchuk, V.: Improvement of operational properties of diesel fuels with additives of different manufacturers. Bull. Lviv. Univ. Trade Econ. **23**, 11–18 (2020)
24. EN 590: 2009. Disel fuel. Euro. Specifications. http://docs.cntd.ru/document/1200108413. Accessed 09 Dec 2022

The Study of Intermolecular Interactions in Bio-Jet Fuel and Substantiation of Its Influence on Fuel Properties

Anna Yakovlieva, Sergii Boichenko, Peter Korba, and Pavol Kurdel

1 Introduction

Modern aviation is one of the main consumers of non-renewable hydrocarbon feedstock in the form of aviation gasoline and jet fuels. Due to the rapid development of the aviation industry, it is important to improve the energy efficiency of fuel and reduce aircraft emissions [1]. Today, in accordance with the state policy of the leading countries of the world in the fuel and energy industry, the organization of alternative motor fuels use, in particular aviation fuel, from renewable feedstock is one of the priority tasks.

It is well known that the aviation industry causes significant damage to the environment because the products of fuel combustion are a source of atmospheric pollution. In addition, the emission of CO_2 and other greenhouse gases makes a significant contribution to global climate change [2]. A set of guiding documents of leading world organizations is devoted to the problem of aircraft emissions. They establish the requirements for continual reduction of CO_2 emissions by 1.5% per year on average with the aim to reduce carbon emissions by 50% by 2050 in comparison with 2005 [1–3].

Among the existing today variety of alternative aviation fuels, preference is given to those derived wholly or partially from renewable feedstock—biofuels. The use of fuels from renewable feedstock has a number of advantages, in particular their natural origin, provision of the closed carbon cycle during the production and use and, therefore, the reduction of CO_2 emissions into the atmosphere, the ease of fuel biodegradation in the environment, availability of the feedstock in different

---

A. Yakovlieva (✉) · P. Korba · P. Kurdel
Technical University of Kosice, Kosice, Slovakia
e-mail: anna.yakovlieva@tuke.sk

S. Boichenko
National Technical University of Ukraine “Igor Sikorsky Kyiv Polytechnic Institute”, Kyiv, Ukraine

S. Boichenko et al. (eds.), *Modern Technologies in Energy and Transport*, Studies in Systems, Decision and Control 510, https://doi.org/10.1007/978-3-031-44351-0_11

regions, and minimizing the adverse impact on environment during fuel storage and transportation [2, 3].

One of the types of aviation biofuels, which are actively studied today, is a bio-jet fuel that is a blend of conventional jet fuel and bio-additives produced from plant oils [3, 4]. According to studies by [5, 6] there is a variety of oil feedstock, which can be used for bio-additives production: rapeseed, sunflower, camelina oil, jatropha, used cooking oil, animal fats in the form of food industry waste, etc. The choice of feedstock usually depends on its availability in the certain region or country and physical–chemical properties of oil. Supply of the feedstock for bio-jet fuels production shouldn't compete with the needs of food industry. Bio-additives are usually produced through the process of esterification of oils with various alcohols (methanol, ethanol, butanol, etc.) and further vacuum distillation. These processes are well-described in works [1, 6].

During the previous studies [3, 6–8] the authors fulfilled a series of experimental researches aimed on analysis of the basic physical–chemical properties of the bio-jet fuels Within these studies the bio-jet fuels based on methyl and ethyl esters of rapeseed and camelina oils were analyzed by the parameters of density, viscosity, fractional composition and freezing point of the fuel [6, 7]. The results have shown a good level of compatibility of conventional jet fuel and bio-additives, satisfactory physical–chemical properties of bio-jet fuels, which correspond to requirements of standard specifications and improvement of certain operation properties. The results have also shown a need in further studies, which should be devoted to optimization of some physical–chemical properties of bio-jet fuels [7, 8]. Another important issue, is possibility to use new type of feedstock—including both, oils and alcohols. Using of new types of renewable feedstock for bio-additives production may contribute to improvement of physical–chemical and operation properties of bio-jet fuels and provide more of feedstock availability.

This article is presented as a continuation of previously fulfilled studies. The main purpose of the work is to determine the nature and role of intermolecular interaction in the system "hydrocarbon jet fuel—fatty acid esters" to explain the mechanism of interaction and substantiate the influence of bio-additives on the physical–chemical properties of bio-jet fuels. Within this study the following bio-additives were analyzed: rapeseed oil fatty acid methyl esters (RO FAME), rapeseed oil fatty acid ethyl esters (RO FAEE), camelina oil fatty acid ethyl esters (CamO FAEE), palm-kernel oil fatty acid ethyl esters (PKO FAEE) and coconut oil fatty acid ethyl esters (CocO FAEE).

2 Analysis of Hydrocarbon Composition of Conventional Jet Fuel and Fatty Acid Composition of Bio-Additives

From the studies by [1, 4] and other researchers it is known that conventional jet fuels are derived from crude oil by straight-run distillation. They are kerosene-gasoil fraction, which boils in a range 140–250 (280) °C and is composed mainly of paraffinic, naphthenic and some amount of aromatic hydrocarbons C5–C16 [1, 5], which is explained by the natural composition of crude oil which is used for production. Depending on the origin of crude oil the ratio of hydrocarbons in fuel may vary in some range.

Fatty Acid Composition of Bio-Additives

Based on the results of the previous authors' researches the comparative analysis of chemical composition (fatty acids composition) of bio-additives used for bio-jet fuel production was developed (Table 1) [6–8].

Data in Table 1 show the content (%, mas.) of each individual fatty acid found in samples of bio-additives. Fatty acid composition of RO FAME, RO FAEE, and CamO FAEE were determined and studied during the previous researches [6–8]. At the same time fatty acid composition of CocO FABE and PKO FAiBE were analyzed for the first time and are also presented in the table for the comparative analysis. The table also contains data about the heat of evaporation ($\Delta H_{\text{evap.}}$) of each of the compounds. Values of the heat of evaporation are individual for each of the compounds and are taken from certain reference literature [9]. Values of $\Delta H_{\text{evap.}}$ will be used for further analysis of intermolecular interactions in the bio-jet fuel.

3 Theoretical Fundamentals of Intermolecular Interactions, Which Can Occur Between Hydrocarbons and Fatty Acids Esters in Bio-Jet Fuel

To study and establish the regularities of the influence of the bio-additives obtained from different plant oils on the physical–chemical properties of petroleum jet fuel, it is necessary to carry out a detailed analysis of the mechanisms of compounding (blending) of jet fuels and bio-additives, as well as the nature of the intermolecular interaction in the system "hydrocarbon fuel—fatty acid esters". Today there is a number of studies is devoted to the questions of fatty acid esters production, analysis, and influence on fuel properties. However, the issue of intermolecular processes and interactions, which take place in blended petroleum fuel, and jet fuel in particular, is insufficiently covered in the modern scientific literature.

Table 1 Fatty acid composition of samples of bio-additives

Fatty acid	Short name	RO FAME		RO FAEE		CO FAEE		PKO FAEE		CocO FAEE	
		Content, %	ΔH_{evap}, kJ/mol	Content, %	ΔH_{evap}, kJ/mol	Content, %	ΔH_{evap}, kJ/mol	Content,	ΔH_{evap}, kJ/mol	Content, %	ΔH_{evap}, kJ/mol
Hexanoic	C6:0	–	–	–	–	–	–	0.8	40.4	–	–
Caprylic	C8:0	–	–	–	–	–	–	19.4	44.4	2.9	44.4
Decanoic	C10:0	–	–	–	–	–	–	7.7	47.9	3.2	47.9
Lauric	C12:0	–	–	–	–	–	–	53.1	50.7	47.1	50.7
Myristic	C14:0	–	–	–	–	–	–	17.4	53.5	16.4	53.5
Palmitic	C16:0	6.0	57.5	6.6	58.6	5.7	58.6	4.7	58.6	8.9	58.6
Stearic	C18:0	1.9	60.1	2.6	60.1	2.5	60.1	1.7	60.1	2.4	60.1
Oleic	C18:1	52.6	59.6	20.0	63.5	48.4	63.5	2.0	63.5	14.3	63.5
Linoleic	C18:2	21.1	62.1	29.6	63.7	30.6	63.7	0.6	63.7	2.5	63.7
Linolenic	C18:3	7.2	61.1	24.5	62.2	9.0	62.2	–	–	–	–
Arachidic	C20:0	0.45	62.2	1.1	61.6	0.4	61.6	–	–	–	–
Eicosenoic	C20:1	1.25	65.3	9.7	67.0	0.8	67.0	–	–	–	–
Heneicosanoic	C21:1	4.2	63.6	–	–	–	–	–	–	–	–
Eicosadienoic	C20:2	–	–	1.3	64.7	–	–	–	–	–	-
Behenic	C22:0	0.23	64.9	–	–	–	–	–	–	–	–
Erucic	C22:1	2.5	67.7	0.9	69.3	0.4	69.3	–	–	–	–
Others		2.57	–	3.7	–	1.2	–	1.6	–	2.3	–

Thus, the works [10, 11] provide data on the solubility of triacylglycerides of vegetable oils in some polar solvents. The works of scientists [12, 13] provide data on the solubility of biodiesel and diesel fuels in various organic solvents. However, information on the mutual solubility of fatty acids esters and hydrocarbons of kerosene-gasoil fractions of oil refining (jet fuels) is not presented in the modern literature. Accordingly, this issue requires study, analysis, and substantiation.

Samples of bio-jet fuels can be considered at the macro level as a two-component system, in which each of the components (petroleum jet fuel and bio-additives) are in the liquid state under normal conditions. At the same time, at the micro level the bio-jet fuel is a multicomponent system, which includes paraffinic, naphthenic, aromatic hydrocarbons, saturated and unsaturated fatty acid esters [14].

In order to study and analyze the processes of compounding (blending) of hydrocarbon fuels and fatty acid esters the fundamentals of physical chemistry: the processes of intermolecular interaction, colloidal chemistry and solution theory were applied [11].

It is well-known that dissolution is a complex physical and chemical process [10, 14]. According to physical theory [14, 15], dissolution is the uniform distribution of dissolved substance particles throughout the solvent volume. According to the chemical theory [14, 15], solutions are systems formed by particles of the solvent, dissolved substance, and unstable chemical compounds formed between them by hydrogen bonds or electrostatic forces of interaction. The modern theory of solutions considers the dissolution process as an interaction between particles of different polarity [15].

It is known from the works [12–14] that the dissolution (mixing) of substances is based on the solvation process—the interaction of solvent particles with the particles of the dissolved substance. In the dissolution process, part of the energy is released as a result of breaking the bonds between the molecules of the dissolved substance, and part is absorbed during the formation of new bonds between the molecules of the solvent and the dissolved substance. That is, the dissolution process is determined by intermolecular interaction of the system components. Van der Waals forces and hydrogen bonds belong to intermolecular interactions [15].

To analyze the process of dissolution of the fatty acid esters in the hydrocarbon fuel it is necessary to establish the presence and role of these forces between the molecules of the esters. As it is known, ester molecule is a fatty acid radical with carbonyl group -C = O, conjugated by hydroxyl oxygen atom with alcohol radical (Fig. 1) [6].

The presence of oxygen atoms indicates the ability of molecules to form hydrogen bonds. Thus, these molecules can be hydrogen bond acceptors. At the same time, hydrogen atoms in ester molecules are bound by strong covalent bonds with carbon atoms in acid and alcohol radicals and can't be hydrogen bond donors [15]. It follows

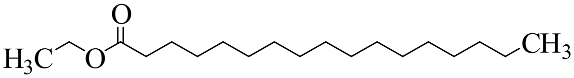


Fig. 1 Molecule of the typical fatty acid ester

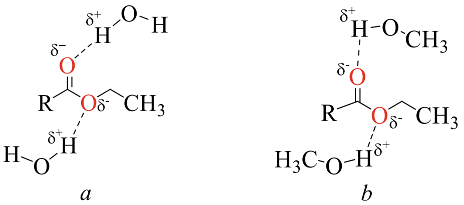


Fig. 2 Intermolecular interaction of esters molecules with low carbon number with water (**a**) and alcohol (**b**) via hydrogen bonds

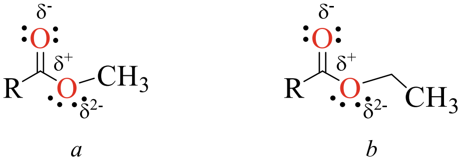


Fig. 3 Induction effect and shift in atoms' charges in a—FAME and b—FAEE

that hydrogen bonds are not formed between the fatty acid esters molecules, and the molecules are not capable of mutual association through hydrogen bonds.

Ester molecules can form hydrogen bonds only with other molecules, being acceptors of such bonds. This explains the solubility of esters with the number of carbon atoms in acyl residues up to 5 in water and alcohols, in polar molecules in which hydrogen atoms interact with electronegative oxygen atoms (Fig. 2). However, as the length of the hydrocarbon chain increases, the solubility of esters in polar solvents decreases.

Hydrogen bonding is a particular case of dipole–dipole or orientational Van der Waals interaction. The basis of the orientational interaction (Kizome forces) is the ability to orient one molecule relative to another with charges opposite in sign [15].

The electronegativity of oxygen atoms (3.5) in a molecule is greater than the electronegativity of carbon (2.5). Undivided pairs of oxygen electrons shift the electron density of neighboring carbon atoms, acquiring partially negative charge (induction effect). In turn, the carbonyl carbon atom acquires a partially positive charge (Fig. 3).

As a result, the ester molecule becomes polar and has a constant electric dipole moment. This peculiarity of the structure of the fatty acid ester molecules explains their ability to orientation interaction.

An ester molecule consists of two parts: a polar hydrophilic part and a nonpolar hydrophobic one. Accordingly, the hydrophilic part of the molecule has the ability to orientation interaction [14]. At the same time, acyl radicals are nonpolar (hydrophobic) and orientation interaction is not typical to them. Dispersive interaction forces (London forces) arise between them. These forces arise due to the appearance of instantaneous dipoles as a result of the shift in the electron density of electron shells that are in constant motion relative to the nuclei [14, 17]. The constant motion of the electrons leads to an asymmetric redistribution of charges in the molecules, and instantaneous dipoles arise in the particles. Thus, nonpolar molecules can become polar for a moment. In general, the dispersion interaction depends on the deformation ability of the molecules and the distance between them.

Fig. 4 Spatial electrostatic model of fatty acid ester molecule

In the spatial electrostatic model of the molecule (Fig. 4) one can see its polar part, where the accumulation of negative charge is shown in red and positive charge in blue. The nonpolar acyl radical is shown in green.

Placed in space, ester molecules are oriented by opposite charge signs, and dipole–dipole bonds are formed between the polar parts of the molecule. Dispersive interaction forces arise between hydrophobic acyl radicals. The longer the radical, the larger the area of its contact and, consequently, the area for the formation of dispersion interaction forces. It follows that as the length of the hydrocarbon chain increases, the force of intermolecular interaction increases. Importantly, as the length of the hydrocarbon chain increases, dispersion interaction forces begin to dominate over orientation forces, and the ester molecule acquires hydrophobic properties. This is revealed by loose of ability to dissolve in polar solvents [16, 18].

The presence of double bonds in acyl radicals of esters has a significant effect on their intermolecular interactions and, accordingly, on the physical–chemical properties of esters. The angle of the valent double bond between the carbon atoms is 120° compared to the angle of a single bond (110°), which makes the shape of the molecule more curved. The distance between the "curved" acyl radicals with one or several double bonds is greater than in the case of straight (saturated) ones. This contribute to weakening of the forces of dispersion interaction between the molecules [12, 14, 16].

In addition to the orientation and dispersion interactions between ester molecules, an inductive interaction can occur: the non-polar parts of the molecule are polarized under the action of the electric field of the polar part of the molecule and acquire an induced dipole moment.

Summarizing the above mentioned it can be concluded that the forces of dispersion interaction between ester molecules prevail. The dispersion interaction energy can be expressed by the London formula [14, 15]:

$$E_{disp} = -\frac{3I}{4}\frac{\alpha^2}{d^6}, \tag{1}$$

where I—ionization energy of the molecule; α—coefficient representing the polarization ability of molecules; d—distance between the moment dipoles.

Formula (1) shows that as the polarization ability α increases, i.e. as their size of the molecules increases, their dispersion interaction energy also increases. At the same time, the ionization energy *I* of ester molecules changes insignificantly with the increase of their linear size [14, 17] and, in general, does not affect the disperse interaction energy. Quantitative values of size of the molecules [9] for fatty acids methyl and ethyl esters are given in Table 2. Therefore, we may expect the rise of polarization ability and energy of dispersion interaction with the increasing of molecules size.

Hydrocarbons of jet fuels can be conditionally divided into two groups: non-polar and non-polar, but capable of polarization—paraffin-naphthenic and aromatic hydrocarbons respectively. Some paraffins as well as naphthenes can give an insignificant reduced dipole moment [10, 17].

The spatial electrostatic models of typical molecules of hydrocarbon jet fuel and fatty acids esters of rapeseed oil are shown in Table 3. Hydrocarbon molecules have smaller sizes compared to ester molecules, correspondingly smaller polarization ability and dispersion interaction energy.

Basing on the analyzed literature and data it has been established that during the process of blending of hydrocarbon jet fuel and fatty acids esters the mutual mixing of components takes place. This mixing occurs under the influence of induction and dispersion forces of Van der Waals interaction, among which the dispersion component prevails. As the proportion of esters in the system ‘hydrocarbon jet fuel—fatty acid esters’ increases, an increase in intermolecular interaction is observed. This is evidenced by an increase in the evaporation heat of its components [9] (Table 4).

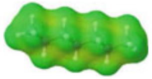
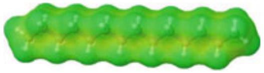
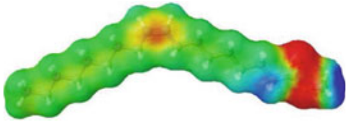
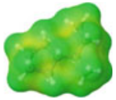
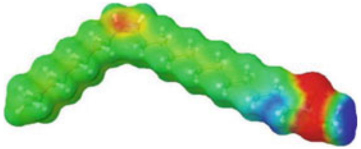
This is explained by an increase in the proportion of the dispersion component in the total intermolecular interaction as a result of an increase in the polarizability of the system molecules. Induction interaction in the system occurs due to polarization by carboxyl groups of naphthenic and aromatic hydrocarbons esters of jet fuels.

The energy of the system decreases by 31–69.3 kJ/mol as the proportion of esters in the hydrocarbon fuel—fatty acid esters system increases. Reduction of the total energy in the system has a direct influence on the physical–chemical properties of bio-jet fuels blended with fatty acids esters.

Table 2 Ability to polarization of fatty acid esters expressed as a molecule size [9]

The ability to polarization, α						
Methyl	–	–	$C_{17}H_{34}O_2$	$C_{19}H_{38}O_2$	$C_{21}H_{40}O_2$	$C_{23}H_{44}O_2$
esters	–	–	$32.7 \cdot 10^{-24}$cm^3	$36.4 \cdot 10^{-24}$cm^3	$40.1 \cdot 10^{-24}$cm^3	$43.8 \cdot 10^{-24}$cm^3
Ethyl	$C_{14}H_{30}O_2$	$C_{16}H_{32}O_2$	$C_{18}H_{36}O_2$	$C_{20}H_{40}O_2$	$C_{22}H_{42}O_2$	$C_{24}H_{46}O_2$
esters	27.2 10^{-24}cm^3	30.9 10^{-24}cm^3	$34.6 \cdot 10^{-24}$cm^3	$38.2 \cdot 10^{-24}$cm^3	$41.9 \cdot 10^{-24}$cм^3	$45.6 \cdot 10^{-24}$cm^3

Table 3 Comparative view of spatial electrostatic models of molecules of jet fuel and fatty acid esters

Hydrocarbon jet fuel		Fatty acid esters	
Compound	Spatial electrostatic models of the compound	Compound	Spatial electrostatic models of the compound
Paraffins		Saturated esters	
Heptane		Methyl-palmitate	
Tetradecane		Ethyl-stearate	
Naphthenes		Non-saturated esters with one double bond	
Trimethylcyclopentane		Methyl-oleate	
Secbuthylcyclopentane		Methyl-erucate	

(continued)

Table 3 (continued)

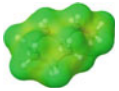
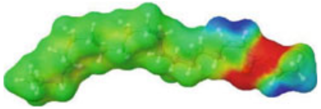
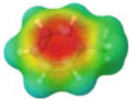
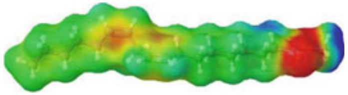
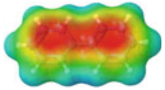
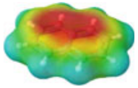
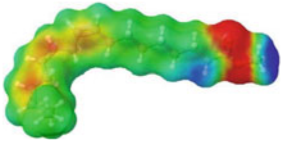
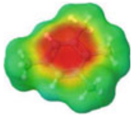
Hydrocarbon jet fuel		Fatty acid esters	
Compound	Spatial electrostatic models of the compound	Compound	Spatial electrostatic models of the compound
Ethylcyclohexane		Ethyl-eicosenoate	
Aromatics		Non-saturated esters with two double bonds	
Toluene		Methyl-linolate	
Biphenyl		Non-saturated esters with three double bonds	
Naphthalene		Methyl-linolenate	
Tetramethylbenzene			

Table 4 Heat of evaporation, ΔH of components of bio-jet fuels [9]

Type of molecules	Heat of evaporation, ΔH		
	Jet fuel hydrocarbons	Methyl esters	Ethyl esters
Heat of evaporation, ΔH, kJ/mol	31.0–47.0	57.5–67.7	40.4–69.3

Table 5 Physical–chemical properties of conventional jet fuel and bio-additives

Property	Jet fuel	Bio-additives				
		RO FAME	RO FAEE	CO FAEE	PKO FAEE	CocO FAEE
Density at 20 °C, kg/m^3	792.0–794.0	880.38	873.22	871.13	860.4	866.92
Viscosity at 20 °C, mm^2/s	1.50–1.58	6.734	7.355	6.422	4.546	4.041
Freezing point, °C	Minus 59–minus 60	Minus 19	Minus 18.5	Minus 7	Minus 13	Minus 12

4 Experimental Analysis of the Influence of Intermolecular Interactions on Some Physical–Chemical Properties of Bio-Jet Fuels

In order to substantiate the influence of intermolecular interactions on properties of bio-jet fuels the experimental study of some of the basic physical–chemical properties has been done. For the study the set of sample of bio-jet fuels were prepared. Each of the bio-additives (RO FAME, RO FAEE, CO FAEE, PKO FAEE and CocO FAEE) were blended with conventional jet fuel in quantity 10%, 20%, 30%, 40% and 50%. Conventional jet fuels of grade Jet A-1 with no bio-additives content was studied as a reference fuel. Such properties as density, kinematic viscosity and freezing point were chosen for the investigation. These properties are determined and substantiated by the chemical composition of fuel and structure of fuel's molecules. Therefore, research and analysis of these of bio-jet fuel properties allows understanding the degree of influence of intermolecular interactions and processes, which take place in fuels.

Table 5 summarizes the values of basic physical–chemical properties of bio-additives samples and conventional jet fuel used during the experiment. These data allow analyzing and understanding the differences in properties basing on research of their structure and composition.

Data in Table 5 shows that quantitative values of density, viscosity and freezing point of bio-additives significantly differ from conventional jet fuel. Typically, density of the fuel depends on its chemical and fractional composition. All the studied bio-additives possess much higher density values comparing to the density of conventional JF.

It is explained by its chemical structure. Unlike hydrocarbons of conventional JFs, which contain 5–16 carbon atoms, acyl radicals of ester molecules contain a wider range of molecules, usually with 8–22 carbon atoms or even more, depending on the feedstock. This is the reason of a strong dispersion interaction forces between them and, consequently, higher density compared to jet fuel.

Influence of Intermolecular Interactions on Density of Bio-Jet Fuels

From Table 5 it may be seen that density of different bio-additives significantly varies (860.4–880.38 kg/m^3). This is explained by the fatty acid composition and content of each of the bio-additive. From Table 1 it is seen that RO FAME and FAEE contain molecules with 16–22 carbon atoms in fatty acids radicals. Moreover, about 90% of all molecules are esters of fatty acids with 16, 18 and 20 carbon atoms (palmitic, oleic, linoleic, linolenic, and eicosenic acids). CO FAEE contains mostly esters of palmitic, oleic, linoleic and linolenic acids (C16–C18). Such content of high-molecular esters results in high values of density. At the same time PKO FAEE and CocO FAEE are composed of molecules with lower carbon number (C8–C18), additionally, PKO FAEE contains some amount of C6 molecules. The weaker intermolecular interaction may be supposed in this case and this results in lower density values (860.4–866.92 kg/m^3).

Next, the density of bio-jet fuels with different content of bio-additives was studied (Fig. 5). The density of the bio-jet fuel samples increases with the increase in the content of bio-additives. For all the samples the change of density has an additive character, and is represented by a straight line. The rise in density values is explained by the increased effect of the forces of dispersion interaction between hydrocarbon molecules and acyl radicals of esters, on the one hand, and the emergence of forces of induction interaction between hydrocarbons of the jet fuel and carboxyl groups of esters, on the other. As it was mentioned, acyl radicals of ester molecules contain higher number of carbon atoms, which leads to high values of the interaction energy between ester molecules and, accordingly, their density. At the same time, samples of bio-jet fuels with PKO FAEE and CocO FAEE have lower density values compared to bio-jet fuels with RO FAME, RO FAEE and CO FAEE, are closer to values typical to jet fuels.

Influence of Intermolecular Interactions on Kinematic Viscosity of Bio-Jet Fuels

The viscosity of fuels is the average value of the viscosities of all its components. The viscosity of hydrocarbon jet fuels depends on the structure of the molecules,

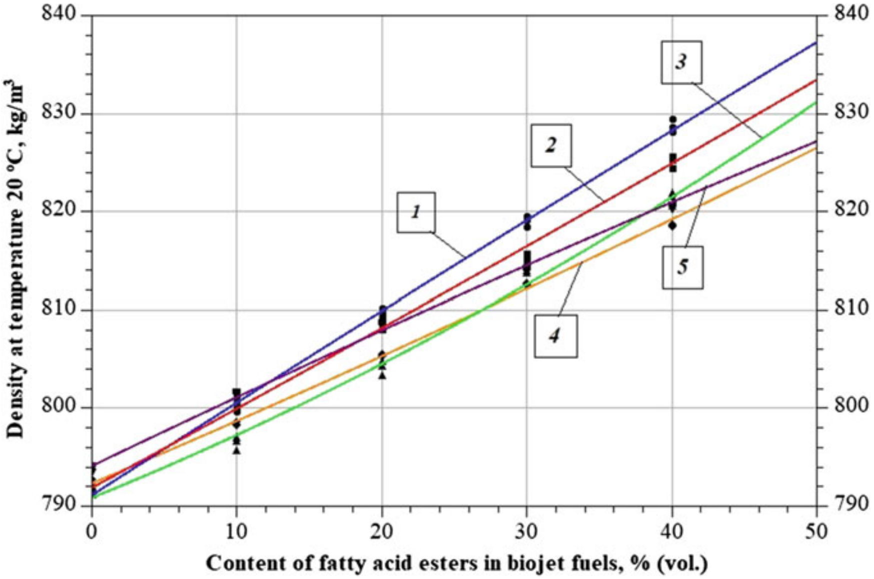


Fig. 5 Dependence of density of bio-jet fuel on the content of bio-additives: *1*—RO FAME, *2*—RO FAEE, *3*—CO FAEE, *4*—PKO FAEE, *5*—CocO FAEE

their interaction and, to a small extent, on their molecular weight. From Table 5 it may be seen that viscosity values of bio-additives (4.041–6.734 mm^2/s) significantly differ from the viscosity of conventional jet fuel (1.50–1.58 mm^2/s).

The reason for this, as mentioned above, is chemical structure of fatty acid esters. The length of the fatty acid radicals determines the large size of the compounds, which leads to a higher energy of their intermolecular interaction. Viscosity, like density, is a property that can be used to characterise the forces of intermolecular interaction in a liquid quite accurately. The higher the energy of intermolecular interaction of fuels, the higher their viscosity. Hydrocarbon molecules do not contain carboxyl groups in their composition and are characterised by much smaller sizes, as a result only dispersion forces act between them, the energy of which is much lower than that of ester molecules.

In addition, from Table 5 it may be seen that PKO FAEE and CocO FAEE have lower values of viscosity compared to RO FAME, RO FAEE, and CO FAEE. Referring to the Table 1 it is seen that RO and CO esters are composed of long-chain esters with 16–22 carbon atoms, while PKO and CocO contain molecules with 8–18 carbon atoms. Due to this, forces of intermolecular interactions in PKO and CocO bio-additives are weaker, and, consequently, viscosity is lower. Moreover, RO and CO bio-additives with approximately 80% composed of esters of unsaturated fatty acids with one and two double bonds, which additionally increases their viscosity. On the contrary, PKO bio-additive contains only about 3% of unsaturated fatty acids

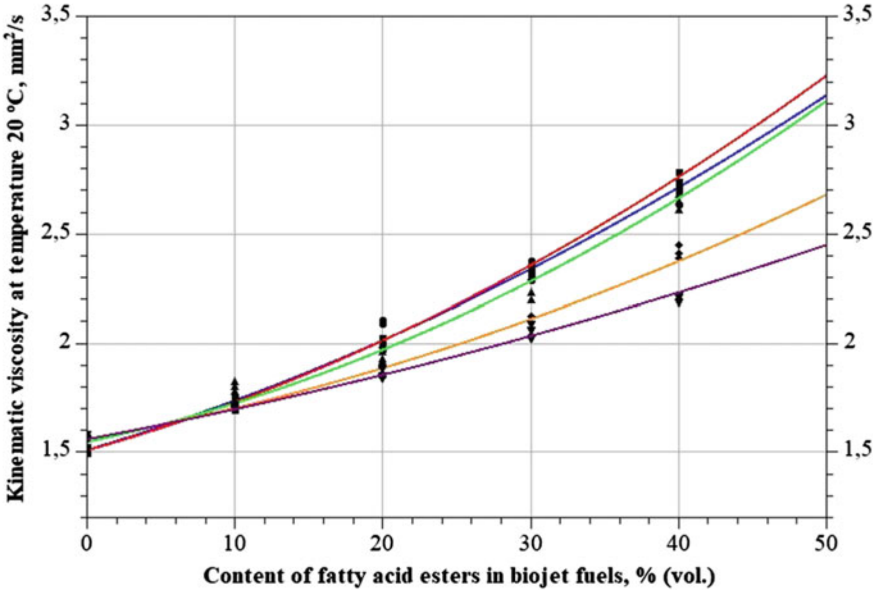


Fig. 6 Dependence of kinematic viscosity of bio-jet fuel on the content of bio-additives: *1*—RO FAME, *2*—RO FAEE, *3*—CO FAEE, *4*—PKO FAEE, *5*—CocO FAEE

and CocO bio-additive—about 17%, which much lower compared to RO and CO esters.

Next, the kinematic viscosity of bio-jet fuels with different content of bio-additives was studied (Fig. 6). It was found that increasing of content of bio-additives in bio-jet fuels results in rising of kinematic viscosity. This phenomenon may be explained by the strengthening of intermolecular interaction forces between hydrocarbon molecules and ester molecules.

It is also seen from Fig. 7 that samples of bio-jet fuels with PKO FAEE and CocO FAEE have lower kinematic values compared to bio-jet fuels with RO FAME, RO FAEE and CO FAEE, and are closer to values typical to conventional jet fuels.

Influence of Intermolecular Interactions on Freezing Point of Bio-Jet Fuels

All of the studied bio-additives based on RO, CO, PKO and CocO have significantly higher values of freezing point compared to conventional jet fuel (Table 5). Such high freezing points of bio-additives are explained by the chemical structure of the molecules and the van der Waals forces that exist between them. The length of the hydrocarbon chain (C8–C22) determines the large size of the compounds, due to

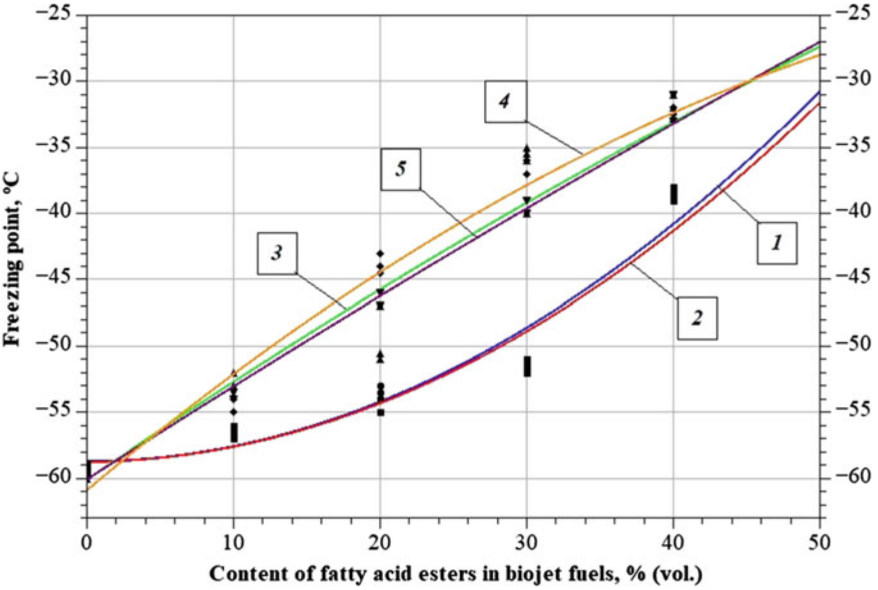


Fig. 7 Dependence of freezing point of bio-jet fuel on the content of bio-additives: *1*—RO FAME, *2*—RO FAEE, *3*—CO FAEE, *4*—PKO FAEE, *5*—CocO FAEE

which the energy of the bonds between the molecules is much higher compared to the conventional jet fuels.

Due to the existence of intermolecular interaction forces, the rate of chaotic movement of fatty acids esters molecules is negligible. As the temperature decreases, their association increases rapidly: on the one hand, due to a decrease in the thermal motion of the molecules, which weakens the bonds between them, and on the other hand, due to a decrease in the mobility of the esters molecules that “interconnect” with each other. With a further decrease in temperature, the viscosity becomes so high that the esters solidify and lose their mobility.

The structure of the bio-additive molecules has a certain influence on the pour point. The presence of double bonds in ester molecules makes their shape curved, which makes it difficult to place them tightly together. The results of the study showed that blending jet fuels with bio-additives increases its freezing point (Fig. 7). At a concentration of bio-additives up to 30% (by volume), their effect on the freezing point is relatively insignificant. At low concentrations of bio-additives, they are evenly distributed in the volume of conventional jet fuel and are at distances insufficient for their interaction. With a further increase in the ester content, the solidification temperature increases and gradually approaches the values typical for pure fatty acid esters.

To explain this effect, the works on the analysis of intermolecular interaction and properties of petroleum products [10, 14] were used. As the content of bio-additives in the bio-jet fuel increases above 30%, the content of relatively large ester molecules becomes sufficient for their association: on the one hand, due to the action of physical forces of attraction, and on the other hand, due to the "adhesion" or "engagement" of molecular chains. A special role in the process of "engagement" is played by unsaturated ester of curved shape. Thus, the associated ester molecules initiate the formation of a structure in the system hydrocarbon jet fuel—fatty acid esters.

From Fig. 7 it may be seen that bio-jet fuels with PKO FAEE and CocO FAEE have higher values of the freezing point compared to RO FAME, RO FAEE, and CO FAEE. The reason for such effect may be explained by the differences in structure of fatty acids radicals. From one side PKO FAEE and CocO FAEE are composed of smaller molecules and weaker forces of interaction should appear between them. However, from the other side, both of these bio-additives are composed mostly of saturated non-curved ester molecules (PKO FAEE—about 93% and CocO FAEE—about 87%). Similar to *n*-paraffins in conventional jet fuels short-chain saturated esters turn into crystals at comparatively high temperatures.

5 Conclusions

The analysis of the nature of intermolecular interactions of fatty acid esters, hydrocarbons of conventional jet fuel and their mixtures allowed to state that during compounding (mixing) of hydrocarbon jet fuel and bio-additives based on fatty acid esters o plant oils, a homogeneous system is formed, in which each of the components is ground to the size of molecules. Interaction between the system components occurs under the action of electrostatic forces of intermolecular interaction (van der Waals forces). In this case, chemical interaction between the system components does not occur. Due to this, hydrocarbon jet fuel is mixed with bio-additives in any ratio and unlimitedly. During the process of storage the absence of stratification of the system is ensured, i.e. the aggregative stability of the fuel is ensured.

Differences in chemical structure of hydrocarbon jet fuel and bio-additives and, therefore, intermolecular interactions appearing between them determine properties of bio-jet fuels. Increasing content of bio-additives in bio-jet fuel leads to rise of the dispersion component in the total intermolecular interaction and graduate reduction of internal energy of the system. This has a direct influence on the physical–chemical properties of bio-jet fuels blended with fatty acids esters. Increasing the content of bio-additives results in rising of fuel density, viscosity and freezing point. Bio-additives based on PKO FAEE and CocO FAEE have molecular composition and weigh, which is closer to composition of conventional jet fuel. Therefore, bio-jet fuels blended with these bio-additives possess properties, which are more similar to properties of hydrocarbon jet fuels.

Acknowledgements This work was supported by the Fellowship for excellent researchers threatened by the conflict in Ukraine (Project code: 09I03-03-V01-00060) within the Slovakia's Recovery and resilience plan Funded by the European Union NextGenerationEU.

References

1. Yakovlieva, A., Boichenko, S., Boshkov, V., Korba, L., Hocko, M.: Experimental study of physical-chemical properties of advanced alcohol-to-jet fuels. Aviation **27**(1), 1–13 (2023). https://doi.org/10.3846/aviation.2023.18564
2. Lee, D.S., Fahey, D.W., Forster, P.M., Newton, P.J., Wit, R.C., Lim, L.L., Owen, B., Sausen, R.: Aviation and global climate change in the 21st century. Atmos. Environ. **43**(22–23), 520–3537 (2009). https://doi.org/10.1016/j.atmosenv.2009.04.024
3. Yakovlieva, A.V., Boichenko, S.V., Zaremba, J.: Improvement of air transport environmental safety by implementing alternative jet fuels. In: MOSATT 2019 – Modern Safety Technologies in Transportation International Scientific Conference*,* Proceedings, 146–151 (2019). https://doi.org/10.1109/MOSATT48908.2019.8944122
4. Dessens, O., Köhler, M.O., Rogers, H.L., Jones, R.L., Pyle, J.A.: Aviation and climate change. Transp. Policy **34**, 14–20 (2014). https://doi.org/10.1016/j.tranpol.2014.02.014
5. Achinas, S., Margry, S., Euverink, G.J.W.: A technological outlook of biokerosene production. In: Applied Biotechnology Reviews, Sustainable Biofuels, pp. 225–246. Academic. https://doi.org/10.1016/B978-0-12-820297-5.00011-6
6. Boichenko, S., Zubenko, S., Konovalov, S., & Yakovlieva, A. (2020). Synthesis of Camelina oil ethyl esters as components of jet fuels. Eastern-Eur. J. Enterprise Techno. **1**(6(103), 42–49. https://doi.org/10.15587/1729-4061.2020.196947
7. Iakovlieva, A., Vovk, O., Boichenko, S., Lejda, K., Kuszewski, H.: Physical-chemical properties of jet fuel blends with components derived from rapeseed oil. Ch&ChT **10**(4), 485–492 (2016). https://doi.org/10.23939/chcht10.04.485
8. Yakovlieva, A., Boichenko, S., Leida, K., Vovk, O., Kuszewski, H.: Influence of rapeseed oil ester additives on fuel quality index for air jet engines. Chem. Technol. Fuels Oils **53**(3), 308–317 (2017)
9. http://www.chemspider.com/
10. Monteiro, R.R.C., da Silva, S.S.O., Cavalcante, C.L., Jr., de Luna, F.M.T., Bolivar, J.M., Vieira, R.S., Fernandez-Lafuente, R.: Biosynthesis of alkanes/alkenes from fatty acids or derivatives (triacylglycerols or fatty aldehydes). Biotechnol. Adv. **61**, 108045 (2022). https://doi.org/10.1016/j.biotechadv.2022.108045
11. Batista, M.M., Guirardello, R.M., Krähenbühl, A.: Determination of the hansen solubility parameters of vegetable oils, biodiesel, diesel, and biodiesel-diesel blends. J. Am. Oil Chem. Soc. **92**, 95–109 (2015). https://doi.org/10.1007/s11746-014-2575-2
12. Beneti, S.C., Priamo, W.L., Lanza, M.: Determination of liquid-liquid equilibrium data for biodiesel containing ternary systems using near infrared technique. Braz. J. Chem. Eng. **30**(01), 23–31 (2013)
13. Yamane, K., Kawasaki, K.: A Study of Polystyrene Solubility in Biodiesel, Biofuels – Status and Perspective, Krzysztof Biernat (Ed.), InTech (2015). https://doi.org/10.5772/59112
14. Yakovlieva, A., Boichenko, S., Lejda, K., Vovk, O.: Modification of Jet Fuels Composition with Renewable Bio-Additives. Center for Education Literature, Kyiv (2019)
15. Fialkov, J.Y.: Physical-Chemical Analysis of Liquid Systems and Solutions, p. 247. Naukova dumka, Kyiv (1992)
16. Li, H., Xia, S., Luo, H., Ma, P.: Experimental and computational study on the compatibility of biodiesel/diesel/methanol blended fuel. Fuel **173**, 52–59 (2016). https://doi.org/10.1016/j.fuel.2016.01.036
17. Holmes, J.L., Lossing, F.P.: Ionization energies of homologous organic compounds and correlation with molecular size. Org. Mass Spectrom. **26**, 537–541 (1991)
18. Karimi-Maleh, H., Rajendran, S., Vasseghian, Y., Dragoi, E.-N.: Advanced integrated nanocatalytic routes for converting biomass to biofuels: a comprehensive review. Fuel **314** (2022). https://doi.org/10.1016/j.fuel.2021.122762

Monitoring the Risks of Microbiological Contamination of Aviation Fuels and Fuel Systems

Iryna Shkilniuk and Nataliia Shevchuk

1 Aviation Fuels as a Factor in Aircraft Flight Safety

Aviation is a factor in the economic success of many countries of the world. Flights have helped develop international trade links and create vital domestic connections that 'stitch' a country together. Accelerating scientific and technological progress, globalization of air transport markets, increased international connectivity and the introduction of the digital economy require continuous monitoring of risks to flight operations and preservation of the infrastructure capacity of air transport to enhance its competitiveness and sustainable development.

The most important part of ensuring the normal operation of aviation is ensuring the safety of ongoing flights.

Aircraft operational safety, together with aviation and environmental safety, is of paramount importance to ensure flight safety. The quality of aviation fuels and lubricants is one aspect of aircraft safety [1]. Generally recognized regulations and requirements have existed and allow for a stable system for maintaining aviation fuel quality and control at every stage of its life cycle.

The reliability and efficiency of aircraft gas turbine engines are highly dependent on the quality of aviation fuels. Operating fluids, including fuels, are complete structural elements of the respective systems from a chemmotologycal point of view. Strict requirements related to reliability, efficiency, and environmental friendliness of aviation transport operations are imposed on aviation fuels used in civil and military aviation.

Low-quality aviation fuels reduce the performance and reliability of aircraft equipment, while higher fuel requirements result in higher fuel prices. Therefore, modern

---

I. Shkilniuk (✉) · N. Shevchuk
National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute", Kyiv, Ukraine
e-mail: i_shkilniuk@ukr.net

S. Boichenko et al. (eds.), *Modern Technologies in Energy and Transport*, Studies in Systems, Decision and Control 510, https://doi.org/10.1007/978-3-031-44351-0_12

aviation fuels and lubricants must meet a number of requirements combining the economy, reliability, and durability of aviation vehicles.

The negative effects of fuel properties are mainly due to uncontrolled changes in its composition and properties caused by variable operating conditions.

One of the strategic safety objectives is to identify and monitor existing aviation safety risks and to develop and implement globally effective and appropriate measures to address emerging risks.

2 Purity and Microbiological Contamination of Motor Fuels

The main link in all civil aviation activities is ensuring flight safety. The most important condition is the use of aircraft within the range of expected operating conditions, taking into account operational constraints. One of these is the appropriate quality of aviation fuel.

Flight safety activities are multifaceted and complex. The main, constituent factor in ensuring flight safety is the interaction between the aviation authorities of the state and the air transport process. The quality assurance of aviation safety, including the occurrence of aviation equipment failures, is a worldwide problem today. ICAO, concerned about the prevailing worldwide trend of contaminated aviation fuel reaching airports, has issued Directive 9977 (Guidelines for the Supply of Aviation Fuels to Civil Aviation). IATA has adopted Standard 1530 (Quality Assurance Requirements for Aviation Fuel Production, Storage and Delivery Systems at Airports). The essence of these documents is that at each stage from the production of aviation fuel to the airport, all parties involved have a shared responsibility to ensure quality, purity and control capability at each point in the production and supply chain.

Fuel purity is an issue in the supply of aviation fuels in vehicles, as well as in the inner cavities of the technological equipment of airfield fuel depots, centralized aircraft refueling systems, and fuel tankers [2]. The purity of fuels is determined by the number of impurities in their composition. Contaminants can be of different natures. Inorganic contaminants are particulates and water. Organic contaminants are residues of other petroleum products, fame. Biological contaminants are microorganisms that require hydrocarbons from fuel to function. The most common contaminants are particulates, water, other petroleum products or their residues, and microbial growth [3, 4].

Sources of contamination of jet fuels are materials and substances in contact with the fuel. Such as:

- Mineral impurities introduced into fuel from refined oil;
- Corrosion products on fuel apparatus parts as well as on process surfaces with which fuel comes into contact during transport or storage;

- Contaminants introduced through the tank breathing system and fuel tank drainage system.

Microorganisms are a specific type of pollution, capable of multiplying and having a complex effect on the habitat, that is the fuel, and the means of using it [5]. More than 150 species of micro-organisms capable of degrading the hydrocarbons that compose aviation fuels have so far been detected and identified [2]. The main representatives of microorganisms are:

1. Anaerobic and aerobic bacteria—Achromobacter, Alcaligenes, Artrobacter, Bacillus, Bacterium, Brevibacterium, Citrobacter, Clostridium, Corynebacterium, Desulfovibrio, Enterobacter, Escherichia, Flavobacterium, Metanobacterium, Micrococcus, Micromonospora, Mycobacterium, Nicrocossus, Pseudomonas, Sarcina, Serratina, Spirillym, Vibrio, Thiobacillus;
2. fungi (or micromycetes)—Alteranga, Aspergillus niger, Aspergillus fumigatus, Hormoconis resinae, Monacus floridanus, Phialophora sp., Cephalosporium, Renicillum;
3. yeasts—Candida, Debaryomyces, Endomycopsis, Hansenula, Rhodotorula, Saccharomyces, Torula, Torulopsis, Trichoderma, Trichosporon.

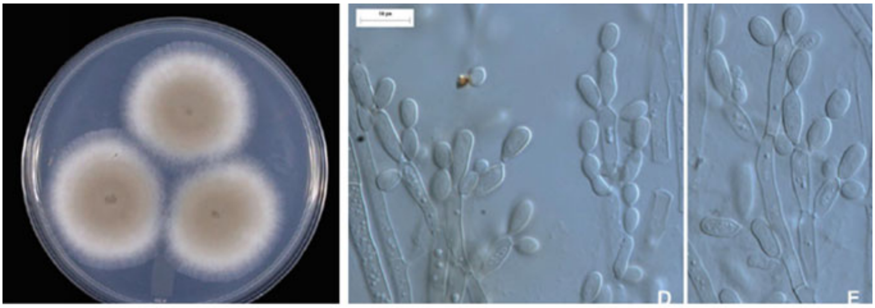
Numerous researchers confirm that among the microorganisms that develop in aviation fuels, fungi are the most common [6, 7]. Fungi are a heterogeneous group of eukaryotic microorganisms that have a core with a core membrane, a cytoplasm with organelles, a cytoplasmic membrane and a strong cell wall. Fungi consist of long thin filamentous fibers (hyphae) with a thickness of 5 μm, which are woven into mycelium Fungi are specific plant organisms that do not have chlorophyll and do not synthesize organic substances. Fungi need ready-made organic substances for their life activity [8].

Hormoconis resinae is an active destructor more commonly found among microorganisms capable of growing in aviation fuels (Fig. 1) [5, 6]. It is also called the "Kerosene fungus". In the natural environment, this fungus inhabits the soils of the subtropical and tropical zone [7]. Research by many scientists confirms the presence of this fungus in aviation fuel samples from Australia, Brazil and California, UK, Denmark, India, Syria, Nigeria, Japan, New Zealand, China. Obviously, the development of aviation and flight geography has contributed to the spread of the fungus to other geographical areas. In the scientific literature, it is known by other names: *Hormodendrum resinae*, *Cladosporium resinae*, *Amorphotheca resinae* [10].

Bacteria are prokaryotic cells that have a cytoplasm surrounded by a cytoplasmic membrane, a cell membrane, a capsule, flagella, villi, etc. Bacteria are characterized by a high reproduction rate. The linear size of the bacteria averages 0.15–3 μm [9].

Yeast is a microscopic unicellular fungus that reproduces by division or budding. The size of yeast is: the diameter of the smallest cells is 1.5–2 μm, the diameter of large cells is 8–10 μm, and the length of some species can reach 20–25 μm [7].

Microorganisms are divided into two groups: aerobic, which grow under conditions of air access, and anaerobic, which can grow without air access. Therefore, the



(a) (b)

Fig. 1 Hormoconis *resinae* on nutrient media (**a**) and under microscope magnification (**b**)

Fig. 2 Visual representation of microbiological contamination of aviation fuels

reproduction process of microorganisms may occur on the surface of the petroleum product and in the fuel itself [11].

Microbiological contamination of fuels is characterized by the formation of a gelatinous, slimy, amorphous mass ranging from light grey to dark brown (Fig. 2).

The enzyme system of a microorganism for carrying out metabolism can change during the individual development of the microorganism. This property of plastic metabolism is necessary because of the very small size of the microorganism cell and the impossibility of accommodating the entire possible range of enzymes. This explains the existence of potentially active microorganisms acquiring the ability to develop in the hydrocarbon environment of fuels [12].

Microorganisms are highly active organisms that function according to a general biological law: the smaller the organism, the more intensive its metabolism. Microbial enzymes are capable of acting on a large volume of nutrient substrate per unit of time. Microorganisms that do not have the appropriate enzyme systems for the oxidation of an unknown product are capable of producing adaptive enzymes in the process of adapting to a new food source [12, 13].

3 Growth Conditions for Microbiological Contamination in the Fuel and Fuel System

The biological nature of microorganisms determines the conditions for their occurrence and growth in fuels as microbiological contamination [14].

The nutrient medium determines the possibility of microbial growth. Hydrocarbons are a nutrient medium for some microorganisms. Aviation fuels consist mainly of highly sensitive and microbiologically susceptible hydrocarbons. Aviation fuels are middle distillates of petroleum. They contain hydrocarbons of various classes, heteroatomic compounds, and inorganic impurities. The hydrocarbon composition of jet fuels consists of different classes of hydrocarbons. The most common of these are paraffin. All paraffin hydrocarbons are subject to biodegradation, but isooctane (with a branched structure) remains resistant to the action of microorganisms. The physiological characteristics of each species of microorganism determine the direction of degradation of individual hydrocarbons and their mixtures, which have varying degrees of resistance to oxidation. The insolubility of hydrocarbons in water causes difficulties in their uptake by microorganisms. The hydrocarbon-water interface must be as large as possible to activate destructive enzymes. All paraffin hydrocarbons are subject to biodegradation, but isooctane (with a branched structure) remains resistant to microbial attack.

Water/moisture is essential for the functioning and evolution of any biological organism. Water is a critical factor in the growth and metabolic activity of microorganisms in aviation fuels. The life activity of microorganisms depends on water, as water constitutes 75–90% of the vegetative cell mass [12].

Jet fuels are hygroscopic. The hygroscopicity of fuels is reversible. Under certain external conditions, the fuel can absorb moisture, which can transfer from the fuel to the environment or form an emulsion of water in the fuel [4]. Over time, droplets of emulsified water will settle and form sludge water as a result of their coalescence by gravity. The water solubility of fuel is governed by Henry's law and is determined by many factors, the main ones being:

- temperature,
- pressure,
- relative humidity of the air in contact with fuel,
- hydrocarbon composition of the fuel.

Individual hydrocarbon molecules in jet fuels are non-polar compounds and are larger in volume than water molecules and are not capable of forming hydrogen bonds with water molecules. The hygroscopic nature of fuels increases with magnification in their content of aromatic hydrocarbons, which are specifically added to aviation fuels and are part of the fuels for air-jet engines. Water solubility in hydrocarbons is very low (not more than 0.01%), but for aromatic hydrocarbons, it is approximately 2–3 times higher. Water in the external environment can be available or inaccessible. The degree to which water is accessible to microorganisms is determined by the activity index of water, which describes the degree to which its molecules are bound.

This index is equal to one for pure free water. The activity index of water is less than one for water in a given interaction with other substances. Microorganisms can grow in media with a water availability coefficient of 0.6–0.9 [15].

The flight of any aircraft can be conventionally characterized by three components—takeoff, horizontal flight, and descent. Each of these flight components is constantly connected with changes in external conditions (temperature, pressure, and humidity air). During altitude climb, there is a decrease in air pressure and temperature and a decrease in the relative humidity of the surrounding air. In horizontal flight, minor changes in air pressure and temperature are possible. The descent section is characterized by an increase in pressure and temperature and an increase in relative air humidity. All these changes outside the aircraft affect the physical and chemical properties of the fuel (density, viscosity, etc.), which in turn leads to changes in its water content and condition. The effect of changes in atmospheric conditions in flight is different for different types and groups of aircraft fuel system tanks.

The evolution of microbiological damage in fuel systems begins in places of water accumulation. Thus, the bottom of aboveground and underground tanks and fuel pipelines are areas of increased risk of microbiological contamination.

Under the influence of external factors, fuel is capable of absorbing moisture, which can transfer from the fuel to the environment or form an emulsion of water in the fuel. Over time, the emulsion water droplets will drain away under the influence of gravitational forces and form settling water. The solubility of water in fuel is determined by many factors, the main ones being temperature, pressure, relative humidity of the air the fuel meets and the hydrocarbon composition of the fuel.

The accumulation of water in fuel during storage in aircraft tanks (reservoirs) can only occur through the ingress of moist air through the drainage system into their above-fuel space. Depending on the changing conditions, the moist air may condense on the cold non-wetted tank (reservoir) walls, on the cold fuel surface, or dissolve directly into the fuel.

The total content of water in jet fuels reaches 0.008–0.012% by weight, including dissolved 0.002–0.007% by weight, during the operation of aviation equipment. The amount of water in the fuel after refueling must not exceed 0.003% by weight. The presence of water has a negative effect on a number of fuel quality parameters.

Air humidity contributes to the watering of the fuel. Accordingly, the water content of jet fuels in storage depends on the period of the year, climate, and geographical location.

Therefore, water is one of the common contaminants of aviation fuels, the occurrence of which is facilitated by a number of environmental factors. Water is a basic requirement for the metabolic activity of microorganisms and is a factor in the formation and development of microbiological contamination.

Some microorganisms are able to survive for months or even years *in dehydrated fuel (e.g. Hormoconis resinae)* [15]. The persistence of *Hormoconis resinae* spores in fuel in the absence of water poses a threat of uncontrolled growth if there is moisture in the fuel and a suitable temperature.

Environmental temperature is the second most important physical factor for microbial growth in fuels. The temperature of the fuel determines the metabolic activity of the microorganisms and the rate of degradation of the hydrocarbons in the fuel. Most of the microorganisms that can grow in fuel belong to the group that develops actively at temperatures of 20–45 °C, i.e. mesophiles. The metabolic potential of microorganisms increases with increasing temperature within the optimum range. Microbial growth slows down at temperatures below the optimum range. If the temperature exceeds the optimum range, microbial cells may die or retard their growth for some time. Studies [16] confirm that *Hormoconis resinae* and *Phialophora sp.* strains are resistant at –57 °C. *Hormoconis resinae* spores are viable for a maximum of 3 days at 60 °C and die at 70 °C. *Phialophora sp.* spores are viable at 55 °C for no more than 24 h and die at 60 °C. Strains of Aspergillus fumigatus isolated from supersonic jet fuel survive at temperatures as low as minus 32 °C and 80 °C.

The area of microbial growth is the accumulation of water in tanks and fuel lines. Water is characterized by its pH value. A neutral pH allows the growth of most microorganisms capable of degrading hydrocarbons in fuels [24]. Fungi grow at pH 4–6; SRB bacteria grow best at pH 7.5. The pH of the tank bottom water is a safe environment for microbial growth as its pH range is 6–9 [15]. The effect of pH on the microbial cell can be direct or indirect. In the case of an indirect effect, the pH affects the nutrient components of the external environment, which in turn affects the penetration of these components into the microbial cell [12]. The pH value can have an effect on the development of different types of microorganisms in the sub-bottom water. Scientists [15] have studied the types of microorganisms which grow in fuel tanks on ships where seawater is used in the ballast system of the ships and accumulates on the bottom of the fuel tanks. The pH of the seawater is 8. The results showed that *Hormoconis resinae* grows in the tanks in the presence of the yeast *Candida sp. Candida sp.* produces acidic metabolites that lower the pH. This ability of the yeast creates conditions for the growth of *Hormoconis resinae*, which reproduces poorly at alkaline pH. Low pH suppresses the development of bacteria that grow on fuel hydrocarbons. High pH suppresses fungal growth. For example, some microorganisms are able to lower the pH by producing organic acids, thereby allowing other oil-degrading microorganisms to proliferate. The pH can influence the development of different types of microorganisms in the sub-bottom water.

The hydrocarbon composition of the fuel, the presence of water, and the ambient temperature determine the occurrence of microbiological contamination. These are interdependent factors in the growth of microorganisms in fuel systems.

Microorganisms grow actively at the fuel-water interface. This is due to the assimilation of fuel hydrocarbons and the ability to carry out biochemical reactions to convert these hydrocarbons into an energy source when water molecules are available. The greatest accumulation of microorganisms and the products of their living activities accumulates in vessels located at the water-hydrocarbon interface (Fig. 2).

There are other factors contributing to microbiological contamination in fuels. These do not directly affect the life activity of the microbial cell. The Ishikawa diagram shows other factors that contribute indirectly to the formation and development of microorganisms in fuels (Fig. 3). One of the tools used to analyze

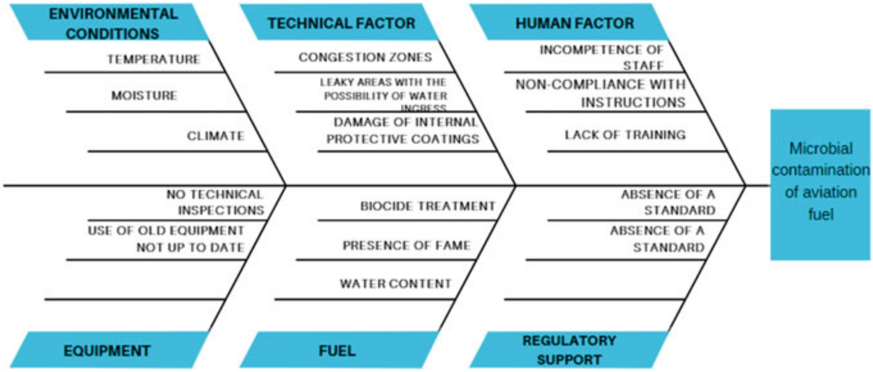


Fig. 3 Ishikawa diagram of the factors that are related to the problem of microbiological contamination of aviation fuels

and visualize the relationship between sources and factors causing microbiological contamination in aviation fuel is Ishikawa diagram. This involves establishing relationships between factors that influence the formation process of a particular adverse phenomenon. The Ishikawa diagram is created after carefully detailing and examining all factors and grouping them into categories.

This diagram shows how to identify and systematize potential factors and relationships for a thorough analysis and selection of methods to prevent or solve the problem of microbial fuel contamination. The results presented in this material can be used by organizations or companies involved in the storage and supply of aviation fuels.

4 Effects of Microbiological Contamination on the Quality of Fuels, Operating Materials, Fuel Systems and Vehicle Operability

Fuel cleanliness is the permissible level of impurities of various origins in the fuel at which the operation of the fuel control and fuel handling equipment is uninterrupted. There are several factors that influence the level of fuel purity. The first is size. Individual microbial cells are very small and do not present a danger to filtration. However, groups of microorganisms (colonies, biofilms) in fuel can be as large as even the human eye can see. Secondly, surfactants are substances released as a result of microorganism metabolism, known as biosurfactants, which have a positive effect on the coagulation of mechanical contaminants in the presence of moisture. Thirdly, the slime-like and sticky properties of microbial colonies or biofilms, adhere to the filter material and disrupt the operation of fuel-regulating equipment [5].

Changes in the group composition of fuels are a result of the microbiological degradation of hydrocarbons. The consumption of a particular type of hydrocarbon is determined by microbial activity and the availability of hydrocarbons for consumption in the fuel environment. The ability to biodegrade hydrocarbon groups depends on the physiological characteristics of the microorganism, in particular the adaptability of its enzymatic apparatus to environmental conditions. Changes in the paraffinic composition of aviation fuels affect the energy properties of the fuel since alkanes have the highest calorific value. In turn, the calorific value affects the efficiency of an air jet engine.

A change in the chemical composition of fuels due to a reduction in alkanes affects physico-chemical parameters such as density, fractional composition, vaporability, flash point. The rate and completeness of combustion of fuel depend on paraffinic hydrocarbons, as they have a lower flash point. These, in turn, affect flight and technical and economic performance [5]. Density is an important physical property and performance indicator for calculating and accounting for fuel. Vaporability is a property of fuel that determines the rate at which a combustible mixture of fuel and air is created, which in turn affects the completeness of fuel combustion and the ease of engine starting. Fractional composition is an indicator related to vaporability and characterizes the vaporability and startability of fuel as well as the safe operation of the aircraft fuel system [2, 5].

The results show a significant increase in the acidity of the samples tested, with the exception of aviation gasoline. Acidity is an indicator of the content of organic acids in fuels and is measured by the amount of alkalinity required to neutralize them [5]. Organic acids improve the anti-wear and protective properties of fuels, but have a negative effect on the corrosive properties of fuels, particularly compatibility with consumables. Therefore, the value of acidity in jet fuels is limited. The increase in acidity in contaminated fuel is explained by the appearance of intermediate products of the metabolism (Krebs cycle) of microorganisms [12].

The presence of microflora in fuels, as determined by fuel surveys, is indicated by:

- presence of biomass clumps in the form of lumps of sticky slime, felt-like formations in the water sediment;
- presence of lumps of sticky slime on internal tank walls;
- swelling of the sealant and corrosion of the surface of the fuel tank;
- clogginsg of filters and pump nets installed in tanks with sticky mass;
- malfunction of fuel metering equipment;
- unpleasant odour.

In the case of the same level of contamination in the fuel (up to 0.005% by weight), the pressure drop across the filter increases more rapidly in the case of microbiological contamination of the fuel than in the case of normal mechanical particles [15]. The differential pressure across the filter increases more rapidly with bacterial contamination than with fungal contamination. Measuring the mass of deposits on the filter when the maximum differential is reached, the mass is 9 g for normal contamination, 8 g for fungal contamination, and 5 g for bacterial contamination. It can be concluded that biological contamination is more dangerous for fuel pumping and filter life than normal contamination. The physiological ability of microorganisms to produce biosurfactants is the reason for this. Biological surfactants promote adhesion to fuel system components and storage material, including the surface of the filter material. Consequently, an easily observed symptom of microbiological heavy fuel contamination is the increased pressure drop and impaired fuel flow. The microbiological effect is one of the most important manifestations of the corrosive and aggressive effects of the environment on metal products and structural elements of aircraft and fuel-supplying equipment in contact with fuel [2]. Corrosion phenomena in fuel tanks begin at the sites of microbial growth on the bottom of fuel tanks at the fuel-water interface.

Microbial corrosion is a complex process of interaction between microorganisms and metal that occurs in a biofilm. The composition and properties of the biofilm influence the development of corrosion processes through metabolic activity and electrochemical reactions. Microorganisms do not only directly "corrode" the metal itself, but often influence chemical, electrochemical and mechanical factors to enhance or mitigate any type of damage. Therefore, despite its widespread occurrence, biochemical corrosion is not always easy to recognize [5].

Thus, microbiological corrosion of metals is part of the complex problem of microbiological contamination of fuels. It occurs under the influence of the products of life activity of microorganisms present in the affected fuel, in the process of cell adhesion to the metal and implementation of electrochemical reactions.

The physiology and developmental characteristics of microorganisms determine their impact on the environment. Microorganisms can affect the environment through their physical presence, nutrient requirements, metabolic products, and biocorrosion capacity. Deterioration of fuel quality, clogging of filters and failure of fuel control devices, and corrosion of metal and rubber surfaces are related to aspects of the physiology of microorganisms that contaminate aviation fuel (Fig. 4).

The interconnectedness of micro-organisms and the negative effects of their development on fuel and means of operation, transportation, and storage demonstrates the complex impact and importance of controlling microbiological contamination of aviation fuel at every stage of its life cycle.

5 Monitoring of Aviation Fuels, Fuel Systems and Fueling Complexes for Risk Assessment of Microbiological Contamination

Aviation fuel supply is complex. Aviation stakeholders face a range of risks that can affect not only the business operations of organizations, but also the lives and health of the people who use their services. Increased demand for air transport, complex designs, new composite materials, and technologies are leading to more costly aircraft grounding incidents.

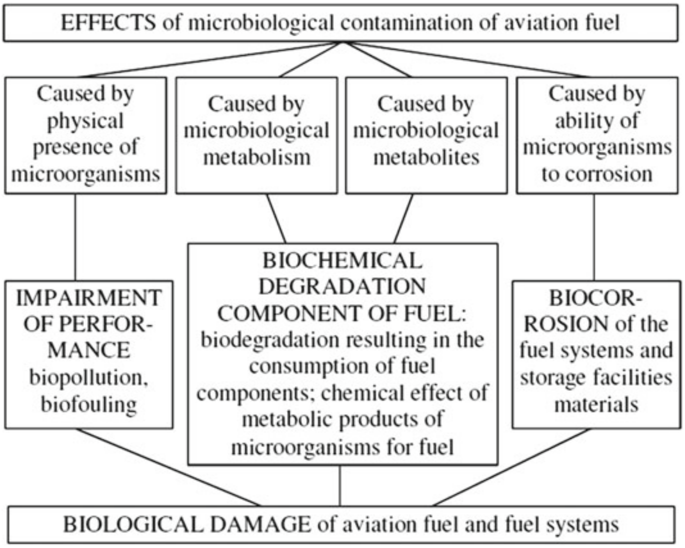
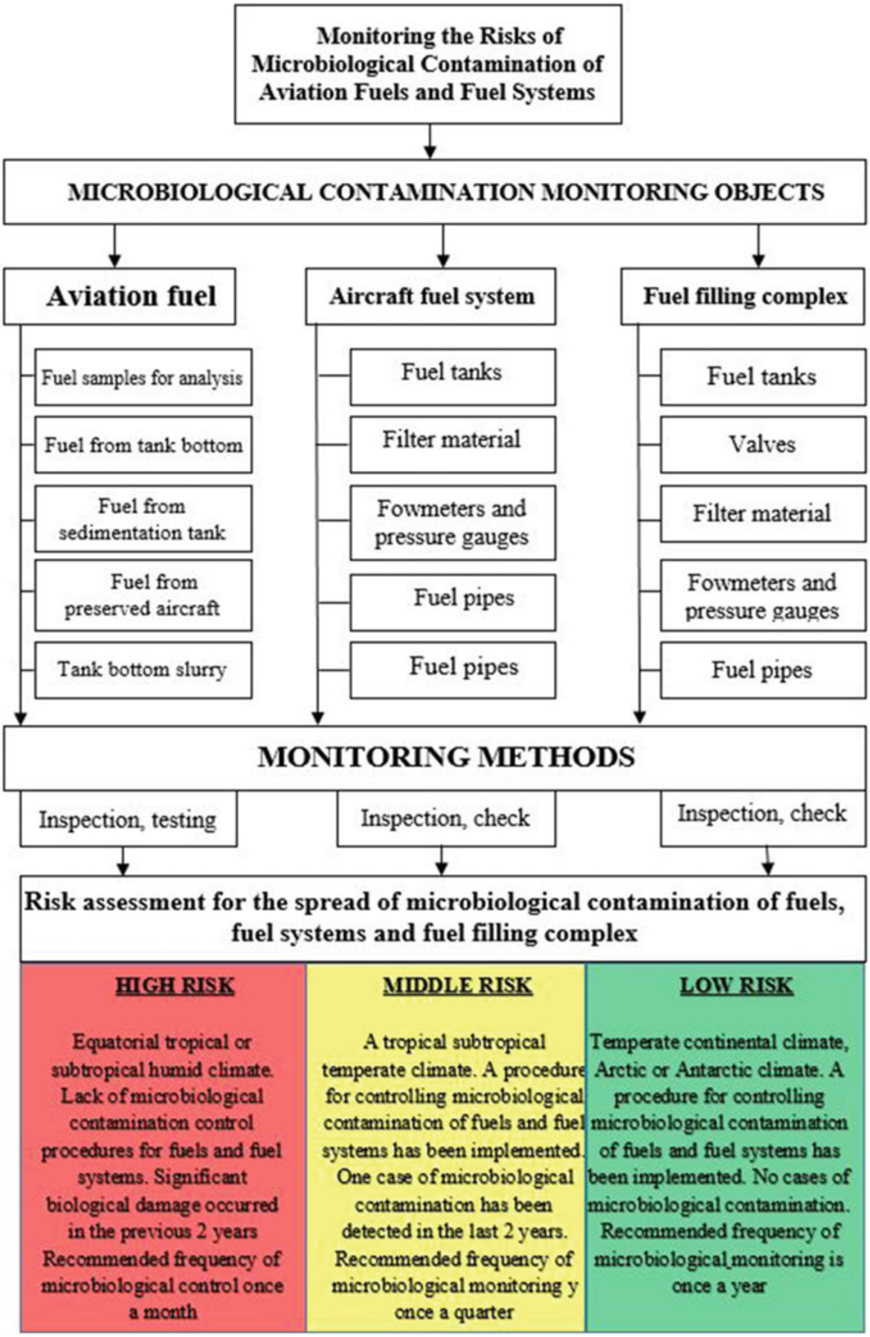


Fig. 4 The risks and consequences of microbial contamination of aviation fuels

The ICAO coordinated risk-based approach to improving aviation safety [159] is the application of logical and systematic methods to identify, analyze, evaluate and manage the risk associated with an aspect of aviation activity in order to reduce the risk or the likelihood of its recurrence. Risk management is a way of anticipating a problem or threat in advance. A risk-based approach makes preventive action part of strategic and operational planning and ensures that risks are considered and assessed.

Scientist Passman [17] developed criteria for evaluating the risk of microbiological contamination of oil products based on average annual precipitation: low risk (average annual precipitation of 64 cm), medium risk (average annual precipitation between 64 and 190 cm), high risk (average annual precipitation over 190 cm) and number of days when it occurs (low risk—less than 100 days per year, medium risk—100 to 200 days per year, high risk—over 200 days per year).

Aviation fuel is one of the elements affecting the flight safety of air transport. A system analysis of existing risk management methods [160–164], in particular in the aviation industry [159, 164–165], helped to implement risk theory approaches to the problem of microbiological contamination of aviation fuels and develop a Monitoring the Risks of Microbiological Contamination of Aviation Fuels and Fuel Systems presented in the form of a scheme (Fig. 5).



HIGH RISK

Equatorial tropical or subtropical humid climate. Lack of microbiological contamination control procedures for fuels and fuel systems. Significant biological damage occurred in the previous 2 years Recommended frequency of microbiological control once a month

MIDDLE RISK

A tropical subtropical temperate climate. A procedure for controlling microbiological contamination of fuels and fuel systems has been implemented. One case of microbiological contamination has been detected in the last 2 years. Recommended frequency of microbiological monitoring y once a quarter

LOW RISK

Temperate continental climate, Arctic or Antarctic climate. A procedure for controlling microbiological contamination of fuels and fuel systems has been implemented. No cases of microbiological contamination. Recommended frequency of microbiological monitoring is once a year

Fig. 5 Monitoring the risks of microbiological contamination of aviation fuels and fuel systems

The proposed system is a generalized algorithm for deciding on the frequency of monitoring objects (aviation fuel, elements of fuel systems, and fueling complexes) and the selection of prevention methods based on a qualitative risk assessment. The algorithm consists of the definition of the monitoring object, the selection of monitoring methods (inspection, testing or verification, depending on the monitoring object), the analysis of monitoring results, and the assessment of the risk of microbiological contamination spreading in fuels and fuel systems, and the selection of methods to prevent or control the development of microbiological phases.

The factors identified in the preliminary analysis and the construction of an Ishikawa cause-effect diagram helped to formulate attributes for each risk level. The first of these is climate (characterized by humidity and temperature). Temperature is an intensifying risk factor.

The principle of risk classification is based on aspects of the physiology of the micro-organisms that can grow in the fuel environment. These are the dependence of the micro-organisms on the nutrient medium and the presence of water. The risk of water in the fuel depends on the humidity of the environment.

The risk of past events indicator is also used to form a risk level indicator. Past events of microbiological contamination of aviation fuel and fuel systems increase the level of risk and influence the selection of actions and organizational measures to minimize it.

The implementation of this system will make it possible to ensure the biological purity of aviation fuel, prevent the occurrence of microbiological contamination in fuel systems and refueling complexes and, as a consequence, eliminate the impact of microbiological fuel contamination on flight safety.

6 Conclusions

Contamination of fuel by microorganisms is incidental. However, this does not negate the existence of certain patterns. Factors such as oxygen, moisture, temperature, nutrients and pH affect the appearance, growth rate and spread of microorganisms in fuel. Natural and climatic conditions determine the numerical and qualitative composition of microorganisms and their activity in the environment. Normal metabolism, growth, and reproduction are possible only in the presence of moisture.

Problems caused by microbiological contamination of fuel systems can be divided into the following categories: problems caused by the physical presence of microbial colonies; problems caused by the metabolism of microbial petrodestructors; problems caused by metabolites of microbial petrodestructors; problems related to the property of microorganisms to cause corrosion.

Microbiological fuel contamination is an indirect sign of a microbial contamination problem in the fuel system and environment of the aircraft and aviation.

References

1. Iakovlieva, A., Boichenko, S., Vovk, O.: Impact of aviation fuel quality on flight safety and environment. Sci. Innovat. **9**(4), 25–30 (2013)
2. Shkilniuk, I.: Investigation of the microbiological stability of traditional and alternative aviation fuels. Int. J. Sustain. Aviat. **2**(2), 111–118 (2016)
3. Vangsness, M.D.: Best practices for fuel system contamination detection and remediation. Physicist University of Dayton Research Institute, USAF AFMC AFRL/RQTF (2015)
4. Behbahani-Pour, M.J., Radice, G.: Fuel contamination on the large transport airplanes. Aeronaut Aerospace Eng. **6**, 4 (2017)
5. Shkilniuk, I., Boichenko, S.: (2020). Biological Risk of Aviation Fuel Supply. In: Babak, V., Isaienko, V., Zaporozhets, A. (eds) Systems, Decision and Control in Energy I. Studies in Systems, Decision and Control, 298. Springer,
6. Harold, W.G. (2003) An analysis of microbial contamination in military aviation fuel systems. Technical report AFIT/GEE/ENV/03–10. Department of the air force Air university Air forceinstitute of technology, p. 221.
7. Kondratyuk, T., Kharkevich, E., Zaharchenko, V., Nakonechnaya, L., Roy, A., Zhdanova, N., Pashkevich, R.: Biodeterioration of aviation fuel TS-1 by microscopic fungi. Mycol Phytopathol **41**(5), 442–448 (2007)
8. Joseph B. Morton (2021) 6 - Fungi, Principles and Applications of Soil Microbiology, pp. 149–170.
9. Mary Ann Bruns (2021) 5 - Bacteria and archaea. Principles and Applications of Soil Microbiology, pp. 112–148.
10. Rafin, C., Veignie, E. (2018) Hormoconis resinae, the kerosene fungus: Handbook of hydrocarbon and lipid microbiology, Springer International Publishing AG, pp. 16–21.
11. Gaylarde, C.C., Bento, F.M., Kelley, J.: Microbial contamination of stored hydrocarbon fuels and their control. Rev de Microbiol **30**, 1–10 (1999)
12. Pirog, T. (2004) General microbiology: handbook, Kyiv, p. 471.
13. Shkilniuk, I., Boichenko, S.: Methodically organizational principles of biological stability providing of aviation fuel. Trans Inst Aviat Warsaw **4**(237), 6–83 (2014)
14. Nezbrytska, I.M., Shamanskyi, S.I., Boichenko, S.V., Kharchenko, G.V.: Some problems of the use of microalgae for nitrogen and phosphorus removal from wastewater (a review). Hydrobiol. J. **57**(2), 62–78 (2021)
15. Robbins, JA., Levy, R. (2004) A review of the microbiological degradation of fuel. In: Directory of microbicides for the protection of materials. Kluwer Academic Publishers, pp. 177–202.
16. Vasilieva, A.A., Chekunova, L.N., Poliakova, A.V.: Influence of temperature on growth and viability of Hormoconis resinae u Phialophora sp., developing in aviation fuels. Mycology and phytopathology, 43(4), pp. 312–316 (2017)
17. Passman, F.J.: Microbial contamination and its control in fuels and fuel system. Int. Biodeterior. **1**(88), 104 (2013)

International Requirements and Modern State in Sphere of Motor Fuels Quality Control: Basic Principles of Monitoring and Control

Olena Sibilieva, Sofiia Dokshyna, and Petro Topilnytskyi

1 The Origin and Supply Chain of Liquid Fuels to the Consumer Market, the Current State of Non-Food Product Quality and International Obligations for Ukraine

Implementation of technical solutions, regulations and directives of the European Union in Ukraine is an urgent task and a key component of ensuring the protection of consumer interests, environmental safety, and national security, including creating conditions for a free trade area for exports and imports of products. Given the challenges of today, on the path of recovery and sustainable development of Ukraine, with the aim of Ukraine's full membership in the EU and bringing the living standards of Ukrainians closer to the European level, the key issues of European integration, trade liberalization, and the removal of trade barriers are the main topical areas of the country. In particular, the Action Programme of the Cabinet of Ministers of Ukraine, approved by the Resolution of the Cabinet of Ministers of Ukraine № 471 dated 12.06.2020, has relevant goals that include the launch of new forms of cooperation with EU countries, updating the Association Agreement between Ukraine, on the one hand, and the European Union, the European Atomic Energy Community and their Member States, on the other hand (hereinafter—the Association Agreement),

---

O. Sibilieva (✉)
State Environmental Inspectorate, Kyiv, Ukraine

S. Dokshyna
National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute", Kyiv, Ukraine
e-mail: dokshyna.sofiia@lll.kpi.ua

P. Topilnytskyi
National University "Lviv Polytechnic", Lviv, Ukraine

S. Boichenko et al. (eds.), *Modern Technologies in Energy and Transport*, Studies in Systems, Decision and Control 510, https://doi.org/10.1007/978-3-031-44351-0_13

concluding an Agreement on Conformity Assessment and Acceptance of Industrial Products, and implementing international acts in Ukraine.

Pursuant to Article 56 of the Association Agreement, in order to guarantee the free movement of products to the EU countries, one of the steps for Ukraine is the obligation to harmonize EU legislation, including the requirements for the implementation of the Regulation (EU) 2019/1020 of the European Parliament and of the Council of 20.06.2019 on market surveillance and compliance of products and amending Directive 2004/42/EC and Regulations (EC) No 765/2008 and (EU) № 305/2011 (hereinafter—Regulation № 1020), the provisions of which provide for a high level of protection of the public interest, increased consumer confidence, fair competition, public safety and environmental protection, which is achieved through enhanced state control, state market surveillance, elimination of risks of non-compliant and dangerous products, ensuring equal conditions for all business entities, with the mandatory introduction of clear, transparent and comprehensive rules, promotion of closer cross-border cooperation between law enforcement and customs authorities [1]. In particular, the provisions of Regulation № 1020 provide for the harmonization of 70 international acts of the EU, including Directive 98/70/EC of the European Parliament and of the Council of 13 October 1998 relating to the quality of petrol and diesel fuels and amending Council Directive 93/12/EEC (hereinafter—Directive 98), Regulation (EC) № 715/2007 of the European Parliament and of the Council of 20 June 2007 on type approval of motor vehicles with respect to emissions from light passenger and commercial vehicles (Euro 5 and Euro 6) and on access to vehicle repair and maintenance information (hereinafter—Regulation № 715), etc.

Motor gasoline and diesel fuel (hereinafter—liquid fuels) are a mixture of liquid hydrocarbons obtained from the refining of crude oil and gas condensate (their mixtures). The transport industry accounts for the bulk of liquid fuels consumption (60%), and their quality is a key to the reliability, efficiency, and environmental friendliness of machines and mechanisms during operation, and an important component in the field of environmental protection, human life and health [2].

Quality control of liquid fuels in Ukraine is carried out in accordance with the Technical Regulations on the requirements for motor petrol, diesel, marine and boiler fuels (hereinafter—the Technical Regulations), including in accordance with the procedure provided for by the Law of Ukraine "On State Market Supervision and Control of Non-Food Products". The Technical Regulation is developed in line with Directive 98 and should include requirements to improve the quality of liquid fuels in terms of air pollution, including the introduction of environmental standards aimed at reducing emissions of gases and vapors from mobile and stationary sources, reducing the share of flavorings, olefins, sulphur, unburned hydrocarbons, carbon monoxide, as well as toxic emissions and secondary pollutants such as ozone, including the introduction of refining technologies for the sale of unleaded petrol, and the prohibition of the sale of leaded petrol due to the threat of air pollution caused by petrol combustion and lead ingress, which poses a threat to human health and the environment [3, 4].

According to the State Customs Service of Ukraine, in 2022, the total volume of imports of certain product subcategories of liquid fuels (Ukrainian Classification of Goods for Foreign Economic Activity codes 27,101,241, 27,101,245, 27,101,249, 2,710,194,300, 2,710,194,600, 2,710,194,710, 2,710,194,790, 2,710,194,800) amounted to 6,943,174.61 tons of products (worth 4,713,148.11 thousand USD) and was 10.6% less than in 2021 (total volume 7,768,738.14 tons, worth 8,302,999.05 thousand USD). In 2022, Ukraine imported liquid fuels from 42 producing countries (Hungary, Greece, the EU, Lithuania, Romania, Belgium, Bulgaria, Belarus, Israel, India, Spain, Italy, Malaysia, the Netherlands, Germany, Turkey, Turkmenistan, Israel, etc.), including the supply of products from 21 countries of origin whose imports were not registered in 2021 (Austria, Georgia, Denmark, Estonia, Egypt, Kazakhstan, China, Cyprus, Latvia, Republic of Moldova, and Ukraine, North Macedonia, Poland, Saudi Arabia, Serbia, Slovakia, Slovenia, Taiwan Province of China, Sweden, Finland, Tunisia, United Arab Emirates (total volume of 820,801.71 tons and worth 1,110,861.77 thousand USD). According to the State Tax Service of Ukraine, as of the beginning of 2022, 54,068 business entities were engaged in the business of liquid fuels in Ukraine, including the number of licenses issued (renewed) for the wholesale trade in fuels in the absence of wholesale trade outlets, was 3489 (328) for the wholesale trade in fuel, in the presence of wholesale trade outlets—711 (68), for fuel production—77 (9), for retail trade in fuel—11,768 (6091), for fuel storage—4010 (233), for fuel storage (exclusively for own consumption or industrial processing)—34,013 (8549) licenses, respectively. Given the origin and supply of liquid fuels to the Ukrainian consumer market, it can be determined that the products reach the consumer from both domestic and foreign producers. Oil products can be transported via main oil pipelines, rail, sea and road transport operators. Liquid fuels reach the consumer market based on the results of their production and on the results of "quality improvement", namely changes in physical and chemical properties by using (adding) additives, dopes and colorants to liquid fuels (Fig. 1). Taking into account the requirements of the Technical Regulations, the Law of Ukraine "On Technical Regulations and Conformity Assessment", Resolution of the Cabinet of Ministers of Ukraine dated 13.01.2016 № 95 "On Approval of Conformity Assessment Modules Used to Develop Conformity Assessment Procedures and Rules for Using Conformity Assessment Modules", for fuels produced or imported in batches, as well as for fuels produced in experimental batches, the manufacturer or an authorized representative must apply the conformity assessment procedure according to module F1, for fuels produced in series (domestic production)—module A1 [5, 6]. Based on the results of the conformity assessment, the manufacturer or an authorized representative must draw up a declaration of conformity, thus confirming by the first party that the liquid fuel meets the requirements of the Technical Regulations and that the specified requirements for the product and/or process have been met. Each batch of liquid fuel that is put into circulation or is in circulation must have a quality document (quality passport) for the fuel, on which the manufacturer or an authorized representative affixes the national conformity mark, which also confirms the fuel's compliance with the requirements of the Technical Regulations [7]. According to the Ministry of Energy of Ukraine, in 2022, based on the results of the conformity assessment to confirm the quality of motor fuels to the requirements of the Technical Regulations, conformity assessment bodies issued 80 certificates of conformity, which was 8.5 times less than in 2021 (682 certificates). A decrease in the number of issued certificates of conformity may indicate the introduction of liquid fuels in the Ukrainian market in the absence of a conformity assessment and non-compliance by business entities with the requirements of the law, and as a result, the introduction and distribution of products of unknown origin with questionable quality. Thus, according to the Department of Strategic Investigations of the National Police of Ukraine, it was established that in 2022 the number of pre-trial investigations into criminal offences related to fuel trafficking amounted to 35 proceedings (including 27 under part one of Article 204; 5—under part two of Article 204 of the Criminal Code of Ukraine; 1—under part three of Article 204 of the Criminal Code of Ukraine; 2—under part one of Article 227 of the Criminal Code of Ukraine), which was 1.4 times higher compared to 2021 (25 pre-trial investigations). According to the State Tax Service of Ukraine, based on the results of the identified violations of tax legislation, in 2022, fines totaling 932.7 million UAH were imposed on business entities engaged in the sale of liquid fuels in Ukraine, which was 3.6 times less than in 2021 (3,367.8 million UAH). In particular, the results of the work of interagency regional working groups on combating illegal fuel trafficking showed that in 2022, 26.4% of fuel retail activities were carried out in the absence of quality documents (quality passports) and declarations of conformity, which is a violation of the Technical Regulations.

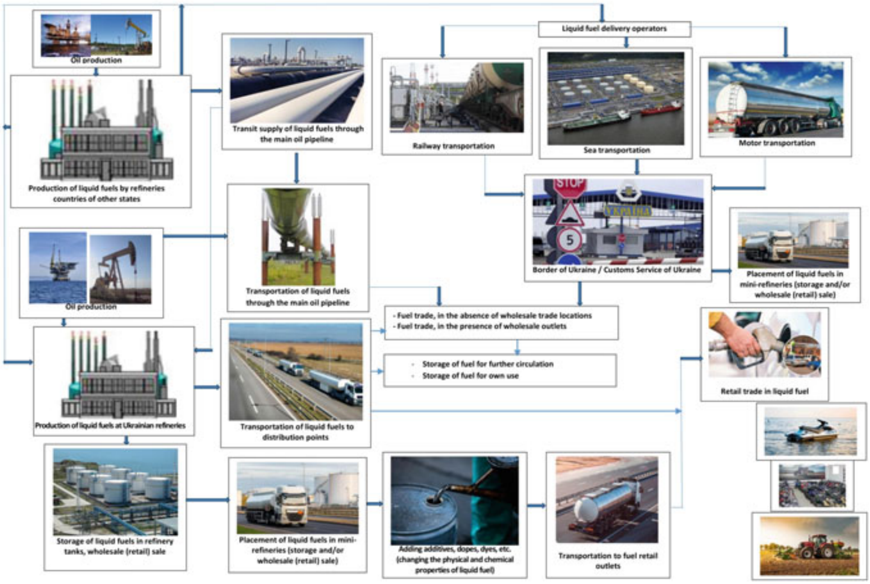


Fig. 1 Origin and supply of liquid fuels to the Ukrainian consumer market (photo from open sources)

2 Environmental Performance of Petrol and Diesel Fuels in Line with International Requirements

Comparing the requirements for environmental performance of petrol set out in Annexes 2 and 8 to the Technical Regulation, Directive 2009/30/EC of the European Parliament and of the Council of 23 April 2009 amending Directive 98/70/EC as regards the specification of petrol, diesel and gas-oil and introducing a mechanism to monitor and reduce greenhouse gas emissions and amending Council Directive 1999/32/EC as regards the specification of fuel used by inland waterway vessels and repealing Directive 93/12/EEC (hereinafter—Directive 2009/30/EC) and Directive 98/70/EC of the European Parliament and of the Council of 13 October 1998 relating to the quality of petrol and diesel fuels and amending Council Directive 93/12/EEC (hereinafter—Directive 98), it can be determined that the quality control of petrol in the EU Community countries (hereinafter—the Community) is examined by 18 parameters, and in Ukraine—by 10 parameters (Table 1) [3, 4, 8].

In accordance with paragraph 1 of Appendix 1 to the Technical Regulations for automobile gasoline, designations are defined, which include such groups as: the first group—letter A, designation of gasoline for automobile engines with forced/spark ignition; the second group—digital designation of the octane number of automobile gasoline (80, 92, 95, 98) according to the experimental method; the third group—ecological class symbols: Euro3, Euro4, Euro5; the fourth group is a symbol for determining the content of bioethanol: E5, E7, E10.

Taking into account the above designations, in the Technical Regulations, the octane number according to the experimental and motor methods differs for gasoline brands A-80, A-92, A-95, A-98 (also taking into account the environmental class: Euro3, Euro4, Euro5), the saturated vapor pressure depends on the period of the year with a range from 45 to 90 kPa, the oxygen content depends on the bioethanol content and is no more than 2.7% for gasoline E0, E5, E7, and no more than 3.7% for gasoline E10.

In accordance with Directive 2009/30/EC, the environmental parameters for gasoline in the Community countries clearly define the content of ethanol as an oxidant and stabilizing component, which may not exceed 10%, and also define the content of such oxidants as methanol—up to a maximum of 3.0%, isopropyl alcohol—up to 12%, isobutyl alcohol—up to 15%, tertiary butyl alcohol—up to 15%, esters—up to 22%, and the indicator "other oxidants"—up to 15%.

According to Annex 2 to the Technical Regulation, the indicator ethanol is absent, however, there is an indicator of bioethanol content, which should be equal to 0% for E0 petrol, no more than 5% for E5, more than 5% and no more than 7% for E7, and more than 7% and no more than 10% for E10. In particular, the notes to Annex 2 to the Technical Regulation state that for E0, E5 and E7 petrols, the use of oxygen-containing additives other than bioethanol is additionally allowed, namely methanol up to 3% by volume, isopropyl alcohol up to 10% by volume, isobutyl alcohol—up to 10% by volume, tertiary butyl alcohol—up to 7% by volume, ethers—up to 15% by volume, other organic oxygen-containing compounds with a boiling point not

Table 1 Environmental performance of petrol

Parameters	Units of measurement	Limits [1]		Limits [2]	
		Min	Max	Min	Max
Octane number by the research method		95	–	95	–
Octane number by motor method		85	–	85	–
Saturated vapour pressure	kPa	–	60.0	Summer: 45–80 Winter: 60–100 Transition period: 50–90	
Distillation:					
– Fraction of evaporation at 100 °C	% v/v	46.0	–	The indicator is absent	
– Fraction of evaporation at 150 °C	% v/v	75.0	–		
Hydrocarbons:					
– Olefins	% v/v	–	18.0	–	<18
– Aromatic (hydrocarbons)	% v/v	–	35.0	–	<35
– Benzene	% v/v	–	1.0	–	<1
Oxygen content	% m/m	–	3.7[3]	–	<2.7 (E0, E5, E7) <3.7 (E10)
Oxidants:					
– Methanol (stabilising agent)	% v/v	–	3.0	Indicators are specified in the notes to Annex 2 of the Technical Regulation, ethanol is equivalent to bioethanol, the content of oxygen-containing compounds depends on the content of bioethanol for E0, E5, E7, E10	
– Ethanol (stabilising agent)	% v/v	–	10.0[3]		
– Isopropyl alcohol	% v/v	–	12.0		
– Tert-butyl alcohol	% v/v	–	15.0		
– Iso-butyl alcohol	% v/v	–	10.0		
– Esters that contain more than 5 carbon atoms	% v/v	–	22.0		
Other oxidants	% v/v	–	15		
Sulphur content	mg/kg	–	10.0	–	<10

(continued)

Table 1 (continued)

Parameters	Units of measurement	Limits [1]		Limits [2]	
		Min	Max	Min	Max
Lead content	g/l	–	0.005	–	<5 mg/dm^3
Volume fraction of bioethanol	%	Not specified		–	0 (E0) < 5 (E5) 5–7 (E7) 7–10 (E10)

Note

[1] *Annex 1 to Directive 2009/30/EC* [4, 8]*;*

[2] *Annex 2 to the Technical Regulation (for A-95 Euro5)* [3]*;*

[3] *For floating vessels and other special and recreational vehicles, in accordance with Directive 98 with a maximum oxygen content of 2.7%, the ethanol content (regardless of octane number by the motor method (95 or 98)) may not exceed 5%*

exceeding 210°C—up to 10% by volume, provided that the mass fraction of oxygen does not exceed 2.7%.

For E10 petrols, the use of oxygen-containing additives other than bioethanol is additionally allowed: methanol—up to 3% by volume, isopropyl alcohol—up to 12% by volume, isobutyl alcohol—up to 15% by volume, tert-butyl alcohol - up to 15% by volume, ethers—up to 22% by volume, other organic oxygen-containing compounds with a boiling point not exceeding 210 °C—up to 15% by volume, provided that the mass fraction of oxygen does not exceed 3.7%.

Taking into account Annex 1 "Quality requirements for motor gasoline with a maximum oxygen content of up to 3.7% (m/m), used especially in vehicles and floating entertainment vehicles equipped with spark ignition engines" to the Regulation of the Ministry of Economy of the Republic of Poland dated 09.10.2015 (hereinafter—Regulation 1680) stipulates that in motor petrols with octane number 95, 98 (without tin), with a maximum oxygen content of up to 3.7% (m/m), used in vehicles and recreational floating craft equipped with spark ignition engines, the ethanol content (as a stabiliser) may not exceed 10% (v/v) [9].

In particular, in accordance with Annex 2 of Regulation 1680, motor gasoline with an octane rating of 95, 98 (tin-free), with a maximum oxygen content of up to 2.7% (m/m), used in vehicles and recreational boats equipped with spark ignition engines, the ethanol content (as a stabilizer) may not exceed 5% (v/v).

Also, in Annexes I-IV of Directive 98, in the Regulation 1680, the indicator bioethanol is absent in the parameters of quality requirements for motor gasoline; methanol, ethanol are indicated as stabilizers; isopropanol, -2-methylpropanol-2, -isobutanol, -esters, other oxygen-containing bonds are parameters of quality requirements for motor gasoline and are defined as the content of organic oxygen-containing bonds [4, 9].

In particular, Directive 98 and Regulation 1680 do not specify whether alcohols belong to biomethanol, bioethanol, biobutanol, their synthetic products, including their use as biocomponents, and taking into account the test reports, that accompanied the fuel for putting into circulation on the territory of Ukraine in 2022 under № PBZ-007071EN of 21-DEC-2022, Gasoline Standard 95/EN228-10 ppm (petrol with octane number 95) contained a limit on ethanol content $\leq$ 5% (v/v), while in fact it was 0.13% (v/v), the limit on oxygen content $\leq$ 2.7% (m/m), in fact—2.19% (m/m); № PBZ-0070759EN of 25-DEC-2022 Gasoline Standard 95/EN228-10 ppm, petrol with octane number 95, oxygen content limit $\leq$ 2.7% (m/m), actually—1.92% (m/m), ethanol content limit $\leq$ 5% (v/v), actually—0.11% (v/v); in the test report under № 4489/BP09/2022 data 2022–08-01 Benzyna Bezolowiowa 95 (petrol with octane number 95), the oxygen content limit was $\leq$ 2.7% (m/m), in fact—2.10% (m/m), the ethanol content limit was $\leq$ 5% (V/V), in fact—4.6% (v/v); № 158746_4591871 data 2022–07-23 UNLEADED PETROL "Premium" grade 95 with oxygen of 2.7% (m/m) (petrol with octane number 95, with a maximum oxygen content of up to 2.7%) the ethanol content limit is $\leq$ 5% (v/v), in fact—0% (v/v).

Thus, the ethanol content in the Community countries is controlled and cannot exceed the established requirements, and international directives and regulations do not specify different designations (names) of petrol based on the share of bioethanol.

Article 1 of Directive 2009/28/EC defines a common framework for encouraging the production of energy from renewable sources, provides mandatory national targets for the share of energy produced from renewable sources in the total final energy consumption, as well as the share of energy produced from renewable sources sources for energy consumption in the transport sector; rules are introduced on statistical transfers between Member States, joint projects between the latter and with third countries, guarantees of origin, administrative procedures, information, training and access to the grid for energy produced from renewable sources; stability criteria for biofuel and biofuel liquids are determined [8].

Article 2 of Directive 2009/28/EC defines that "energy produced from renewable sources" means energy produced from non-fossil renewable sources (wind, solar, geothermal, hydrothermal, marine and hydroelectric, biomass energy, landfill gas, gas from sewage and biogas treatment plants); "biomass" —part of products subject to biological decomposition, waste and residues of biological origin obtained from agriculture (including substances of plant and animal origin), forestry and related industries, including fishing and aquaculture, as well as part of industrial and municipal waste, which is biodegradable, "biofuel liquid" means a liquid fuel produced from biomass and intended for energy use other than transport, including electricity generation, heating or cooling, "biofuel" means a liquid or gaseous fuel produced from biomass that is used for transport.

In particular, in accordance with Annex 3 of Directive 2009/28/EC, it is defined that bioethanol is ethanol produced from biomass, bio-ETBE is ethyl tert-butyl ether produced from bioethanol, biomethanol is methanol produced from biomass and is used as biofuel.

Thus, in the Technical Regulation, the indicator "bioethanol" needs to be clarified regarding its use, including taking into account the way of its extraction and use in liquid fuel in the territory of Ukraine.

Comparing the requirements for environmental performance of diesel fuel set out in Annexes 3 and 9 to the Technical Regulation, Directive 2009/30/EC and Directive 98, it can be determined that diesel fuel quality control in the Community countries is mainly based on 6 parameters, while in Ukraine—on 8 parameters, in particular, Directive 98 and Directive 2009/30/EC do not define the indicators "flash point in a closed cup", "maximum filterability temperature", "lubricity" (diameter of wear spot at 600 °C), which are given in the Technical Regulation, and vice versa, Annexes 3, 9 to the Technical Regulation do not contain such a quality indicator as diesel density at 15 °C, which are specified in international documents (Table 2).

Table 2 Environmental parameters of diesel fuels

Parameters	Units of measurement	Limits [1]		Limits [2]	
		Min	Max	Min	Max
Cetane number		51.0	–	Summer: 51 winter: 49 arctic: 48	–
Density at 15 °C	kg/m^3	–	845.0	The indicator is absent	
Distillation or fractional composition 95% by volume distilled at	ºC	–	360.0	–	< 360
–Polycyclic aromatic hydrocarbons	% m/m	–	8.0	–	< 8
Sulphur content	mg/kg	–	10.0	–	< 10
–Flash point in a closed crucible	ºC	The indicator is absent		–	> 55
Filtration limit temperature	ºC	The indicator is absent		–	Summer minus 5 Winter minus 20 Arctic minus 30
Lubricity (wear scar diameter at 60 °C)	micrometres	The indicator is absent		460	–
Volume fraction of methyl/ethyl esters of fatty acids	% v/v	–	7,0	–	For DP [in Ukrainian] B0—0; for DP [in Ukrainian] B5—no more than 5; for DP [in Ukrainian] B7—more than 5 and not more than 7

Note

[1] *Annex 2 to Directive 2009/30/EC* [8]*;*

[2] *Annex 3 to the Technical Regulation (for Euro 5)* [3]

Paragraph 2 of Annex 1 to the Technical Regulation contains the following groups of diesel fuel designations: the first group includes the letters DP [in Ukrainian], the designation of diesel fuel for automotive diesel engines; the second group includes the letter designation of the climatic period: L [in Ukrainian] (summer), Z [in Ukrainian] (winter), Ark [in Ukrainian] (arctic); the third group includes environmental class symbols: Euro3, Euro4, Euro5; the fourth group is a symbol for determining the content of methyl/ethyl esters of fatty acids: B0 (in their absence), B5, B7.

Thus, in Ukraine, the parameters of diesel fuel in terms of cetane number, maximum filterability temperature, and volume fraction of methyl/ethyl esters of fatty acids differ both by climate period (summer, winter), environmental class symbol (Euro3, Euro4, Euro5), and the content of methyl/ethyl esters of fatty acids, the value of which is not reflected in international directives.

In accordance with the requirements for the characteristics of motor gasoline and diesel fuel set out in Annexes 2, 3, 8, 9 to the Technical Regulations, in 2022, amendments to paragraph 26 of the Technical Regulations (Resolution of the Cabinet of Ministers of Ukraine № 292 dated 16.03.2022) removed paragraphs two and three of paragraph 26 of the Technical Regulations, namely, the deadline for the introduction into circulation of automobile gasoline and diesel fuel of the environmental class Euro 3 by December 31, 2015 and Euro 4 by December 31, 2017 has been canceled.

In particular, taking into account the requirements of Annexes 1, 2, 3, 8, 9 of the Technical Regulation, from March 16, 2022, the introduction of automobile gasoline and diesel fuel of the environmental class Euro 3 and Euro 4 with the appropriate designation of the environmental class into circulation on the market of Ukraine is again allowed: for gasoline according to the content bioethanol (E0, E5, E7, E10) and octane number (80, 92, 95, 98); for diesel fuel—according to the content of methyl/ethyl esters of fatty acids (B0, B5, B7) [3].

Thus, the above-mentioned requirements of the Technical Regulation allow the introduction into circulation in Ukraine of liquid fuels according to the environmental class Euro 3 and Euro 4, with a sulfur content for gasoline from 50 to 150 mg/kg, diesel fuel from 50 to 350 mg/kg, which does not correspond international requirements, which create conditions for exceeding the standard emissions of maximum permissible concentrations of toxic substances, heavy metals into the atmospheric air (nitrogen dioxide, carbon oxides, others) and, as a result, pollution of the atmospheric air and the environment as a whole.

3 Implementation of a Fuel Quality Monitoring and Control System as a Key to Reducing Hazardous Substances Emissions and Ensuring Environmental and Human Health Safety

Commission Regulation (EC) № 692/2008 of 18 July 2008 implementing and amending Regulation (EC) № 715/2007 of the European Parliament and of the Council on type-approval of motor vehicles with respect to emissions from light passenger and commercial vehicles (Euro 5 and Euro 6) and on access to vehicle repair and maintenance information (hereinafter—Regulation № 715) is a legal document of the Community countries, which aims and regulates the determination of specific technical requirements for the control of emissions from vehicles, including the approval of the type of mechanical vehicles taking into account emissions into atmospheric air from light passenger and cargo vehicles, approval of the type of mechanical vehicles taking into account the specification of fuel according to the environmental class Euro 5 and Euro 6 [10].

Thus, in accordance with paragraph 3 of Article 1 of Regulation № 715, gaseous pollutants are emissions of carbon monoxide and nitrogen oxide expressed in terms of nitrogen dioxide (NO_2) equivalent and have the following ratios: $C_1H_{1.89}O_{0,016}$ for petrol (E5), $C_1H_{1.86}O_{0,005}$ for diesel fuel (B5), $C_1H_{2,525}$ for liquefied petroleum gas (LPG), C_1H_4 for natural gas (NG) and biomethane, and (E85) $C_1H_{2.74}O_{0,385}$ for ethanol.

In accordance with the requirements of Regulation № 715, in order to determine the suitability of a vehicle for operation, the manufacturer shall conduct exhaust gas toxicity tests, measure fuel consumption and CO_2 emissions, and other measures, based on the results of which the manufacturer receives official approval of the vehicle type from the competent authority in terms of emissions into the atmosphere.

In particular, the provisions of Regulation № 715 introduce mass and quantity limits for exhaust particle emissions, requirements for the conformity of production and goods during the operation of vehicles, requirements for the approval of the type of pollution control devices, as well as requirements for easily accessible information on on-board diagnostics, repair and maintenance.

Directive 2009/30 amended Directive 98 on petrol and diesel fuel specifications, introducing a mechanism for monitoring and reducing greenhouse gas emissions with regard to the protection of the environment and human health, and reducing greenhouse gas emissions, emitted during the entire life cycle of road vehicles and off-road mobile machinery (including inland navigation vessels when not at sea), agricultural and forestry tractors and recreational vessels, and appropriate changes in the environmental parameters of petrol and diesel fuel [8].

The requirements of such technical specifications are the introduction of petrol with a maximum sulphur content of 10 mg/kg, oxygen 2.7%, ethanol 5% (oxygen 3.7%, ethanol 10% for floating vessels and other special and recreational vehicles). For the Community countries with low summer ambient temperatures (Denmark, Estonia, Finland, Ireland, Latvia, Lithuania, Sweden, the United Kingdom), it is allowed to sell ethanol-containing petrol with a maximum vapour pressure of 70 kPa during the summer period, and 60 kPa for other countries. It also stipulates that Community countries may continue to allow the sale of small quantities of leaded petrol with a lead content not exceeding 0.15 g/l, up to a maximum of 0.03% of total sales, for use in older vehicles.

As of 1 January 2011, the maximum permissible sulphur content of gas oils shall be 10 mg/kg and Community Member States shall ensure that liquid fuels other than gas oils may be used in inland navigation and pleasure craft, agricultural, forestry tractors and recreational vessels only if the sulphur content of such liquid fuels does not exceed the maximum permissible content of such gas oils. In particular, for the Community Member States with severe winter weather, the maximum distillation point for 65% should be at 250 °C, for diesel fuel and gas oil—10% at 180 °C [8, 10–13].

According to the 2021 Annual Summary Report by Poland to the European Commission on the sulphur content of light fuel oil, heavy fuel oil, inland navigation fuel oil and marine fuel used in ships, it was determined that two exceedances of the permissible value for sulphur content (0.14% (m/m) and 0.12% (m/m)) were detected on ships out of 249 samples taken. The lowest sulphur content by weight was 0.00062% (m/m), and the highest was 2.42% (m/m). And the highest sulphur content value of 2.42% (m/m) was recognized as meeting the quality requirements, given the use of equipment with an exhaust gas cleaning system on the ship [14].

Taking into account the photo materials shown in Fig. 2, it can be determined that the type of fuel in the retail network of car and gas filling stations of some countries of the Community and in the city of Kyiv differs significantly, namely, in the countries of the EU Communities, mainly gasoline is introduced into the circulation of products with an octane number according to the motor method 95, 98, diesel fuel, liquefied gas. In the city of Kyiv, the sale of liquid fuels, the difference between gasoline with an octane number of 92, 95, 100, diesel fuel and liquefied gas, including the sale of various types of gasoline and diesel fuel with an octane number of 92, 95, 100 branded as “Shebel”, “Shell V –Power”, “Premium”, “Energy”, “Mustang”, “Euro Plus”, “Brand oil” others, which are put into circulation taking into account the change in their physical and chemical properties by adding additives, dopes, dyes to liquid fuels (fuel dopes) and the sale of liquid fuel products under its own brand.

According to some open sources, fuel dopes should be added to improve the quality of liquid fuels, improve performance, environmental and ergonomic characteristics, improve the combustion process, increase the octane or cetane number, as well as to increase their compression and reduce corrosion or oxidation in the working mechanisms of vehicles [15, 16].

According to data from some open sources, fuel dopes should be added in order to improve the quality of liquid fuels, to improve operational, environmental and ergonomic characteristics, to improve the combustion process, to increase the octane or cetane number, as well as to increase their compression and reduce corrosion or oxidation in working mechanisms of vehicles [15, 16].

According to some authors, there are currently more than 40 fuel additives that differ in purpose and brand (anti-detonation, cetane-enhancing antioxidant, anti-smoke, anti-carbon, antistatic, biocidal, depressants, detergents, anti-corrosion, etc.) [15, 17].

In addition to liquid fuel producers, fuel dopes are widely used in Ukraine by fuel distributors for marketing purposes and to create their own brand on the consumer liquid fuel market. In particular, given the absence of officially defined requirements and procedures for the use of such additives, dopes, colourants, as well as the identification of less harmful ones for use, their uncontrolled use in the country creates conditions for the introduction of liquid fuels of dubious and dangerous quality for vehicles, human health and the environment in general.

The requirements of the World Fuel Charter and Directive 98 define strict requirements for the use of fuel additives for various functional purposes by manufacturers, which are added to the mixture of liquid fuels during the production process, with compliance of fuel parameters with the requirements of technical standards, in particular, they clearly define the specification of liquid fuels according to the Euro 5 and Euro 6 environmental class [4, 10].

In particular, in some Community countries, in order to reduce toxic emissions and comply with the Euro 6 environmental standard, AdBlue is used as an additional operating fluid for diesel engines, which is placed in a separate tank (fuel dispenser) and used at the request of the consumer during refuelling. For cars and trucks, AdBlue is used in an average of 1.5–2.5 L per 1000 km (Fig. 3).

All European Union countries are required to check the quality of liquid fuels sold at petrol and gas stations. The obligation was established in view of the differences in legislation and administrative regulations adopted by the Member States on fuel specifications, in particular, it was recognized that differences in requirements create obstacles to trade within the Community, and therefore directly affect the functioning of the internal market, the international competitiveness of both the European automotive industry and the oil refining industry.

According to paragraph 8 of Regulation 2009/30, the combustion of road fuels is responsible for around 20% of greenhouse gas emissions in the Community. One approach to reducing these emissions is to reduce greenhouse gas emissions throughout the life cycle. Reducing such emissions involves a gradual reduction of greenhouse gas emissions by up to 10% per unit of energy through the use of biofuels, alternative fuels and reduced combustion at production sites, including through the use of environmentally friendly carbon capture and storage technologies and the use of electric vehicles.

In addition, the protection of human health and the environment was taken into account, as air pollutants, nitrogen and sulphur oxides, unburned hydrocarbons, particulate matter, carbon monoxide, benzene and other toxic substances emitted in vehicle exhaust gases pose a direct and indirect threat. Therefore, in 2003, the European Parliament adopted Directive 2003/17/EC amending Directive 98, setting new, more stringent environmental requirements for fuels on the market.

Warsaw, Poland, sales of 95 gasoline, diesel fuel, liquefied gas

The Hague, Netherlands, sales of gasoline grade 95, diesel oil, scrap gas

Görlitz, Germany, sales of 95 gasoline, diesel fuel, liquefied gas

Basel, Switzerland sales of 95 and 98 gasoline and diesel fuel

Kyiv, Ukraine

Fig. 2 Photo materials of the type of fuel in the retail network of fuel stations (car gas filling stations) in some Community countries and Kyiv (photo August–September 2022)

According to the requirements of Regulation 2009/30, suppliers or suppliers responsible for the monitoring and reporting of greenhouse gas emissions designated by the Member States of the Community report on the greenhouse gas emissions during the life cycle of the fuel they supply and on the extent of their reduction from 2011, which are formed during the life cycle per unit of supplied fuel energy [8].

The fuel quality control system in the Community countries is based on European standards, including EN 14,274:2003 “Automotive fuels—Assessment of petrol and diesel quality—Fuel quality monitoring system” and EN 14,275:2003 “Automotive fuels—Assessment of petrol and diesel fuel quality—Sampling from retail site pumps and commercial site fuel dispensers”. This standard defines in detail the rules for

Fig. 3 Distribution complex at a gas station for the sale of diesel fuel and AdBlue reagent in Germany (photo August 2022)

sampling and the minimum number of samples, the method of sampling at petrol stations, the rules for their transportation, storage, examination, requirements for accredited laboratories, etc.

Each Community country has its own specifics and elements that distinguish it from other EU countries (legal framework, institutions involved in the organization of the system), however, each state is obliged to comply with the requirements of Directive 98, Directive 2009/30/EC, EN 14,274: 2003 standard, including the obligation to report annually to the Council of Ministers (by 31 July) on the quality of liquid fuels, the quality of liquid biofuels, liquefied petroleum gas (LPG) and compressed natural gas (CNG), and to the European Commission (by 31 August) on the quality of fuels sold on its territory, to organize a fuel quality control system based on EU principles and to carry out relevant analysis.

In particular, since 2012, the European Commission has been reporting every two years to the European Parliament and the Council on third countries and Community Member States that are sources of biofuels or feedstocks for biofuels consumed within the Community and on national measures taken to meet sustainability criteria, and to protect soil, water and air.

Given the practice of fuel quality control in Poland, since January 1, 2007, the main regulatory document governing the functioning of the fuel quality monitoring and control system is the Act of 25 August 2006 "On the Fuel Quality Monitoring and Control System" [19, 20].

The Head of the Competition and Consumer Protection Authority is responsible for the functioning of the control system, which is supported by the Trade Inspectorate responsible for fuel control. The control and monitoring of the quality of fuels is divided into summer and winter periods, with samples taken for examination every month, as well as systematic statistical observations of the quality of fuels placed on the market.

Samples are collected at petrol and gas filling stations by oblasts. Sampling locations are selected randomly for each type of fuel and are proportional to the share of liquid fuel sales in that region and the total liquid fuel sales in the country.

Within the national part, the control system is aimed not only at detecting cases of fuel trade that does not meet quality standards, but also provides for the inspection of liquid fuels to which changes in physical and chemical parameters (quality improvement) are applied where violations have been identified, including as a result of previous inspections of drivers' complaints, information received from the police.

Systematic monitoring is carried out for all types of fuel (unleaded gasoline of the 95 and 98 grades, diesel fuel, liquid biofuel (diesel fuel with a 20% content of complex esters (B20) and methyl ester of fatty acids as an independent fuel (B100)) and covers the entire chain of circulation operators fuel, namely:

- entrepreneurs who store fuel;
- entrepreneurs who carry out activities in the field of fuel transportation (control at the request of the police);
- owners and operators of fuel stations (car gas filling stations) of car parks;
- state and corporate gas stations where control of liquid biofuel, liquefied petroleum gas (LPG) and compressed natural gas (CNG) is carried out;
- farmers who produce liquid biofuel for their own use;
- entrepreneurs who sell light petroleum products, light and heavy fuel oils [20, 21].

Control over the quality of fuels also includes control over compliance by business entities with the obligations to sell motor petrol with a bioethanol content of up to 5% (10%) at petrol stations (filling stations) with the appropriate labelling of fuel dispensers offering such petrol in order to identify for the consumer the percentage of such biocomponents in this fuel, as well as to inform that the proposed fuel can be used in an engine that allows its use. In addition, the labelling of fuel dispensers used at petrol stations or factories for the sale of liquid fuels containing metal dopes must be marked with the inscription "Contains metal dopes".

The Office for Competition and Consumer Protection in Poland is responsible for preparing reports for the European Commission and the Council of Ministers. The report contains information on: the quality of liquid fuels and the quality of liquid biofuels, liquefied petroleum gas (LPG), compressed natural gas (CNG); sulphur content in light fuel oil, heavy fuel oil. The reports are generated on the basis of data from the Chief Environmental Inspector or Directors of Maritime Offices if the data relate to motor fuel oil for inland navigation and/or fuel used on marine vessels.

The relevant reports are available at the following links in the public domain [14, 22]. The fuel quality monitoring and control system in Germany is different from others, it does not belong to any model that operates according to EN 14,274:2003 - and is considered a national system. The control system mainly provides requirements for the labeling and quality of automobile gasoline, motor oils and liquid gaseous fuel in accordance with the Law of the Federation "On Protection from Emissions" and other standards [23].

Monitoring of fuel quality does not involve checking all the parameters contained in the European standards, but only indicators of particular importance for the environment, consumer protection, or indicators of product non-compliance that have been established as a result of previous inspections.

The Ministry of the Environment is responsible for submitting an annual report to the European Commission. The report is based on data provided by the Federal Environment Agency and on information provided by the German federal states, as well as statistics from the Federal Office for Economic Affairs and Export Control.

The fuel quality monitoring and control system in Austria is implemented throughout the country and covers the quality of motor petrol and diesel fuel sold at petrol stations. All parameters of liquid fuels are measured in accordance with EN 14,274:2003. The examination (testing) of the parameters is carried out in accredited laboratories of the Federal Office for Consumer Protection and the Federal Environment Agency. And since Austria has only one refinery (Schwechat), whose products cover a significant part of the national demand, the entire territory of Austria is considered as one region for control [18, 23].

In Ireland, the control over the quality of gasoline and diesel fuel in circulation is checked by the Revenue Service. The selected samples are tested by the National Laboratory. Information on the annual volume of fuel sales is collected and provided by the Department of Transport, and the Department of Environment, Heritage and Local Government is responsible for the preparation and submission of the annual fuel quality monitoring report to the European Commission.

There is one refinery operating in Ireland, all products are inspected by the refinery operator before shipment and transported by road and sea to customers. Samples of fuel products are taken by the tax service once every three months at fuel terminals and after each refueling at the National Bank of Fuel Reserves. Also, samples are taken from gas stations, tankers, trucks and minibuses. The monitoring and quality system includes inspections by the Irish Petroleum Industry Association, which takes its own samples for testing at car parks and at the refinery in July–August and December each year.

In Ukraine, according to the List of types of products for which state market surveillance bodies carry out state market surveillance, the State Ecological Inspection of Ukraine is a state market surveillance body for compliance with the requirements of the Technical Regulation.

Control of fuels is carried out on time and in the prescribed manner in accordance with the Law of Ukraine "On State Market Supervision and Control of Non-Food Products" (hereinafter—the Law). In particular, checking the characteristics of liquid fuel products is carried out on a scheduled basis exclusively at distributors of such products (fuel stations (car gas filling stations)) within 4 days, and unscheduled at distributors of liquid fuels in the presence of substantiated appeals-complaints from consumers regarding the non-compliance of products, at manufacturers (within 5 days)—in case of establishment of non-conformity of the products based on the results of the examination, which was taken from the distributors. Control of importers, authorized persons who introduce liquid fuels into the territory of Ukraine is carried out based on the results of the customs suspension of products and the corresponding notification of the state market surveillance authority by the customs authority [24].

Thus, in Ukraine, control over the quality of liquid fuels does not cover business entities that store fuel, store and/or use liquid fuels for their own needs, transport, fleet operators, state and municipal enterprises, as well as business entities engaged in wholesale trade in fuel, importers, authorized persons, and manufacturers on a routine basis.

In particular, according to Article 27 of the Law, sampling of liquid fuels and their examination (testing) are carried out on the basis of a reasoned written decision of the head of the market surveillance authority or his/her deputy (chairman and members or an authorized person of the state collegial body). Thus, the procedure for taking samples of liquid fuels requires, first of all, formal processing (analysis) of documents provided by the business entity that must accompany the fuel batch, secondly, signing the decision on sampling, and thirdly, organizing and conducting the sampling procedure.

Under such conditions, it takes time to take a sample of products and conduct their examination. In practice, sampling takes place in one to three days, which leads to conditions where products may be generally absent according to the documents provided on the first day of the inspection by the market surveillance authority, or to the creation of conditions that lead to certain actions on the part of business entities, namely the replacement of the full volume of such products at the fuel station (car gas filling station), and as a result, inappropriate sampling measures, spending unnecessary budgetary costs during further examination (testing).

The standard EN 14,274:2003 defines a system for monitoring the quality of fuels to assess their quality, which is sold in any country of the Community. According to the internal regulations of CEN/CENELEC, national standardization organizations of such countries as Austria, Belgium, the Czech Republic, Denmark, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Luxembourg, Malta, the Netherlands, Norway, Slovakia, Spain, Sweden, Switzerland, Great Britain are required to implement the EN 14,274:2003 standard [18].

The EN 14,274:2003 standard contains statistical justifications and describes a fuel quality monitoring system in accordance with European Directive 98/70/EC and cannot be adjusted in a specific region, however, it can be extended to achieve additional goals.

Due to the specific parameters of the European fuel specifications, EN 228 and EN 590 standards state that each country should select limit values from a certain set of values and take into account such limit values for a specific country, taking into account geographical and climatic factors. Such values may differ, therefore the specific parameters in the monitoring and quality system of the Community countries are different.

According to EN 14,274:2003, a country should be treated as a single region for sampling purposes. The number of samples for the purpose of checking their quality depends on the size of the country, taking into account the total amount of fuel sold in this country (a small country—15 million tons or less are sold per year, a large country—a total of more than 15 million tons are sold per year), places of sale (dispensing) of fuel (object of retail or wholesale trade). The calculation of the necessary number of such samples is determined by each country of the Community separately, at the same time, their minimum number should be such that the data are effective and representative for the overall assessment of the monitoring system for that country. In particular, it is noted that the country may, at its own discretion, use more than the minimum number of samples, but not less.

According to the requirements of the EN 14,274:2003 standard, taking into account the specification of liquid fuels, the minimum number of samples for each type varies from 50 to 200 samples. Fuel quality is tested twice a year: once in winter and once in summer.

In accordance with the requirements of EN 14,274:2003, the Community countries shall establish a list of sampling sites, which shall be updated annually. Such a list should contain information on the region in which the facility is located and be divided into facilities based on their turnover.

In order to determine the amount of each type of liquid fuel to be assessed, information on the total amount of fuel sold in the country, sources of supply and the supply chain with distribution in the network, and, if available, data on the population and number of vehicles with their respective regional distribution are taken into account.

Accredited laboratories performing tests for fuel quality monitoring are determined by the competent authority in each Community and take into account the eligibility criteria, which include the qualifications and competence of the staff to take and examine fuel samples and prepare an analytical report.

In Ukraine, the selection of samples of liquid fuels is carried out by officials of the market surveillance body in accordance with the requirements of DSTU [in Ukrainian] 4488:2005 "Oil and petroleum products. Sampling methods", the Procedure for selecting product samples to determine their quality indicators and the form of the act of selecting product samples, approved by Resolution № 1280 of the Cabinet of Ministers of Ukraine dated 30.10.2007. Examination (testing) is carried out in accredited laboratories based on the results of tender procurement and conclusion of contracts with business entities for the lowest value proposition [25, 26].

Thus, an official who takes samples of liquid fuels must be qualified to conduct such sampling at high-risk facilities, including being provided with the necessary equipment, facilities, personal protective equipment, with mandatory specialized training on occupational health and safety, and admission to such work, etc.

Liquid fuels in EU countries are checked mainly for all quality indicators provided for by Directive № 98. According to the report in Poland for 2021, non-compliance with the parameters is noted by the indicators of oxygen content, organic oxygen-containing compounds, ethanol (A-95) and saturated vapor pressure (A-98). The highest excess of sulfur content was registered in Poland in 2005 and was more than fifty times the established norm (more than 2734 mg/kg) [19].

Taking into account data from open sources, it is noted that the lowest non-compliance with quality standards in the studied fuel samples is noted in Germany, Ireland, Latvia and Austria (below 1%), a little more—in the Czech Republic and Poland (1–5%), and the effective effect is emphasized of the implemented system of monitoring and control of fuel quality from year to year, which was launched in 2004 [16, 23].

In Ukraine, non-compliance with the requirements of the Technical Regulation in products of the type "diesel fuel" is noted by indicators of sulfur content, flash point in a closed crucible, in products of the type automobile gasoline—by sulfur content, volume fraction of benzene, mass fraction of oxygen, detonation resistance according to experimental and by the motor method, as well as by the volume fraction of “bioethanol”.

In particular, in products of the diesel fuel type, the sulfur content exceeded the established requirements by 3–3.5 times (49.4 ± 62.4 mg/kg), the flash point in a closed crucible was 1.3 times lower (42.43 ± 9.85 °C). In gasoline samples, the indicator of detonation resistance according to the experimental method was 1–2 times lower (90.8 ± 0.43 units), the sulfur content exceeded the established requirements by 4–10 times (49.4 ± 62.4 mg/kg), the volume fraction of benzene and the mass fraction of oxygen are 2–2.5 times (2.7 ± 3.43%) and 2.5 times (6.71 ± 3.1%), respectively.

Non-compliance with the requirements of the Technical Regulations was noted both in products of the type: A–92–Euro5–E5, A–95–Euro5–E5, DP–Z–Euro5–B0 [in Ukrainian], DP–L–Euro5–B0 [in Ukrainian], and in products of the 95–Euro5 brand –E5 “Premium”, 95–Euro5–E5 “Shebel”, DP–Z–Euro5–B0 [in Ukrainian] “Shell V–Power”, DP–Z–Euro5–B0 [in Ukrainian] “Premium”, DP–Z–Euro5–B0 [in Ukrainian] “Energy”, in imported fuel and fuel of domestic production. In general, the ratio of non-conformity to fuel compliance was 1:4 in gasoline samples, 1:5 in diesel fuel [27].

A significant part of the vehicles used in the world are equipped with spark ignition engines (gasoline engines), the rest are compression ignition engines (diesel engines), which are the most economical and environmentally friendly today [28, 29].

Gasoline, which is a product of crude oil processing, is usually used to power spark-ignition engines. The fuel used in compression ignition engines is diesel, and like gasoline it is a mixture of hydrocarbons separated from crude oil by distillation, but unlike gasoline, diesel distillates have a higher boiling point. Differences in the design and principles of operation of gasoline and diesel engines are different, therefore the requirements for their physical and chemical properties are also different [2, 17].

During storage, transportation and distribution in the fuel supply system, liquid fuels are exposed to physical and chemical influences that change their quality. Therefore, the fuel that is in the tank of the vehicle may have different properties than when it was produced at the refinery.

The potential for fuel to become contaminated with water during storage, transportation or distribution is just one of many factors that cause fuel quality to vary from production to consumer market. And on the way to determine the main factors that can cause changes in the physical and chemical properties of liquid fuels, one can include improper decantation, storage of fuels in containers that exclude their tightness, interaction of fuel with oxygen in the air, and ingress of dust during distribution in the network, evaporation of light fractions, ingress of solid impurities of corrosion products from tanks, pipelines during their oxidation and polymerization.

Thus, the system of control and monitoring of the quality of liquid fuels should be organized at all stages of production, storage, transportation and their distribution, as well as apply to each market operator, economic entity that carries out appropriate measures in the way of introduction into circulation, application and /or storage.

Pursuant to the Regulation 1680, fines in Poland for the production, transportation, storage or sale of liquid fuels, liquid biofuels, liquefied petroleum gas (LPG), compressed natural gas (CNG) or light fuel oil that do not meet the quality requirements are:

- from 50,000 to 500,000 PLN (425,000-4,250,000 UAH) (or imprisonment for up to 3 years);
- from 100,000 to 1 million PLN (850,000-8,500,000 UAH) or imprisonment for a term of 3 months to 5 years if the fuel is property of significant value;
- from 10,000 to 25,000 PLN (85,000-212,500 UAH) in case of lesser severity;
- from 25,000 to 250,000 PLN (212,500-2,125,000 UAH) for unintentional actions that led to product non-compliance.

In addition, fines of 5,000 PLN (42,500 UAH) are provided for farmers who produce liquid biofuels that do not meet quality requirements, including those used for their own needs; owners or users of a vehicle fleet that use liquid biofuels that do not meet quality requirements.

Business entities are also liable for the production, storage or sale of liquid biofuels in tanks that are not labelled in accordance with the established procedure, including for failure to post information on fuel stations (car gas filling stations) about the content of biocomponents in liquid fuels sold at fuel stations (car gas filling stations). In particular, the fine is imposed on the day of the inspection based on an administrative decision made by an inspector of the Trade Inspection.

Pursuant to Article 44 of the Law, fines for business entities that have put products on the market (importers, authorized persons, manufacturers) are imposed in the event of non-fulfilment or incomplete fulfilment of a decision to take restrictive (corrective) measures with respect to products that do not meet the established requirements and/or pose a risk of 102,000 to 170,000 UAH, and for distributors—from 68,000 to 119,000 UAH. The penalty is imposed upon failure to comply with such decisions, drawing up a protocol or resolution, and may be applied within 30 days.

Thus, taking into account the legislation of Ukraine, liability for business entities in the Community countries is more economically severe and demanding, and applies to the range of all entrepreneurs involved in the circulation of fuels from production, management, distribution to storage and use, and is generally aimed at bringing to justice for non-compliance with emission reduction requirements, failure to implement measures to use alternative fuels, and misleading consumers.

Taking into account the above, on the way to complying with the requirements of the Association Agreement, with the aim of Ukraine's accession to the countries of the European Community, as well as the creation of conditions for the acceptance of liquid fuels for the creation of a free trade zone, a number of problematic and urgent issues arise in Ukraine that need to be resolved, and which are inevitable in today's.

The solutions to such issues will be directed and connected primarily with the implementation of the requirements of Directive 98, Directive 2009/30/EC, standard EN 14,274:2003, internal regulations of CEN/CENELEC, European specifications EN 228 and EN 590, including a comprehensive restructuring in the organization, the creation of an appropriate system of control and monitoring of the quality of liquid fuels on the territory of Ukraine, secondly, the introduction of effective levers for the implementation of special legislation, strategies, complex programs and the determination at each stage of competent executive authorities responsible for their implementation.

The control and monitoring system should provide for both internal and external control for business entities, regulatory authorities and take into account the origin and chain of introduction and distribution of liquid fuels, and should be aimed at reducing emissions into the atmosphere, ensuring the protection of consumer interests, safety environment, and national security of the state.

References

1. Regulation (EU) 2019/1020 of the European Parliament and of the Council of 20 June 2019 on market surveillance and compliance of products and amending Directive 2004/42/EC and Regulations (EC) No 765/2008 and (EU) No 305/2011 (20 June, 2019). Verkhovna Rada Ukrainy [in Ukrainian]. https://zakon.rada.gov.ua/laws/show/984_012-19#Text
2. Boichenko, S.V., Leida, K., Yakovleva, A.V., et al.: Influence of rapeseed oil ester additives on fuel quality index for air jet engines. Chem. Technol. Fuels Oils **53**, 308–317 (2017). https://doi.org/10.1007/s10553-017-0807-5
3. On the approval of the Technical Regulations on motor gasoline, diesel, marine and boiler fuels: Resolution of the Cabinet of Ministers of Ukraine № 927. (2013, August 1). Verkhovna Rada Ukrainy [in Ukrainian]. https://zakon.rada.gov.ua/laws/show/927-2013-п#Text
4. Directive 98/70/EC of the European Parliament and of the Council of 13 October 1998 relating to the quality of petrol and diesel fuels and amending Directive 93/12/EEC. (1998, October 13*)*. EUR-Lex. https://eur-lex.europa.eu/resource.html?uri=cellar:9cdbfc9b-d814-4e9e-b05d-49dbb7c97ba1.0008.02/DOC_1&format=PDF
5. About technical regulations and conformity assessment № 124-VIII. (2015, January 15). Verkhovna Rada Ukrainy [in Ukrainian]. https://zakon.rada.gov.ua/laws/show/124-19#Text
6. On the approval of conformity assessment modules, which are used to develop conformity assessment procedures, and rules for the use of conformity assessment modules: Resolution of the Cabinet of Ministers of Ukraine № 95. (2016, January 13). Verkhovna Rada Ukrainy [in Ukrainian]. https://zakon.rada.gov.ua/laws/show/95-2016-п#Text
7. On approval of the form, description of the mark of compliance with technical regulations, rules and conditions of its application: Resolution of the Cabinet of Ministers of Ukraine № 1184. (2015, December 30). Verkhovna Rada Ukrainy [in Ukrainian]. https://zakon.rada.gov.ua/laws/show/1184-2015-п#Text
8. Directive 2009/30/EC of the European Parliament and of the Council of 23 April 2009 amending Directive 98/70/EC as regards the specification of petrol, diesel and gas-oil and introducing a mechanism to monitor and reduce greenhouse gas emissions and amending Council Directive 1999/32/EC as regards the specification of fuel used by inland waterway vessels and repealing

Directive 93/12/EEC. (2009, April 23). EUR-Lex. https://eur-lex.europa.eu/legal-content/EN/TXT/?qid=1520077936157&uri=CELEX:02009L0030-20160610
9. Act of 23 October 2015 on quality requirements for liquid fuels: Regulation of the Minister of Economy. (2015, October 23). Minister Gospodarki [in Polish]. https://isap.sejm.gov.pl/isap.nsf/download.xsp/WDU20 150001680/O/D20151680.pdf
10. Commission Regulation (EC) No 692/2008 of 18 July 2008 implementing and amending Regulation (EC) No 715/2007 of the European Parliament and of the Council on type-approval of motor vehicles with respect to emissions from light passenger and commercial vehicles (Euro 5 and Euro 6) and on access to vehicle repair and maintenance information. (2008, July 18). Ligazakon [in Ukrainian]. https://ips.ligazakon.net/document/view/EU080011
11. Regulation (EC) № 443/2009 of the European Parliament and of the Council of 23 April 2009 setting emission performance standards for new passenger cars as part of the Community's integrated approach to reduce CO2 emissions from light-duty vehicles. (2009, April 23). EUR-Lex. https://eur-lex.europa.eu/legal-content/EN/ALL/?uri=celex%3A32009R0443
12. Directive 2010/75/EU of the European Parliament and of the Council of November 24, 2010 on industrial emissions (integrated approach to pollution prevention and control). (2010, November 24). Verkhovna Rada Ukrainy [in Ukrainian]. https://zakon.rada.gov.ua/laws/show/984_004-10#Text
13. Comission decision of 15 December 2010 amending Decision 2006/944/EC determining the respective emission levels allocated to the Community and each of its Member States under the Kyoto Protocol pursuant to Council Decision 2002/358/EC. (2010, December 15). EUR-Lex. https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32010D0778&from=FR
14. Reports for the Council of Ministers on fuel quality. Urzad Ochrony Konkurencji i Konsumentow [in Polish]. https://uokik.gov.pl/szukaj.php?szukaj=raporty_+jakosc_paliw
15. Liakh, M.A., Demianiuk O.S., Barylko, O.S.: Regarding the issue of using fuel additives abroad and in Ukraine. Zbirnyk naukovykh prats Viiskovoho instytutu Kyivskoho natsionalnoho universytetu imeni Tarasa Shevchenka, 17 [in Ukrainian] (2009)
16. World-wide fuel charter. International Organization of Motor Vehicle Manufacturers. https://www.oica.net/worldwide-fuels-charter/
17. Yakovlieva, A., Boichenko, S.: Energy efficient renewable feedstock for alternative motor fuels production: solutions for Ukraine. In: Babak, V., Isaienko, V., Zaporozhets, A. (eds.), Systems, Decision and Control in Energy I. Studies in Systems, Decision and Control, vol. 298. Springer, Cham (2020). https://doi.org/10.1007/978-3-030-48583-2_16.
18. EN 14274:2013 – Automotive fuels – Assessment of petrol and diesel quality – Fuel quality monitoring system (FQMS). ITEH. https://standards.iteh.ai/catalog/standards/cen/6bcedd74-c5e0-48c4-bbb0-0a0783dc9a04/en-14274-2003
19. Reports for the European Commission on fuel quality. Urzad Ochrony Konkurencji i Konsumentow [in Polish]. https://uokik.gov.pl/ raporty_jakosc_paliw.php#faq1499
20. Act of 25 August 2006 on the fuel quality monitoring and control system. (2006, August 25). ISAP. Internetowy System Aktow Prawnych. https://isap.sejm.gov.pl/isap.nsf/DocDetails.xsp?id=WDU20061691200
21. Żmijewski, K., Sokołowski, M.: The development of power grids in Poland in the context of regulatory acts of the climate and energy package. Acta Energetica, 86–94 (2010)
22. Raport z kontroli paliw ciekłych w 2021 roku. (2022). Urzad Ochrony Konkurencji i Konsumentow [in Polish]. https://uokik.gov.pl/search.php?szukaj=raport+dla+Komisji+Europejskiej
23. Description of the fuel quality monitoring and control system. Urzad Ochrony Konkurencji i Konsumentow [in Polish]. https://uokik.gov.pl/opis_systemu_monitorowania_i_kontrolowania_jakosci_paliw.php#faq3757
24. On state market supervision and control of non-food products № 2735-VI. (2010, December 2). Verkhovna Rada Ukrainy [in Ukrainian]. https://zakon.rada.gov.ua/laws/show/2735-17#Text
25. Yakovlieva, A., Boichenko, S., Boshkov, V., Korba, L., Hocko, M.: Experimental study of physical-chemical properties of advanced alcohol-to-jet fuels. Aviation **27**(1), 1–13 (2023). https://doi.org/10.3846/aviation.2023.18564

26. On the approval of the Procedure for the selection of product samples to determine their quality indicators and the form of the product sample selection act: Resolution of the Cabinet of Ministers of Ukraine № 1280. (2007, October 30). Verkhovna Rada Ukrainy [in Ukrainian]. http://online.budstandart.com/ua/catalog/doc-page?id_doc=59378
27. DSTU 4488:2005 [in Ukrainian]. Oil and oil products. Sampling methods. (2006, October 1). K.: Upravlinnia Derzhspozhyvstandartu, 34 p. [in Ukrainian].
28. Sibilieva, O.V.: The quality of automobile gasoline and diesel fuel on the market of Ukraine. Ekolohichni nauky, No **4**(43), 100–106 (2022). [in Ukrainian]
29. Topilnytskyy, P., Romanchuk, V., Boichenko, S., Golych, Y.: Physico-chemical properties and efficiency of demulsifiers based on block copolymers of ethylene and propylene oxides. Ch&ChT **8**(2), 211–218 (2014)

Analysis of Conventional and Nonconventional GTL Technologies: Benefits and Drawbacks

Viktoriia Ribun, Sergii Boichenko, Hubert Kuzhewski,
and Pawel Wos

1 Introduction

Since the world's population continues to grow and national economies develop, the demand for energy increases significantly as well. At the same time, the search for clean sources of energy to reduce the impact of combustion products on the environment is increasing. Soon, natural gas demand is likely to outpace demand for other fossil fuels. The International Energy Agency (IEA) predicts an increase in demand for natural gas by more than 50% by 2035. Especially if a significant part of shale gas will be used [1]. Some countries, for example, the USA, actively produce shale gas and use GTL technologies to convert excess gas into liquid motor fuels and lubricants [2]. Ukraine also has large gas reserves. The total volume of technically recoverable shale gas resources in Ukraine is estimated at 4.8 trillion m^3 (1.75% of the world reserve), 3.6 trillion m^3 of which are concentrated in the two largest fields—Yuzivskyi field in the Donetsk and Kharkiv regions, and 1.2 trillion m^3 are concentrated in the Oleske field, which is located in the west of Ukraine. In addition, Ukraine has quite wide possibilities for the production of biogas, which contains 50–60% of methane and 30–35% carbon dioxide, and 10 billion m^3/year of biomethane [3]. Therefore, the development and implementation of technologies for motor fuel or their components production through the conversion of natural gas is a promising scientific direction for Ukraine.

V. Ribun (✉)
Chemical-Analytical Laboratory of PJSC Ukrnafta, Kyiv, Ukraine
e-mail: ribun.vika@gmail.com

S. Boichenko
National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute", Kyiv, Ukraine

H. Kuzhewski · P. Wos
Rzeszow University of Technology, Rzeszow, Poland

S. Boichenko et al. (eds.), *Modern Technologies in Energy and Transport*, Studies in Systems, Decision and Control 510, https://doi.org/10.1007/978-3-031-44351-0_14

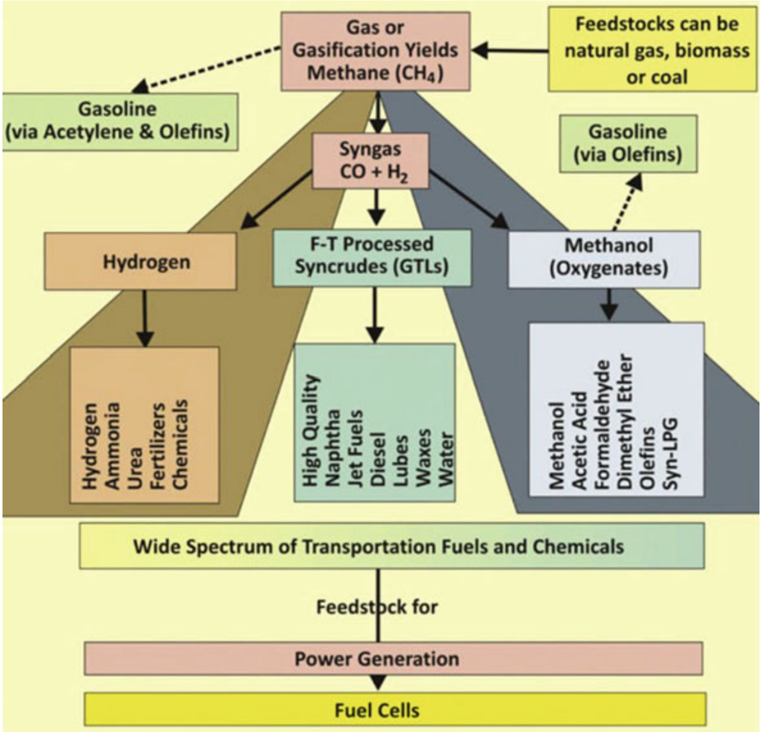


Fig. 1 Conversion of natural gas into liquid fuels and petrochemical products

The most common way of converting natural gas into liquid hydrocarbons is the Fischer–Tropsch method, that requires a pre-conversion of natural gas to synthesis gas, which is the most expensive stage of the technology. However, in recent decades, a number of alternative technologies for converting natural gas into high-quality liquid fuels have emerged, including sulfur free diesel with high cetane number, and jet fuel. Such technologies make it possible to obtain motor fuels using both ways—including the stage of synthesis gas and without conversion of natural gas to a mixture of carbon monoxide and hydrogen, which actually is synthesis gas (Fig. 1) [4].

2 The Role of Global Gas Reserves for the Development of GTL Technology Development

Global natural gas reserves are increasing faster than its consumption. An increase in unconventional gas production in North America and Australia in recent years has accelerated this trend. Indeed, taking into account the future development of unconventional gas production, such as shale gas, for energy-scarce countries, this trend is likely to continue for at least several decades. An additional resource is significant amounts of associated natural gas that is burnt or released during oil production in some countries of Africa (Nigeria) and the Middle East. Gas conversion can play a major role in reducing flaring if the technology becomes more available and cost-effective [5].

According to forecasts of the International Energy Agency (IEA), it is possible to achieve natural gas production of about 5.1 trillion m^3 in 2035, 32% of which will be unconventional natural gas. Most of this gas is currently delivered to consumers via pipelines, and approximately 30% of the gas exported from producing countries is transported as liquefied natural gas (LNG). However, a significant part of the world's natural gas reserves are either located far from consumers or are located in regions where demand for gas is limited. Transportation of natural gas by vehicles is a technologically complex process, because the gas must be compressed up to 600 times. GTL technology is an alternative and offers the chemical conversion of methane into long-chain hydrocarbon molecules that exist in a liquid state under atmospheric conditions. Methane itself can be obtained from natural gas, associated petroleum gas, gasification of coal and biomass [6].

OPEC predicts an increase in the need for diesel fuel to 37 million barrels/day by 2035 [7]. GTL technologies can make a significant contribution to the production of the necessary amount of transport fuels since demand for transport fuels increases every year (Fig. 2). The dependence on oil products for the transport sector is considered to be a threat to the energy and environmental security of country. High consumption in turn has contributed to the development of alternative fuels (biodiesel, bioreactive fuels, etc.), which can compete with GTL fuels [8]. However, GTL may benefit from increasingly stringent demands from consumers, environmentalists, governments and car manufacturers for fuel purity and efficiency. GTL diesel produced by FT processes has significantly higher quality than diesel fuel produced by typical crude oil refining processes. GTL diesel has a high cetane number (about 70 units compared to 45–55 units of petroleum diesel), low sulfur content (< 5 ppm), low content of aromatic substances (<1%), which leads to a decrease in density and improvement of low-temperature properties of diesel fuel [9].

3 Chemistry of the Fischer–Tropsch GTL Process

GTL (gas-to-liquid) and CTL (coal-to-liquid) technologies were first introduced in Germany in the 1920s using a process that became known as Fischer–Tropsch (FT) synthesis when Germany found itself short on oil, but had significant reserves of coal [10]. The need to provide liquid fuel led to the opening of factories that turned coal into gas and then into liquid using the high-temperature synthesis of FT. Despite the fact that the FT process was technically successful, it could not economically compete with the processing of crude oil, so the technology was used only to cut the lack of transport fuels. Recently, there has been renewed interest in the synthesis of

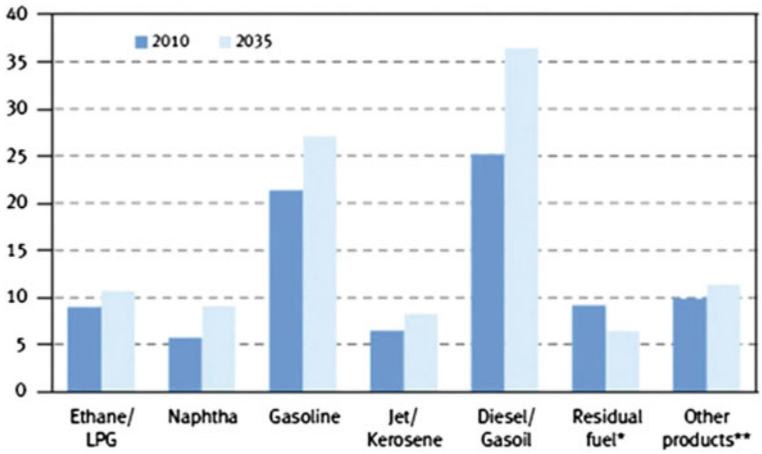


Fig. 2 Global product demand [9]

GTL fuels using low-temperature conversion of natural gas by the FT method into middle distillates [11]. It is caused by the limited supply of crude oil and the global desire to obtain cleaner high quality transport fuel.

The conversion of natural gas into liquid hydrocarbons can be accomplished through several chemical transformation steps leading to a variety of products. Currently, GTL technology based on Fischer–Tropsch synthesis is the most common. The process consists of three main stages, which require significant supporting infrastructure and a safe supply of natural gas for highly efficient synthesis [12].

1. Synthesis gas production. Natural gas is treated with steam and/or partial oxidation. The produced syngas consists mainly of carbon monoxide and hydrogen [13–17].
2. Catalytic (FT) synthesis. Depending on the technology, syngas is converted in reactors of various designs, into a variety of paraffinic hydrocarbons (crude synoil) with a long carbon chain ($\approx$ 100 carbon atoms in the molecule) [18–20].
3. Cracking of FT synthesis products. Crude synoil is cracked as in a traditional oil refinery to produce diesel fuel and commercial lubricants. Cracking of long-chain hydrocarbons can be adjusted to obtain products that market demands. The highly profitable target products of FT synthesis usually are middle distillate diesel fuel, jet fuel, and lubricating materials. Modern facilities are designed to obtain target products [21–26].

Fischer–Tropsch processes are not limited only to the use of conventional natural gas. Coal seam gas, associated gas, coal or biomass can be also processed using FT technologies by changing the catalyst, pressure and temperature conditions of synthesis [27]. A constant and safe supply of feed gas, regardless of origin, is essential to the commercial viability of large-scale FT GTL plants. The integration of mining and processing processes allows developers of GTL projects to earn profits with less potential risk [28].

4 Syngas Syngthesis

Syngas is usually obtained by the method of partial oxidation or conversion with water steam [29]. Syngas production is an intermediate step for many petrochemical processes, including a number of alternative GTL technologies.

Production of syngas by partial oxidation of methane (1) requires separation stage to remove nitrogen from the air and obtain oxygen of high purity [30].

$$CH_4 + 1/2O_2 \rightarrow CO + 3H_2. \tag{1}$$

Typical schemes of partial oxidation usually include:

- section for burning gas with pure oxygen. It contains a combustion chamber and operates at high temperatures (1200–1500° C) without catalysts;
- heat removal section, since the reaction is exothermic;
- carbon removal section [31].

The steam reforming process is widely used to obtain synthesis gas as a feedstock for a number of petrochemical processes and to produce hydrogen used in hydrocracking refineries. Reforming occurs according to reaction (2).

$$CH_4 + H_2O \rightarrow CO + 3H_2. \tag{2}$$

Steam reforming is usually carried out in the presence of a catalyst and under operating conditions that include temperatures of 850–940° C and a pressure of approximately 3 MPa. The process, as a rule, is carried out in tubular reactors using the heat of flue gases to preheat the source gas or to obtain steam in boilers [32].

In the autothermal reforming (ATR) synthesis gas production combines steam reforming with partial oxidation. The heat generated as a result of partial oxidation is used to heat the steam reforming reaction. The gases from the combustion chamber are mixed with steam and directed to the steam reformer, which makes the process autothermal. In autothermal processes, the heat is produced only by the reaction [33].

5 Fischer–Tropsch Synthesis

The The Fischer–Tropsch synthesis is one of the common technologies for increasing the carbon chain to obtain long-chain hydrocarbon molecules:

$$CO + 2H_2 \rightarrow -CH_2 - + H_2O(\text{exotermic}). \tag{3}$$

However, in practice, the process occurs according to Eq. (4).

$$2CO_{(gas)} + H_{2\,(gas)} \rightarrow (-CH_2-)_{nliquid} + CO_{2\,(gas)} + H_2O. \quad (4)$$

Carbon dioxide and water are formed as by-products. The FT reaction competes both the methane forming reaction (reverse steam reforming reaction 5) and reaction leading to the formation of propane and butane.

$$\mathrm{CO} + 3\mathrm{H_2} \rightarrow \mathrm{CH_4} + \mathrm{H_2O}. \quad (5)$$

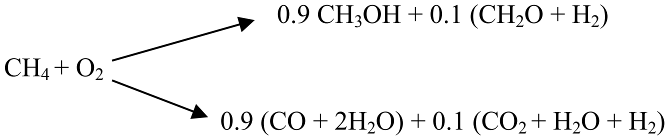
To promote the FT reaction and limit the methane forming reaction, the synthesis is carried out at low temperatures (220–350 °C), pressure 2–3 MPa and using cobalt-based catalysts [34].

There are two types of FT technologies based on natural gas: high-temperature (HTFT) and low-temperature (LTFT) Fischer–Tropsch synthesis. As a result of HTFT synthesis, if the process conditions are chosen correctly and are used the appropriate catalysts, obtained crude syn-oil contains a high percentage of short-chain hydrocarbons (<10 carbon atoms) and significant amount of propane, butane and other olefins (for example, propylene and butylene). These short-chain hydrocarbon gases are usually extracted from tail gases using cryogenic separation. The resulting tail gas is returned to the technological process for further processing. The high-temperature (HT) process of FT GTL based on an iron catalyst allows to obtain such fuels as gasoline and diesel, which are quite similar to traditional fuels obtained by refining conventional oil. The resulting GTL fuel is sulfur free, but contains some aromatic hydrocarbons. Typical operating conditions of the HTFT process are a temperature of about 320° C and a pressure of about 2.5 MPa. The HTFT process can be quite efficient (conversion > 85%), but not all products are ready for use. As a rule, high-temperature Fischer–Tropsch synthesis is carried out in reactors with a circulating fluidized bed [35].

The low-temperature Fischer–Tropsch process (LTFT) is carried out at a low temperature with cobalt based catalyst in slurry reactors with a bubbling column (for example, the Sasol) or in tubular reactors with a fixed bed (for example, the Shell). A synthetic diesel fuel (GTL diesel) obtained during LTFT process does not contain sulfur and aromatic substances. Typical operating conditions of the LTFT process are temperature of approximately 220–240 °C and pressure of approximately 2.0–2.5 MPa. The LTFT conversion is usually only about 60%. The main direction of most large-scale projects based on FT synthesis in the current market conditions is the production of high-quality GTL diesel fuel with low emissions, jet fuel and synoil (as petrochemical feedstock or gasoline addition) [36].

6 Alternative GTL Technologies

The problem of developing a chemical process for obtaining liquid fuels from natural gas without the most expensive stage of obtaining synthesis gas (60% of the cost price), has been raised for a long time. The most common way to obtain gasoline from natural gas is the conversion of methane to methanol, and methanol, in turn, to gasoline. Moreover, the production of methanol takes place without the synthesis gas stage. Currently, several technologies for converting natural gas into methanol have been developed. They do not include the synthesis gas stage – direct oxidation of methane to methanol (OMM) (6) and oxidative coupling of methane (OCM) [37]. OMM is conducted under high pressure (70–80 atm) and relatively low temperatures (400–450 °C). The main products with the same selectivity (40–50%) are methanol and carbon monoxide.



$$\begin{array}{lll} & \nearrow & 0.9\,CH_3OH + 0.1\,(CH_2O + H_2) \\ CH_4 + O_2 & & \\ & \searrow & 0.9\,(CO + 2H_2O) + 0.1\,(CO_2 + H_2O + H_2) \end{array} \qquad (6)$$

Recently, scientists have been developing the OCM method, the main products of which are olefins, mainly ethylene, carbon monoxide and a small amount of hydrogen. The technology is based on the cracking of heavy components of natural and associated gases (C3 +). The process is carried out under atmospheric pressure and high temperatures (≈750 °C). The interaction of methanol or olefins with CO makes it possible to obtain a wide range of GTL products. Direct partial oxidation with simultaneous oligomerization can be an alternative way of GTL technology, which does not include the step of synthesis gas obtaining (7), (8) [38].

$$CH_3OH \rightarrow CH_3{-}O-CH_3 \rightarrow C_nH_{2n}(\text{olefins}); \qquad (7)$$

$$C_nH_{2n} \rightarrow \text{polymerization, cyclization} \rightarrow C_nH_{2n+2}, \text{ cycloparaffins, arenes.} \qquad (8)$$

The Mobil company has developed the first plant, where the technology of conversion of methanol into gasoline is implemented. The plant produces sulfur-free gasoline (octane number 92 units). Methanol is converted into diethyl ether, and then into light olefins C5 + and further into paraffins, naphthenes and aromatic compounds (8). Catalysts used in the process promote the synthesis of hydrocarbons containing less than ten Carbon atoms. The product contains 53% paraffins, 9% naphthenes and 26% aromatichydrocarbons. Methanol is loaded into a system of reactors with a fixed catalyst bed, where it is completely converted into hydrocarbons and water, which are separated into a propane-butane mixture, crude gasoline and water. Crude gasoline is divided into liquefied automobile gas (C3–C4), light gasoline, and heavy gasoline. Heavy gasoline is hydrotreated to reduce duren (1,2,4,5-tetramethylbenzene) content, and then recombined with light gasoline into a finish product that contains no sulfur. The yield of gasoline is usually only 38% [39].

A small Texas company, Synfuels International, has developed a process in which methane at high temperature is converted to acetylene (C_2H_2). Then acetylene is converted using a specially designed catalyst (acetylene conversion $\approx$98%) into ethylene, which in turn is converted into a number of different types of fuel, in particular gasoline. A small demonstration plant was also created [40]. Other companies are also looking for ways to convert gas into gasoline.

7 Experience in Small-Scale FT Plants Operation

Some companies have developed small-sized modular plants for the processing of associated petroleum gas, for example, the British company Compact GTL. This approach consists of such steps as processing of feedgas into a steam methane reformer to produce synthesis gas, feeding it to a FT reactor that converts the feedstock into synthetic crude oil, water, and "tail gases" containing hydrogen, carbon monoxide, and light hydrocarbons gases. Then, the synoil is exported to a conventional oil refinery for further processing. Petrobras' CENPES research and development center has successfully completed a three-year qualification test program for the small-scale GTL technology. This approach enables expansion of GTL technology opportunities [41].

Another company that deals with small-scale FT GTL processes is Velocys. It owns a modular system with a capacity of 1,000 barrels per day. The system is designed to obtain acetylene for the production of diesel and synthetic oil [42].

Although small-scale GTL technologies exist and are commonly used, most of the capital investments in GTL remain concentrated in large-scale FT GTL technologies. Most built capacities that based on FT GTL technologies are owned by two companies. Sasol has developed its GTL technology, which uses autothermal reforming to produce syngas, a slury FT reactor and Sasol's patented cobalt catalyst. The resulting products are subjected to isocracking that is developed by Chevron. Sasol has implemented its technology by building the Oryx plant in Qatar, which has a design capacity of 32,400 barrels per day. Water produced as a byproduct of the GTL plant is used for irrigation in Qatar [43]. Sasol is planning a project to build GTL factories in Uzbekistan, the USA and Canada.

In 1993, Shell put into operation the first commercial GTL plant in the world in Malaysia, and later the Pearl plant in Qatar. Synthesis gas is obtained by partial oxidation with oxygen, and FT synthesis is carried out in a reactor with a fixed layer of cobalt catalyst. Varying the conditions of FT synthesis, the company manufactures a wide range of GTL products: motor fuels, high-quality oils and lubricants, and a number of chemicals that are raw materials for organic synthesis [44].

8 Experience in Large-Scale FT Plants Operation

Although small-scale GTL technologies exist and are commonly used, most of the capital investments in GTL remain concentrated in large-scale FT GTL technologies. Most built capacities that based on FT GTL technologies are owned by two companies. Sasol has developed its GTL technology, which uses autothermal reforming to produce syngas, a slury FT reactor and Sasol's patented cobalt catalyst. The resulting products are subjected to isocracking that is developed by Chevron. Sasol has implemented its technology by building the Oryx plant in Qatar, which has a design capacity of 32,400 barrels per day. Water produced as a byproduct of the GTL plant is used for irrigation in Qatar [43]. Sasol is planning a project to build GTL factories in Uzbekistan, the USA and Canada.

In 1993, Shell put into operation the first commercial GTL plant in the world in Malaysia, and later the Pearl plant in Qatar. Synthesis gas is obtained by partial oxidation with oxygen, and FT synthesis is carried out in a reactor with a fixed layer of cobalt catalyst. Varying the conditions of FT synthesis, the company manufactures a wide range of GTL products: motor fuels, high-quality oils and lubricants, and a number of chemicals that are raw materials for organic synthesis [44].

9 Comparison of FT GTL Products with Conventional Oil Refining Products

Installations basing on FT GTL technology can be desined to produce a wide range of products, from base oils and lubricants to transport fuels and special chemicals. Most of developed technological lines are aimed at production of diesel fuel (C14–C20) along with jet fuel (C10–C13), gasoline (C5–C10), lubricants (>C50) and small amounts of liquefied petroleum gas (C3–C4). Choosing the operating conditions in the Fischer–Tropsch reactor, the mixture of the obtained products can be adjusted. So, GTL products are obtained in such quantities that allow them to complement the market of traditional oil products produced at conventional oil refineries [45].

However, typical FT GTL products are quite different from refinery products, which are obtained as a result of catalytic cracking (Fig. 3). As a rule, the yield of FT GTL diesel fuel is about 70%, that is rather higher than in oil refineries, where diesel fuel yield is usually about 40% [46]. In most oil refineries, the final product is low quality fuel oil and the yield depends on the quality of the processed crude oil, the type and capacity of the plants. In contrast to traditional plants, the products of FT GTL are high-value (compared to crude oil) light and middle distillates. Moreover, the yield of middle distillates is higher in comparison with typical oil refinery [47].

As noted above [9], the world demand for diesel fuel is growing by about 3% per year faster than for other refined products. Produsers face significant challenges in

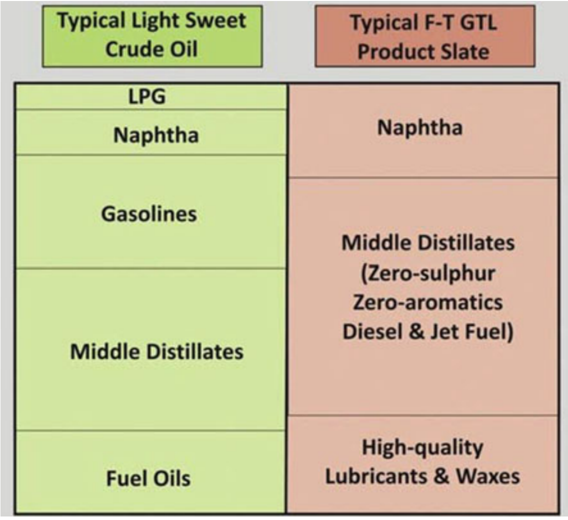


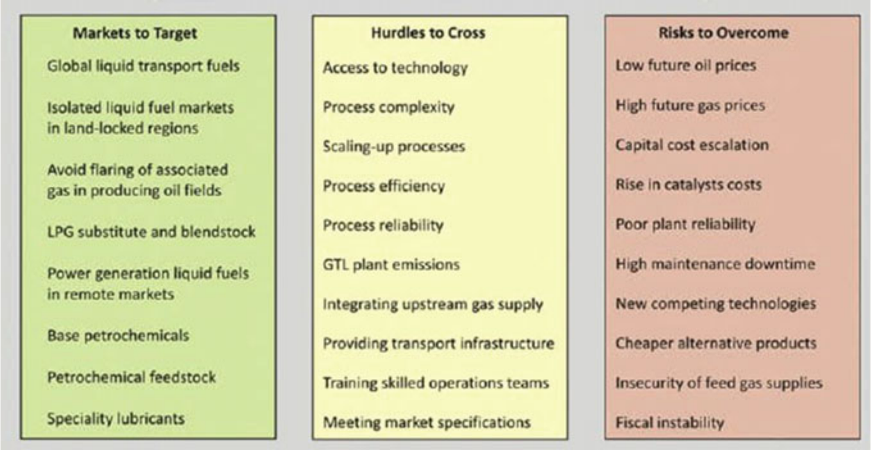
Fig. 3 Refinery volume yield versus FT GTL yield

meeting demand and requirements of diesel fuel, as the supply of crude oil becomes more difficult due to resource exhaustion of resources. Forecasts for the next decades show that demand for diesel fuel will continue to grow (Fig. 2).

10 SWOT-Analysis of GTL Technologies

The current state of development of GTL technologies involves a number of challenges and treas. The main challenges are the high technological complexity of the process, significant capital investments in expensive equipment and investment risks. However, despite the mentioned threats, there are certain opportunities to overcome them. For example, the integration of mining processes and small-scale processing plants, the development of cheap catalysts that increase the selectivity of target products, etc. In order to stimulate innovation and enable new technology, one should consider following points that provide opportunities and prospects for GTL technology:

- reduce complexity. Robust technology can be optimized, but it is difficult to make already complex technology robust;
- reduce capital by innovation. Develop new technology based on improving common GTL process, e.g. small-scale GTL plants;
- explotation of smaal deposits of natural gas and unconventional gas. Use biogas and biomethan as feedstock for GTL process;



Markets to Target	Hurdles to Cross	Risks to Overcome
Global liquid transport fuels	Access to technology	Low future oil prices
Isolated liquid fuel markets in land-locked regions	Process complexity	High future gas prices
Avoid flaring of associated gas in producing oil fields	Scaling-up processes	Capital cost escalation
LPG substitute and blendstock	Process efficiency	Rise in catalysts costs
Power generation liquid fuels in remote markets	Process reliability	Poor plant reliability
Base petrochemicals	GTL plant emissions	High maintenance downtime
Petrochemical feedstock	Integrating upstream gas supply	New competing technologies
Speciality lubricants	Providing transport infrastructure	Cheaper alternative products
	Training skilled operations teams	Insecurity of feed gas supplies
	Meeting market specifications	Fiscal instability

Fig. 4 The GTL industry: opportunities and chelrnges

- improve FT synthesis developing new catalysts to reduce costs of process and its complexity.

The main challenges and risks of GTL technologies are shown in Fig. 4 [48].

11 Conclusions

GTL technologies can contribute to reducing global dependence on transport fuels produced from crude oil. They offer significant opportunities for the development of unconventional natural gas deposits, in particular shale gas and biogas, which is quite promising for Ukraine.

However, the technologies are complex, expensive, patents for key processes are held by several companies. Therefore, the development of simple small-scale GTL installations is an important scientific and technological problem.

Currently, large GTL plants are operating using FT syntesis. However, alternative GTL technologies for converting methane into methanol or olefinic hydrocarbons with their subsequent conversion into gasoline without obtaining syngas are developing quite quickly. Such technological installations can replace traditional oil refineries and petrochemical plants and significantlly reduce the cost of common GTL process.

The GTL industry is influenced with oil and gas prices. Market price fluctuation for crude oil and natural gas complicate capital investment calculations for new GTL projects. While refineries are only affected by oil prices, GTL operations are affected by both oil and natural gas prices. Therefore, the future is in small-scale hybrid installations, which allow to reduce capital investment and monetize natural gas into more expensive, high-quality, cleaner and demanded transport fuels.

References

1. Li, J., et al.: Integrated tuneable synthesis of liquid fuels via Fischer-Tropsch technology. Nat. Catal. **1**, 787–793 (2018). https://doi.org/10.1038/s41929-018-0144-z
2. Geletukha, G., Kucheruk, P., Matveev, Y.: Prospects and potential for biomethane production in Ukraine. Ecol. Eng. Environ. Technol. **23**(4), 67–80 (2022). https://doi.org/10.12912/27197050/149995
3. Energy balance of Ukraine for 2020. State Statistics Service of Ukraine. 2021. http://www.ukrstat.gov.ua/
4. Iakovleva, A., Boichenko, S., Gay, A.: Cause-effect analysis of the modern state in production of jet fuels. Ch&ChT **8**(1), 107–116 (2014). https://doi.org/10.23939/chcht08.01.107
5. AlNouss, A., McKay, G., Al-Ansari, T.: A techno-economic-environmental study evaluating the potential of oxygen-steam biomass gasification for the generation of value-added products. Energy Convers. Manage. **196**, 664–676 (2019). https://doi.org/10.1016/j.enconman.2019.06.019
6. Kumar, N.R., Aarthi, V.: From biomass to syngas, fuels and chemicals – a review. AIP Conf. Proc. **2225** (2020). https://doi.org/10.1063/5.0005864
7. Coppola, G., Papurello, D.: Biogas cleaning: activated carbon regeneration for H_2S removal. Clean Technol. **1**, 40–57 (2018). https://doi.org/10.3390/cleantechnol1010004
8. Georgiadis, A.G., Charisiou, N.D., Goula, M.A.: Removal of hydrogen sulfide from various industrial gases: a review of the most promising adsorbing materials. Catalysts **10**, 521–547 (2020). https://doi.org/10.3390/catal10050521
9. Jeske, K., et al.: Design of Cobalt Fischer – Tropsch catalysts for the combine production of liquid fuels and olefin chemicals from hydrogen – rich syngas. ASC Catal. **11**, 4784–4798 (2021). https://doi.org/10.1021/acscatal.0c05027
10. Chun, D.H., et al.: Highly selective iron-based Fischer – Tropsch catalysts activated by CO_2-containing syngas. J. Catal. **317**, 135–143 (2014). https://doi.org/10.1016/j.jcat.2014.06.014
11. Cheng, K., et al.: Support effects in high temperature Fischer – Tropsch synthesis on iron catalysts. Appl. Catal. A **488**, 66–77 (2014). https://doi.org/10.1016/j.apcata.2014.09.03312
12. Griboval, A., et al.: Cobalt and iron species in aluminia supported bimetallic catalysts for Fischer – Tropsch reaction. Appl. Catal. **481**, 116–126 (2014). https://doi.org/10.1016/j.apcata.2014.04.047
13. Nakanishi, M., et al.: Effects of preparation method on the properties of cobalt β-zeolite catalysts for Fischer – Tropsch synthesis. Catal. Today **291**, 124–132 (2017). https://doi.org/10.1016/j.cattod.2017.01.017
14. Guttel, R., Kunz, U., Turek, T.: Reactors for Fischer – Tropsch synthesis. Chem. Eng. Technol. **31**, 746–754 (2008). https://doi.org/10.1002/ceat.200800023
15. Onsan, Z.I., Avci, M.K.: Multiphase catalytic reactors: theory, design, manufacturing and applications. Chapter 12 (2016). https://doi.org/10.1002/9781119248491.ch12
16. Yong, S., et al.: Effect of Co conversion upon product distribution using bimetallic Co-Ni mesoporous silica catalyst for Fischer – Tropsh synthesis: comparative study of fixed bed reactor and slurry continuous stirred tank reactor. Asia – Pacific J. Chem. Eng. **12**, 518–526 (2017). https://doi.org/10.1002/apj.2094
17. Gabril, J.K., et al.: Gas-to-liquid (GTL) technology: targets for process design and water-energy nexus. Curr. Opin. Chem. Eng. **5**, 49–54 (2014). https://doi.org/10.1016/j.coch.2014.05.001
18. Tang, M., Xu, L.: Progress in oxygen carrier development of methane based chemical – looping reforming: a review. Appl. Energy **151**, 143–156 (2015). https://doi.org/10.1016/j.apenergy.2015.04.017
19. Zahedy Nezhad, M., Rowshanzamir, S., Eikani M.H.: Autothermal reforming of methane to synthesis gas: modeling and simulator. Int. J. Hydr. Energy **34**, 1292–1300 (2009). https://doi.org/10.1016/j.ijhydene.2008.11.09
20. Liu, T., Temur, H., Veser, G.: Autothermal reforming of methane in a reverse-flow reactor. Chem. Eng. Technol. **9**, 1358–1366 (2009). https://doi.org/10.1002/ceat.200900203

21. Zain, M.M., Mohamed, A.R.: An overview on conversation technologies to produce value added products from CH_4 and CO_2 as major biogas constituents. Renew Sustain. Energy 9**8**, 56–63 (2018). https://doi.org/10.1016/j.rser.2018.09.003
22. Izguiero-Colorado, A.: Excess-methane dry and and oxidative reforming on Ni-containing hydrotalcite-derived catalysts for biogas upgrading into synthesis gas. Int. J. Hydr. Energy **43**(27), 11981–1989 (2018). https://doi.org/10.1016/j.ijhydene.2018.04.237
23. Srinivals, S., Field, R.P., Herzog, H.J.: Modeling tar handling options in biomass gasification. Energy Fuels **9**, 2859–2873 (2013). https://doi.org/10.1021/ef400384u
24. Frilund, C., et al.: Desulfurization of biomass syngas using ZnO-based adsorbents: long-term hydrogen sulfide breakthrough experiments. Energy Fuels **34**, 3316–3325 (2020). https://doi.org/10.1021/acs.energyfuels.9b04276
25. He, Z., et al.: Synthesis of liquid fuel via direct hydrogenization of CO_2. Proc. Natl. Acad. Sci. **116**(26), 12654–12659 (2019). https://doi.org/10.1073/pnas1821231116
26. Cheng, K. et al.: Advances in catalysis for syngas conversation to hydrocarbons. Adv. Catal. **60**, 125–208 (2017). https://doi.org/10.1016/bsacat.2017.09.003
27. De Moor, B.A., Reyniers, M.F., Marin, G.B.: Physisorption and chemisorption of alkanes and alkenes in H-FAU: a combined ab initio-statistical thermodynamics study. Phys. Chem. Chem. Phys. **11**, 2939–2958 (2009). https://doi.org/10.1039/B819435C
28. Shi, B.C., Davis, B.H.: Fischer–Tropsch synthesis: accounting for chain-length related phenomena. Appl. Catal. Gener. **277**, 61–69 (2004). https://doi.org/10.1016/j.apcata.2004.08.032
29. Schulz, H., Claeys, M.: Reactions of alpha-olefins of different chain length added during Fischer-Tropsch synthesis on a cobalt catalyst in a slurry reactor. Appl. Catal. Gener. **186**, 71–90 (1999). https://doi.org/10.1016/S0926-860X(99)00165-9
30. Bukur, D.B., Nowicki, L., Lang, X.S.: Fischer-Tropsch synthesis in a slurry reactor – pretreatment effect studies. Energy Fuel **9**, 620–629 (1995). https://doi.org/10.1006/jcat.1995.1218
31. Sajjad, H.: Engine combustion performance and emission, characteristics of gas to liquid(GTL) fuels and its blends with diesel and bio-diesel. Renew. Sustain. Rev. **30**, 961–986 (2014). https://doi.org/10.1016/j.rser.2013.11.039
32. Yakovlieva, A., Boichenko, S., Boshkov, V., Korba, L., Hocko, M.: Experimental study of physical-chemical properties of advanced alcohol-to-jet fuels. Aviation **27**(1) (2023). https://doi.org/10.3846/aviation.2023.18564
33. Sabeg, M.A., Ahmed, S.F., Steiti, A.K.: Transient 3D simulations of turbulent premixed flames of gas-to-liqud (GTL) fuel in a fan-stirred combustion vessel. Fuel **291**, 120184–120200 (2021). https://doi.org/10.1016/j.fuel2021.120-184
34. Seifcar, N. et al.: Biomass to liquid fuels pathways: a techno – economic environmental evaluation, 148 (2015)
35. Behroozsarand, A., Zamaniyan, A.: Simulation and optimization of an integrated GTL process. J. Clean. Prod. **142**, 2315–2327 (2017). https://doi.org/10.1016/j.jclepro.2016.11.045
36. Nasir, M.A., Al-Lagtah, S., Al-Habsi, S.A.: Onaisi. Organization and performance improvement of Lekhwair natural gassweetening plant using Aspen HYSYS. J. Nat. Gas Sci. **26**, 367–381 (2015). https://doi.org/10.1016/j.jngse.2015.06.030
37. Behroozsarand, A., Shafiei, S.: Optimal control of amine plant using non-dominated sorting genetic algorithm-II. J. Nat. Gas Sci. Engin. **2**, 284–292 (2010). https://doi.org/10.1016/j.jngse.2010.11.001
38. Chen, Z., Prasad, P., Yan, Y., Elnashaie, S.: Simulation for steam reforming of natural gas with oxygen input in a novel membrane reformer. Fuel Process. Technol. **83**, 235–252 (2003). https://doi.org/10.1016/S0378-3820903000072-9
39. de Kok, P.J., Rob, R., Overtoom, M.: Perl GTL: multy purpose dynamic simulator (MPDS), an integrated simulation tool to support design and Flawless Start-up. Proc. 3rd Gas Process. Sympos. **3**, 157–164 (2012). https://doi.org/10.1016/B978-0-444-59496-9.0024-2
40. Abed, A.M., Alghoul, M.A., Yazds, M.H., Al-Shamanim, A.N.: The role of enhancement techniques on heat and mass transfer characteristics of shell and tube spray evaporator: a

detailed review. Appl. Therm. Eng. **75**, 923–940 (2015). https://doi.org/10.1016/j.applthermaleng.2014.10.020

41. Zomez, E., Kerke, S., Sheller-Wolf, A., Sicomandi, N.: Strategic analysis of technology and capacity investments in the lsqquefied natural gas industry. Eur. J. Oper. Res. **226**, 100–114 (2013). https://doi.org/10.1016/j.ejor.2012.10.042
42. Top-Jorgensen, J.: Topsoe integrated gasoline synthesis – the Tigas process. Stud. Surf. Sci. Catal. **36**, 293–305 (1988). https://doi.org/10.1016/j.50167-2991(09)60523-1
43. Wang, T., et al.: Conversion of Methanjl to aromatics in fluidized bed reactor. Catal. Today **233**, 8–13 (2014). https://doi.org/10.1016/j.cattod.2014.02.007
44. Lopez-Sanches, J.A., et al.: Reactivity of Ca_2O_3 clusters on Zeolite ZSM-5 for the conversion of methanol to aromatics. Catal. Lett. 1049–1056 (2012)
45. Ilias, S., Bhan, A.: Mechanism of the catalytic conversion of methanol to hydrocarbons. ACS Catal. **1**, 18–31 (2013). https://doi.org/10.1021/cs3006583
46. Du, J., et al.: Experimental study on combustion and particle size distribution of a common rail diesel engine fueled with GTL/diesel blends. Appl. Therm. Eng. **70**, 430–440 (2014)
47. Iakovlieva, A., Vovk, O., Boichenko, S., Lejda, K., Kuszewski, H.: Physical-chemical properties of jet fuel blends with components derived from rapeseed oil. Ch&ChT **10**(4), 485–492 (2016). https://doi.org/10.23939/chcht10.04.485
48. Schaberg, P, Botha, J, Schnell, M, Hermann, H.O., Pelz, N., Maly, R.: Emissions performance of GTL diesel fuel and blends with optimized engine calibrations. SAE paper, 2005–01–2187 (2005)

Metallurgical Coke Production with Biomass Additives. Part 2. Production and Characterization of Laboratory Biocokes

Andrii Koveria, Lina Kieush, Pavlo Saik, and Vasyl Lozynskyi

1 Introduction

The development of technological processes in the modern world follows the path of reducing the environmental impact, using renewable sources of energy and raw materials while simultaneously obtaining products of the required quality [1–4].

Based on the results of the annual UN conferences on climate change [5], further commitments are planned to reduce greenhouse gas emissions globally [6, 7]. This requires a significant modernization of production to ensure the environmental sustainability of the industrial development of the metallurgy [8–10].

In the next five years, a significant proportion of the world's existing integrated steel plants will reach the 60-year age limit and be decommissioned. In addition, it is expected that in 2040–2060 blast furnaces (BF) with a total production of about 200 million tons per year will be decommissioned before reaching final depreciation. There will probably be no need to build new blast furnaces.

Ensuring the sustainable development of metallurgy, particularly in light of future restrictions on CO_2 emissions, requires the modernization of the industry with the introduction of innovative technologies and the improvement of the existing ones [11–14].

Coke production technology greatly impacts the natural environment due to using fossil coal. The primary consumer of coke is blast furnace production, the technology of which imposes specific requirements on the quality of the coke [15–17]. To meet the high requirements, which are constantly increasing, it is necessary to use raw

---

A. Koveria (✉)
Department of Chemistry, Dnipro University of Technology, Dnipro, Ukraine
e-mail: koverya.A.S@nmu.one

L. Kieush · P. Saik · V. Lozynskyi
Department of Mining Engineering and Education, Dnipro University of Technology, Dnipro, Ukraine

S. Boichenko et al. (eds.), *Modern Technologies in Energy and Transport*, Studies in Systems, Decision and Control 510, https://doi.org/10.1007/978-3-031-44351-0_15

materials with suitable initial characteristics (according to proximate analysis, coking ability, and coarseness) to produce coke.

Along with the blast furnace industry, which uses up to about 70% of the coke produced, several other industries use coke and have related requirements. For example, for ferroalloy production, using more reactive coke with a grain size of 10–25 mm is desirable. For the sintering of ores, coke fines (<10 mm) are needed, along with high reactivity. In foundry production, coke should be coarse and low-reactive [15]. Non-blast furnace consumers need coke for high-temperature reactions. The function of carbon materials in these processes is to provide the necessary temperature for reactions and carbon transfer for carbonization.

As an alternative to fossil fuels, renewable energy sources from organic raw materials are increasingly used [17–23]. The most important of them is the vegetable raw material formed in photosynthesis. Biomass is the product of converting solar energy into chemical energy. Plant biomass is a valuable renewable chemical raw material from which unique compounds and fossil fuel substitute products can be obtained.

It is known that charcoal was widely used in the production of cast iron until the middle of the twentieth century [24]. Charcoal is used as the main fuel and reducing agent in small blast furnaces in Brazil [25–27]. However, charcoal is mainly used in the blast furnace process for injection into the BF via the tuyeres [25, 28–31], as well as the carbon iron ore composite [32] and steel recarburazer [33]. At the same time, Brazil is one of the leading countries in using charcoal for steel production [34].

The advantages of using charcoal in the BF process, as opposed to coal coke, are low ash, sulfur, and high porosity. As an injecting component, charcoal has high reactivity and low mechanical strength. However, the use of charcoal for feeding into BF is ineffective precisely because of these features of mechanical and chemical properties.

At the current state of industry development, biomass is important as a renewable source of raw materials that do not increase the amount of CO_2 in the atmosphere. Biomass, as a substitute for fossil fuels, is actively used to produce biofuels [35–39], in the energy [38, 40–42], obtaining nanomaterials [43–47], bioplastics [48–51], as an effective adsorbent [52–55], as well as fertilizer [56–58].

Over the past couple of decades, the issue of using biomass and its products in the metallurgical process, namely in the BF process [59–63], sintering ores [64–71], electrical arc furnace (EAF) to enable carburizing and slag foaming [72, 73], submerged arc furnace (SAF) [74–76], reduction of iron [77–79] has been actively studied. At the same time, the amount of replacing the use of reducing raw materials instead of the conventional one depends on the type of process and the properties of biomaterials. Studies demonstrate that it is possible to increase the share of biomass use and its efficiency through the use of biocoke [80–83].

Co-pyrolysis of biomass and coal can be considered as one of the possible ways of controlling the thermochemical conversion of coal and the formation of molecular structure and physical and chemical properties of the solid residues. However, for the effective use of biomass as a fuel and raw material for chemical products, it should be considered that biomass from different sources has different properties [84].

Studies on the effect of biomass additives on the caking process and coke properties show that a minor proportion of some biomaterials (up to 3 wt.%) in the mixture does not significantly affect the caking of coals [85, 86]. When studying the behavior of the removal of volatile matters from mixtures of biomass and coal, some authors found that no interaction occurs, and the yield of pyrolysis products is associated only with the amount of biomass and coal in the blend [87–90]. Other authors have observed interactions between coal and biomass in co-combustion [91] and co-pyrolysis of biomass and brown coal [92].

When studying the issue of using biomass for co-processing with coal, it is necessary to have a clear, theoretically substantiated, confirmed-by-practice understanding of the processes of thermal destruction of the mixture with the formation of a solid residue and chemical products (tar, gas). Analysis of publications on the co-pyrolysis of coal and biomass [93, 94] highlights the main patterns of ongoing processes, depending on the temperature stage of processing (Table 1). At the same time, lignocellulosic biomass is considered a natural polymer consisting of hemicellulose, cellulose, and lignin, the thermal destruction of which has its characteristics [95].

Thus, the relevance of the use of biomass in metallurgy, as well as a small number of studies on the production and analysis of biocokes, formed the main aim of the chapter is to establish the effect of biomass additives on the yield and quality of biocokes. Co-pyrolysis of coal blend and various types of biomass was carried out via a laboratory shaft furnace with different portions of biomass additives (up to 45 wt.%) and their forms (pellets and chips). The supplementary aim considered in this chapter is to analyze the influence of the type of biomass, its quantity, and form on the technical and physical–mechanical properties of biocokes and quality analysis of biocoke for compliance with the requirements of metallurgical processes.

2 Materials and Methods

Materials

Table 2 shows the characteristics of the coals that were used to prepare the coal blend. Coals are characterized by high sulfur content, typical for Ukrainian caking coals. It should be noted that the thickness of the blend's plastic layer (y, mm) was 12 mm, which is 2 mm less than conventional coal blends used for industrial coking. The indicators of the proximate analysis of coals were determined according to ASTM D3172-13 [96] and plastometric values according to [97–99].

Indicators of reflectance of vitrinite, vitrinite reflectogram, and petrographic composition of the coal used in the research are given in Table 3. The indicators were determined according to [100–102].

The average vitrinite reflectance (R_o) is 1.01%, while the values corresponding to industrial charges with good coking characteristics are 1.1–1.2% [97].

Table 1 Main processes that occur during the pyrolysis of biomass and hard coal

Temperature range, °C	Component	Description	Main processes
up to 105 °C	Hemicellulose	Moisture removal. The duration of the stage is determined by the moisture content and the weight of the charge	Dehydration. Evaporation of water occurs in a narrow range of about 100 °C This stage determines the subsequent course of the pyrolysis process in terms of the temperature field formation of the charge
	Cellulose		
	Lignin		
	Hard Coal		
105–270 °C	Hemicellulose	Drying and start of decomposition at temperatures of about 200 °C	Removal of adsorbed moisture Formed mainly CO, CO_2, and acetic acid
	Cellulose	Drying and decomposition start early, even at 240 °C	
	Lignin	Drying and minor decomposition start early, even at 260 °C	
	Hard Coal	Removal of colloidal moisture and occluded gases (CO_2, CO). Drying	Removal of adsorbed moisture Pre-plastic state
270–350 °C	Hemicellulose	Active decomposition	Isolation of combustible gases CO, H_2, CH_4, CO_2, acetic acid, methanol, acetone, etc., and tar
	Cellulose		
	Lignin	Beginning of active decomposition	
	Hard Coal	Softening of coal with the beginning of the formation of coal plastic layer	Pre-plastic state
350–420 °C	Hemicellulose	Completion of decomposition	The release of combustible gases CO, H_2, and CH_4, along with CO_2, acetic acid, methanol, acetone, etc., and tar
	Cellulose		
	Lignin	Active decomposition	
	Hard Coal	Plastic state	The main process of pyrolysis. Active physical and chemical processes with the participation of coal plastic layer and the release of volatiles
420–500 °C	Hemicellulose	–	Formation of charcoal
	Cellulose	–	

(continued)

Table 1 (continued)

Temperature range, °C	Component	Description	Main processes
	Lignin	Completion of active decomposition	
	Hard Coal	End of the plastic state	Beginning of resolidification after the plastic layer formation stage. Intensive formation of volatile substances and tar
500–550 °C	Hemicellulose	–	Formation of charcoal Completion of carbonization of charcoal
	Cellulose	–	
	Lignin	Further decomposition	
	Hard Coal	Semi-coke formation and its further decomposition. The transformation of semi-coke into medium-temperature coke occurs above 700 °C, and after 950 °C, the formation of high-temperature coke	Accompanied by shrinkage processes and the release of volatile matter, mainly hydrogen, and hydrocarbons

Table 2 Characteristics of coals and blend

Coal type	Amount within the blend, %	Proximate analysis, %				Plastometric indicators, mm	
		W^a	A^d	V^{daf}	$S^d{}_t$	y	x
Coal A	30	1.5	11.3	37.6	1.92	12	32
Coal B	30	1.6	7.6	34.1	2.38	18	10
Coal C	30	1.7	9.5	22.3	1.67	16	11
Coal D	10	2.0	6.8	17.6	1.51	<6	20
Blend	100	1.6	9.2	30.0	1.37	12	21

As is known, coals' size strongly influences their thermal processing processes [103–105]. To exclude the influence of coal particles of different distributions on the quality of coke, a stable granulometric composition of coal of various types was taken, which was maintained during the preparation of coal blends. Firstly, coal of a specific granulometric composition was prepared, and afterward, it was mixed to the particle size distribution according to Table 4.

Wood, sunflower husks, and straw were used as biomass additives in the form of pellets with a diameter of 8 mm and a length of 4 to 12 mm. Additionally, for comparison, when coking the blend, wood chips were used as an additive. The biomass additives' properties are summarised in Table 5.

Table 3 Average reflectance of vitrinite, petrographic composition, and reflectogram of vitrinite of coal

Coal type	R_o, %	Vt, %	Sv %	I, %	L %	$\sum$OK, %	Reflectogram of vitrinite, %						
							<0.5	0.5–0.64	0.65–0.89	0.9–1.19	1.2–1.39	1.4–1.69	1.7– > 2.2
Coal A	0.75	71	1	20	8	21		3	89	8			
Coal B	0.93	87	1	9	3	10		14	34	31	21		
Coal C	1.18	93	1	6	–	7			1	65	16	18	
Coal D	1.52	88	2	10	–	12				5	10	65	20
Blend	1.01	84	1	12	3	13		5	37	32	12	12	2

Table 4 Particles size distribution of coals

Coal type	Content of sizes, %				
	10–6 mm	6–3 mm	3–1.5 mm	1.5–0.5 mm	<0.5 mm
Coal A	4	10	31	30	25
Coal B	4	22	30	24	20
Coal C	3	17	24	33	23
Coal D	2	8	27	32	31
Blend	3.5	15.5	28.2	29.3	23.5

Table 5 Characteristics of additive properties, wt.%

Type of additive	Moisture (W_t^r)	Volatile matters (V^r)	Total sulfur content (S_t^d)	Ash (A^r)
Wood	9.4	81.3	0.01	1.0
Sunflower husks	9.6	75.7	0.01	2.6
Straw	4.7	75.0	0.01	5.4

Methods

Laboratory Coking

Coking was carried out in a laboratory shaft furnace [80] at 800 °C. The load was 1 kg, and after being charged in a retort, it was placed into a heated furnace. After finishing coking, the retort with the obtained coke was taken out and left to cool to room temperature. The coking time was 80 min.

Yield of Coke

After naturally cooling to room temperature, the obtained cokes were subjected to the analysis of the yield, %. The yield was calculated using Eq. 1.

$$Yield = \mathrm{B} \times 100/A,\ \% \tag{1}$$

where A is the initial mass of the blend, g; B is the mass of coke/biocoke after coking, g.

Particle Size Distribution of Coke

Further, the resulting cokes were sieved into sizes > 40, 40–25, 25–10, and < 10 mm according to ASTM D293/D293M-18 [106].

Structural Strength

To determine the structural strength, coke and biocoke samples of 6–3 mm were prepared. Then samples were charged into two special steel cylinders according to [107]. Likewise, five steel balls were placed in the cylinders. These two cylinders were set through screws in the cross-to-cross position in brackets, which were put on a shaft rotating with 0.417 s^{-1} (25 rpm). During the tests, the cylinders performed 1000 revolutions, after which the contents of each cylinder were poured separately on a sieve with a mesh of 3 mm and 1 mm. Coke or biocokes were sieved to separate into 3–1 mm and 1–0 mm fractions. The yield of more than 1 mm from the initial weight in percent characterizes the structural strength.

Abrasive Hardness

The abrasive hardness was determined by the abrasion of an aluminium plate against coke or biocoke powder and the evaluation of its mass loss. 4–5 g of samples of less than 0.5 mm in size was filled on an aluminum plate. A stamp was placed on top of the samples of coke or biocoke, which were loaded so that a pressure of 0.25 MPa was obtained. During the rotation of the rotor (500 rev.), the samples abraded the aluminum plate. The weight loss of the aluminium plate during the test run (in milligrams) was taken as the value of the abrasive hardness. Five tests were conducted for each sample.

Electrical Resistivity

The electrical resistivity measurement was carried out according to [108]. The method aims to determine the electrical resistivity of the particles with a size < 2 mm placed in the cylinder between two stainless steel plungers under a pressure of 3 MPa. The resistivity measured using a four-point mode is advantageous because it allows measuring resistivity close to the actual resistivity of the sample [109].

3 Results and Discussions

The characteristics of biocokes obtained from coking are summarized in Table 6. The yield of laboratory biocokes decreases with an increase in biomass additive, which has a higher yield of volatile matter than coal. The ash content of biocokes decreases due to the lower content of mineral components in the biomass. There is also a decrease in sulfur content since biomass additives practically do not add it to the mixture.

The yield of volatile matters of biocokes is determined by the level of readiness and varies from 0.8 wt.% to 2.5 wt.%. However, there is a tendency that with an increase in the proportion of biomass addition, the yield of volatile matters of the obtained biocokes increases.

The effect of biomass additives on the physical and mechanical properties of biocokes is more significant. The amount of 1 wt.% and 3 wt.% pellets of three types of biomass, as well as 5 wt.% wood pellets do not cause a deterioration in the particles size distribution of biocokes compared to the reference coke. At the same time, the use of wood chips has a more noticeable effect on the size of biocokes in the direction of a decrease in large sizes (>25 mm) and an increase in small ones (<10 mm). In general, with an increase in the proportion of the additive, there is a trend towards a decrease in the yield of large sizes and a corresponding increase in small ones.

Adding up to 3 wt.% of sunflower husks and straw pellets has a positive effect on structural strength. The additives of wood pellets and wood chips reduce the structural strength. At the same time, the negative effect of using chips is more pronounced than for pellets (Fig. 1). Similar dependences are observed when studying the impact of biomass additives on the abrasive hardness of the obtained biocokes (Fig. 2).

Thus, the addition of sunflower husk pellets up to 5 wt.% and straw up to 3 wt.% led to an increase in abrasive hardness, as well as the use of wood chips up to 3 wt.%. At the same time, adding 3 wt.% chips significantly increases the abrasive hardness index, although adding wood pellets decreases this index. This can be because fine coke (<0.5 mm) is used to study abrasive hardness. Therefore the value of the index depends to a greater extent on the degree of biocoke readiness, the number of charcoal particles in the sample, and their distribution.

Electrical resistivity as an indicator that characterizes the structural features of carbon materials shows an improvement in the structural ordering of biocokes when using sunflower husk additives up to 3 wt.% compared to the reference one. The use of other additives leads to a decrease in the quality of biocokes in this indicator (Fig. 3). With an increase in the number of additives, electrical resistivity increases, although not linearly.

Therefore, the addition of sunflower husk up to 3 wt.% leads to an improvement in the physical and mechanical properties of biocokes, which can be explained by the presence of a certain amount of oily substances [110, 111], which during thermal destruction, positively affect the process of formation and properties of biocoke. Straw pellet additives up to 3 wt.% positively affect structural strength and abrasive

Table 6 Yield, proximate analysis indicators, particles size distribution, and physical and mechanical properties of biocokes obtained from coal mixtures with biomass additives

Sample		Yield, %	Proximate analysis, %			Particles size distribution, %					Structural strength, %	Abrasive hardness, mg	Electrical resistivity, mΩ·m
Blend			A^d	V^d	S_t^d	>40 mm	40–25 mm	25–10 mm	10–5 mm	<5 mm			
Reference coke		73.9	11.9	1.0	1.36	88.4	5.1	0.9	1.2	4.4	72.3	105.0	13.57
Biocokes (wood chips addition, wt. %)	1	72.8	11.9	1.3	1.35	86.9	4.0	1.6	1.1	6.4	69.3	106.1	14.26
	3	71.4	11.8	1.5	1.32	83.2	5.5	2.1	1.4	7.8	64.7	119.3	14.99
	5	69.4	11.6	2.0	1.29	82.1	5.8	2.0	1.6	8.5	61.6	84.7	15.36
	10	66.7	11.3	1.9	1.22	80.4	6.2	2.3	1.8	9.3	55.3	76.5	15.82
Biocokes (wood pellets addition, wt. %)	1	73.0	11.9	2.0	1.34	90.1	1.3	1.8	1.6	5.2	70.2	96.7	13.98
	3	71.7	11.8	1.2	1.31	87.1	4.3	3.5	1.7	3.4	71.1	88.2	14.17
	5	69.8	11.6	2.1	1.28	90.2	2.5	2.5	1.1	3.7	66.2	80.0	14.58
	10	67.3	11.4	1.5	1.2	85.9	2.7	2.3	1.5	7.6	62.0	70.0	15.18
	15	64.8	11.1	2.5	1.13	72.9	6.4	4.9	2.9	12.9	58.6	55.1	16.88
	30	59.0	10.0	2.5	1.05	31.4	23.9	9.5	12.8	22.4	49.2	44.0	17.57
	45	52.6	6.6	1.5	0.95	9.5	21.3	12.7	24.7	31.8	36.1	32.6	19.64
Biocokes (sunflower husk addition, wt. %)	1	73.1	11.8	1.4	1.34	92.9	1.4	0.7	1.0	4.0	75.4	119.5	13.48
	3	72.0	11.6	0.8	1.32	93.2	0.9	0.7	1.4	3.8	76.1	126.8	13.34
	5	70.2	11.4	2.0	1.29	80.0	6.5	4.2	1.4	7.9	68.7	106.0	13.62
Biocokes (straw addition, wt. %)	1	73.1	11.9	1.1	1.35	90.0	3.4	1.4	1.1	4.1	73.8	127.4	13.80
	3	71.9	11.7	2.0	1.33	91.0	1.6	1.5	1.6	4.3	73.4	123.0	14.67
	5	70.0	11.6	1.8	1.30	85.8	2.0	3.8	1.7	6.7	67.4	101.2	15.18

Fig. 1 Effect of addition of biomass on structural strength of biocokes

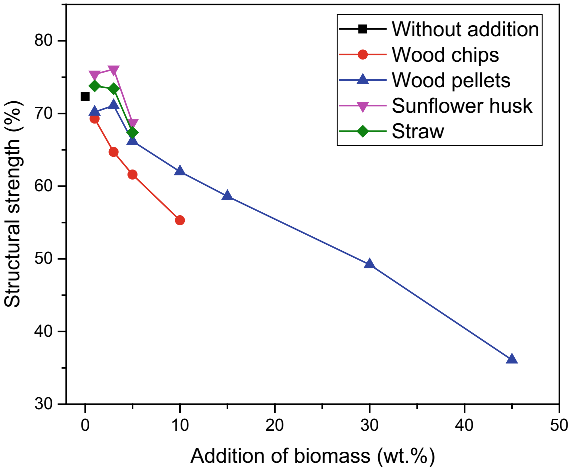
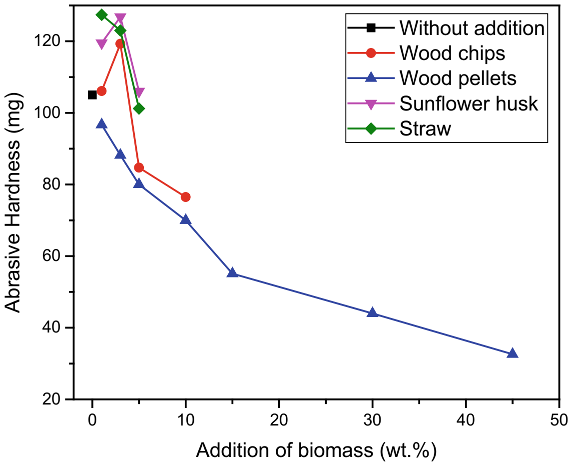


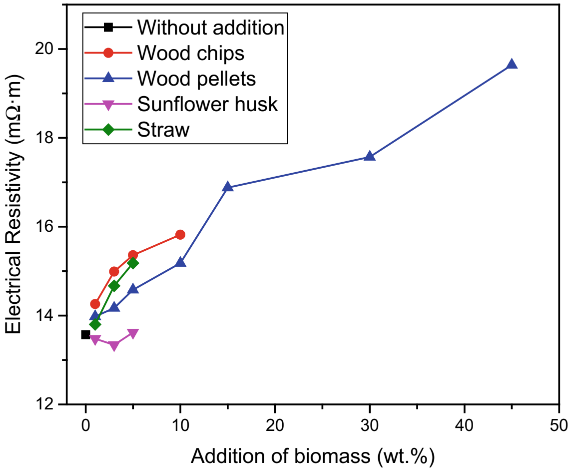
Fig. 2 Effect of addition of biomass on the abrasive hardness of biocokes



hardness, but electrical resistivity increases when using this type of additive. The use of wood additives shows a tendency to reduce the physical and mechanical properties of biocokes. At the same time, the use of pellets has a less negative effect on the structural features of biocokes (structural strength, electrical resistivity) than the addition of chips.

A study of the effect of adding a high proportion of wood pellets on the quality of biocokes demonstrates notable dependencies. Thus, the yield of biocokes decreases non-linearly and increases the yield from the expected one. The physical and mechanical properties of biocoke obtained with additives of 15 and 30 wt.% remain acceptable for non-BF productions. At the same time, inclusions of charcoal in the form of pellets are clearly observed, which, with an increase in the amount, are better separated from the bulk of the solid residue of coal pyrolysis.

Fig. 3 Effect of addition of biomass on electrical resistivity of biocokes



Therefore, the results of earlier studies are confirmed [80, 83], which shows the local effect of wood pellet additives on the change in the properties of the resulting biocoke.

Analysis of the obtained results shows that biomass additives affect the process and quality of biocoke production. The effect of influence is determined by qualitative and quantitative factors, namely the type, form, and proportion of the additive in a mixture with coal. The mechanism of the influence of biomass additives can be explained by the scheme of the co-pyrolysis of coals and biomass, which is presented in Fig. 4.

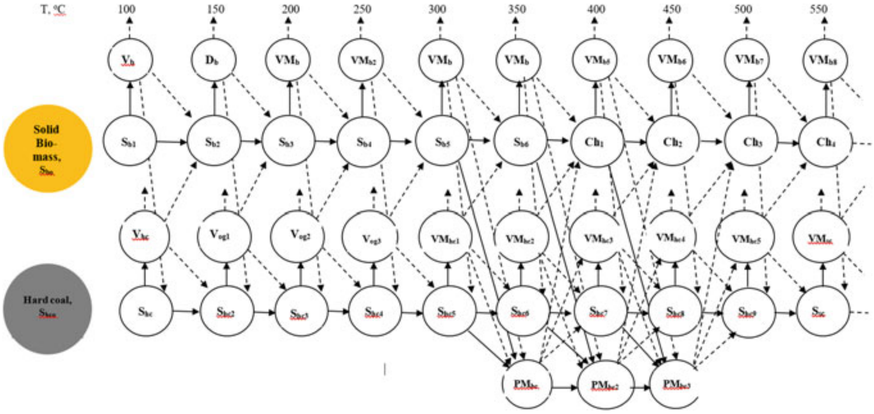


Fig. 4 Scheme of the mechanism of co-pyrolysis of coal and biomass: V_b—vapor of water from biomass; S_b—solid biomass; VM_b—volatile matter from raw and pyrolyzed biomass; V_{hc}—water vapor from hard coal; V_{og}—occluded gas from hard coal; S_{hc}—solid hard coal; VM_{hc}—volatile matter from hard coal; PM_{hc}—plastic layer from hard coal

The scheme shows the course of the process of co-pyrolysis of biomass and coal, namely drying and subsequent parallel and sequential processes of dehydration and condensation with the formation of liquid and solid products and depolymerization processes with the formation of volatile and tarry liquid substances, in the case of biomass pyrolysis; as well as dehydration processes followed by sequential-parallel polycondensation reactions with the formation of metastable phases in the case of coal pyrolysis.

Consequently, there is a transition from the solid state to the solid, a systematic but limited at each stage, decrease in the mass of the solid, a change in the yield of volatile matters, and the appearance, growth, and disappearance of the plastic layer of coal. The pyrolysis process is non-isothermal and continuous, forming and destroying new compounds. As can be seen from the scheme, during the co-pyrolysis of biomass and coal, different phases interact.

Biomass, namely cellulose and hemicellulose, begins to decompose before coal; thus, the volatile decomposition products formed in the charge further process the coal. Considering the predominantly oxygen-containing composition of volatile biomass, their effect on coal is oxidative, which ultimately reduces the caking ability of coals [82, 112–115].

The treatment of biomass with volatile pyrolysis products should affect the kinetics of the yield of steam-gas products of coal. In turn, with increasing temperature, higher molecular weight volatile products of coal act on solid biomass degradation products, processing charcoal.

In the coal pyrolysis process, all phases interact with each other, and each is involved in polycondensation. As a result, new metastable products are synthesized, namely liquid, solid and gaseous, forming phases of the next stage. Evidence of this should be the formation of various amounts of vapor–gas, liquid, and solid products. The most active changes occur within the temperature range of 250–500 °C when biomass decomposes and the coal plastic layer is formed.

It is also important to consider that under higher temperatures and industrial conditions, thermal degradation of biomass pyrolysis tar and light products of primary coal tar will take place. The yield level of various products is determined by the depth of transformations that coal and biomass undergo at the stages of pyrolysis. Therefore, it is necessary to distinguish between conclusions on the co-pyrolysis of biomass and coal, obtained based on pyrolysis under laboratory conditions, and industrial-scale ones.

Additionally, essential to note that during pyrolysis, the destruction-synthesis processes are limited by the rate of thermochemical transformations of the coal substance and not by heat transfer inside the coal particle.

Thus, the addition of biomass actively affects the process of thermal destruction of the charge and, subsequently, the qualitative indicators of the solid residue: proximate analysis, physical–mechanical and physical–chemical properties. Accordingly, using biomass additives makes it possible to obtain biocoke of different qualities for various production processes.

4 Conclusions

Studies on the production of biocoke under laboratory conditions and its study showed that the addition of biomass in the form of wood pellets, wood chips, pellets from sunflower husks, and pellets from straw into coal blend leads to a change in the properties of coke: yield, particles size distribution, structural strength, abrasive hardness, and electrical resistivity.

The use of up to 3 wt.% biomass pellet additives and 5 wt.% wood pellets do not lead to a deterioration in the granulometric composition of biocokes. At the same time, the output of large sizes (>25 mm) and small sizes (< 10 mm) changes noticeably when using the addition of wood chips and with more than 5 wt.% pellet additions.

Regarding structural strength, abrasive hardness, and electrical resistivity, biocokes obtained with the addition of sunflower husks have better characteristics. This can be explained by the presence of a residual amount of oily substances, which improve the caking of coal particles. The addition of sunflower husks generally carries fewer oxygen-containing groups, negatively affecting the co-pyrolysis process with coal.

Straw pellet additions up to 3 wt.% also do not adversely affect the particle's size distribution and structural strength, with a noticeable improvement in abrasive hardness. However, the electrical resistivity of biocokes obtained with the participation of straw increases.

The addition of wood leads to a decrease in the physical and mechanical properties of biocokes. However, the deterioration of properties is not linear, which is more clearly seen when studying the effect of increased wood pellet addition. At the same time, using chips compared to pellets has an even more negative impact. Therefore, the effect of the pellets is local in nature on the change in the properties of the resulting biocoke, and the effect of the chips can be considered volumetric due to the uniform distribution of the chips in the charge volume.

Using biocoke as a metallurgical fuel and reducing agent can improve the technical and economic performance of non-blast furnace industries by using carbon material with more suitable physical, mechanical, and physicochemical properties than conventional coke. In addition, using biomass additives is an environmentally friendly approach to obtaining carbon fuels. The advantages of using biomass as a component of coal blends in the coking process are the utilization of biomass; use of renewable raw materials, instead of fossil fuels, in particular, deficient coking coal; obtaining a new product, namely biocoke, the properties of which meet the modern requirements of consumers; reducing the negative impact on the environmental situation in the region and the world. The cost of biocoke may be lower than that of obtaining the corresponding grades of conventional coke. Therefore, using biomass additives to produce coke will solve complex problems in industrial regions and enterprises of ferrous metallurgy, agriculture, the chemical industry, and many others that process biomass.

Acknowledgements The presented results have been obtained within the framework of the scientific-research projects GP-512 "Co-gasification of carbon-containing raw materials during ultrathin coal seams gasification with a focus on hydrogen production" and GP-516 "Scientific and practical bases of low-rank coal gasification technology", state registrations No. 0123U100985 and No. 0123U101757 of the Ministry of Education and Science of Ukraine.

References

1. Gielen, D., Saygin, D., Taibi, E., Birat, J.: Renewables-based decarbonization and relocation of iron and steel making: a case study. J. Ind. Ecol. **24**, 1113–1125 (2020). https://doi.org/10.1111/jiec.12997
2. Vogl, V., Olsson, O., Nykvist, B.: Phasing out the blast furnace to meet global climate targets. Joule **5**, 2646–2662 (2021). https://doi.org/10.1016/j.joule.2021.09.007
3. Development of a Low CO2 Iron and Steelmaking Integrated Process Route for a Sustainable European Steel Industry (2018)
4. Communication from the Commission to the European Parliament, the European Council, the Council, the European Economic and Social Committee and the Committee of the Regions. The European Green Deal
5. United Nations Climate Change conference. https://en.wikipedia.org/wiki/United_Nations_Climate_Change_conference. Accessed 14 Apr 2023
6. Ritchie, H., Roser, M., Rosado, P.: CO2 and greenhouse gas emissions country profiles. https://ourworldindata.org/co2-and-greenhouse-gas-emissions. Accessed 14 Apr 2023
7. UNCTAD sets out actions to support least developed countries in the global low-carbon transition. https://unctad.org/news/unctad-sets-out-actions-support-least-developed-countries-global-low-carbon-transition. Accessed 14 Apr 2023
8. Tong, D., Zhang, Q., Zheng, Y., et al.: Committed emissions from existing energy infrastructure jeopardize 1.5 °C climate target. Nature **572**, 373–377 (2019). https://doi.org/10.1038/s41586-019-1364-3
9. Vogl, V., Åhman, M., Nilsson, L.J.: Assessment of hydrogen direct reduction for fossil-free steelmaking. J. Clean. Prod. **203**, 736–745 (2018). https://doi.org/10.1016/j.jclepro.2018.08.279
10. Bataille, C.G.F.: Physical and policy pathways to net-zero emissions industry. WIREs Clim Change 11 (2020). https://doi.org/10.1002/wcc.633
11. Diez, M.A., Centeno, T.A., Amado-Fierro, Á.: Coal use for iron and steel production in low-carbon transition scenarios. In: The Coal Handbook, pp 493–546. Elsevier (2023)
12. Swennenhuis, F., de Gooyert, V., de Coninck, H.: Towards a CO2-neutral steel industry: justice aspects of CO2 capture and storage, biomass- and green hydrogen-based emission reductions. Energy Res. Soc. Sci. **88**, 102598 (2022). https://doi.org/10.1016/j.erss.2022.102598
13. Blast Furnace 2030- a vision for sustainable iron production. https://www.mpiuk.com/downloads/industry-papers/SI-Series-Paper-04-Blast-Furnace-2030-A-Vision-for-Sustainable-Iron-Production.pdf. Accessed 14 Apr 2023
14. Kim, J., Sovacool, B.K., Bazilian, M., et al.: Decarbonizing the iron and steel industry: a systematic review of sociotechnical systems, technological innovations, and policy options. Energy Res. Soc. Sci. **89**, 102565 (2022). https://doi.org/10.1016/j.erss.2022.102565
15. Koveria, A., Kieush, L., Svietkina, O., Perkov, Y.: Metallurgical coke production with biomass additives. Part 1. A review of existing practices. Can. Metall. Q. **59**, 417–429 (2020). https://doi.org/10.1080/00084433.2021.1916293
16. Suopajärvi, H., Kemppainen, A., Haapakangas, J., Fabritius, T.: Extensive review of the opportunities to use biomass-based fuels in iron and steelmaking processes. J. Clean. Prod. **148**, 709–734 (2017). https://doi.org/10.1016/j.jclepro.2017.02.029

17. Lyalyuk, V.P., Tarakanov, A.K., Kassim, D.A.: Influence of the reactivity of coke on blast-furnace performance. Coke Chem **54**, 47–52 (2011). https://doi.org/10.3103/S1068364X11020050
18. Wang, C., Wei, W., Mellin, P., et al.: Utilization of Biomass for Blast Furnace in Sweden-Report I: Biomass Availability and Upgrading Technologies. KTH (2013)
19. Oliveira, T.L., Assis, P.S., Leal, E.M., Ilídio, J.R.: Study of biomass applied to a cogeneration system: a steelmaking industry case. Appl. Therm. Eng. **80**, 269–278 (2015). https://doi.org/10.1016/j.applthermaleng.2015.01.002
20. Wiklund, C.-M., Helle, M., Kohl, T., et al.: Feasibility study of woody-biomass use in a steel plant through process integration. J. Clean. Prod. **142**, 4127–4141 (2017). https://doi.org/10.1016/j.jclepro.2016.09.210
21. Anand, A., Gautam, S., Ram, L.C.: Feedstock and pyrolysis conditions affect suitability of biochar for various sustainable energy and environmental applications. J. Anal. Appl. Pyrol. **170**, 105881 (2023). https://doi.org/10.1016/j.jaap.2023.105881
22. Fu, J.-X., Zhang, C., Hwang, W.-S., et al.: Exploration of biomass char for CO2 reduction in RHF process for steel production. Int. J. Greenhouse Gas Control **8**, 143–149 (2012). https://doi.org/10.1016/j.ijggc.2012.02.012
23. Ahmed, H.M., Mousa, E.A., Larsson, M., Viswanathan, N.N.: Recent Trends in Ironmaking Blast Furnace Technology to Mitigate CO2 Emissions: Top Charging Materials. In: Cavaliere, P. (ed.) Ironmaking and Steelmaking Processes, pp. 101–124. Springer International Publishing, Cham (2016)
24. Straka, T.J.: Charcoal as a fuel in the ironmaking and smelting industries. AHS **06**, 56–64 (2017). https://doi.org/10.4236/ahs.2017.61004
25. da Rocha, E.P., Guilherme, V.S., de Castro, J.A., et al.: Analysis of synthetic natural gas injection into charcoal blast furnace. J. Market. Res. **2**, 255–262 (2013). https://doi.org/10.1016/j.jmrt.2013.02.015
26. Babich, A., Senk, D., Fernandez, M.: Charcoal behaviour by its injection into the modern blast furnace. ISIJ Int. **50**, 81–88 (2010). https://doi.org/10.2355/isijinternational.50.81
27. Scarpinella, C.A., Cyro, T., Tagusagawa, S.Y., et al.: Charcoal Ironmaking: A Contribution for CO2 Mitigation. Cancun, Mexico (2011)
28. Feliciano-Bruzual, C.: Charcoal injection in blast furnaces (Bio-PCI): CO2 reduction potential and economic prospects. J. Market. Res. **3**, 233–243 (2014). https://doi.org/10.1016/j.jmrt.2014.06.001
29. Ueda, S., Watanabe, K., Yanagiya, R., Inoue, T.: Optimization of biomass utilization for reducing CO2 in ironmaking process. J. Iron. Steel Res. Int. **16**, 593–599 (2009)
30. Wang, C., Larsson, M., Lövgren, J., et al.: Injection of solid biomass products into the blast furnace and its potential effects on an integrated steel plant. Energy Procedia **61**, 2184–2187 (2014). https://doi.org/10.1016/j.egypro.2014.12.105
31. Mousa, E., Sjöblom, K.: Modeling and optimization of biochar injection into blast furnace to mitigate the fossil CO2 emission. Sustainability **14**, 2393 (2022). https://doi.org/10.3390/su14042393
32. Ahmed, H.M., Viswanathan, N., Bjorkman, B.: Composite pellets - a potential raw material for iron-making. Steel Res. Int. **85**, 293–306 (2014). https://doi.org/10.1002/srin.201300072
33. MacPhee, J.A., Gransden, J.F., Giroux, L., Price, J.T.: Possible CO2 mitigation via addition of charcoal to coking coal blends. Fuel Process. Technol. **90**, 16–20 (2009). https://doi.org/10.1016/j.fuproc.2008.07.007
34. Brazil at steel decarbonization crossroads; charcoal, gas short-term options
35. Khawaja, A.S., Zaheer, M.A., Ahmad, A., et al.: Advances in limitations and opportunities of clean biofuel production to promote decarbonization. Fuel **342**, 127662 (2023). https://doi.org/10.1016/j.fuel.2023.127662
36. Malode, S.J., Prabhu, K.K., Mascarenhas, R.J., et al.: Recent advances and viability in biofuel production. Energy Conv. Manage.: X **10**, 100070 (2021). https://doi.org/10.1016/j.ecmx.2020.100070

37. Kiehbadroudinezhad, M., Merabet, A., Ghenai, C., et al.: The role of biofuels for sustainable MicrogridsF: a path towards carbon neutrality and the green economy. Heliyon **9**, e13407 (2023). https://doi.org/10.1016/j.heliyon.2023.e13407
38. Sharma, S., Kundu, A., Basu, S., et al.: Sustainable environmental management and related biofuel technologies. J. Environ. Manage. **273**, 111096 (2020). https://doi.org/10.1016/j.jenvman.2020.111096
39. Jha, S., Nanda, S., Acharya, B., Dalai, A.K.: A review of thermochemical conversion of waste biomass to biofuels. Energies **15**, 6352 (2022). https://doi.org/10.3390/en15176352
40. Freiberg, A., Scharfe, J., Murta, V.C., Seidler, A.: The use of biomass for electricity generation: a scoping review of health effects on humans in residential and occupational settings. IJERPH **15**, 354 (2018). https://doi.org/10.3390/ijerph15020354
41. Janiszewska, D., Ossowska, L.: The role of agricultural biomass as a renewable energy source in European union countries. Energies **15**, 6756 (2022). https://doi.org/10.3390/en15186756
42. Scarlat, N., Dallemand, J.-F., Fahl, F.: Biogas: developments and perspectives in Europe. Renew. Energy **129**, 457–472 (2018). https://doi.org/10.1016/j.renene.2018.03.006
43. Sangeetha, J., Shettar, A.K., Thangadurai, D.: Nanomaterials from biomass: an update. In: Kharissova, O.V., Martínez, L.M.T., Kharisov, B.I. (eds.) Handbook of Nanomaterials and Nanocomposites for Energy and Environmental Applications, pp. 1–18. Springer International Publishing, Cham (2021)
44. Zhang, Y., Xu, W., Wang, X., et al.: From biomass to nanomaterials: a green procedure for preparation of holistic bamboo multifunctional nanocomposites based on formic acid rapid fractionation. ACS Sustain. Chem. Eng. **7**, 6592–6600 (2019). https://doi.org/10.1021/acssuschemeng.8b05502
45. Raja, S., Mattoso, L.H.C., Moreira, F.K.V.: Biomass-derived nanomaterials. In: Balakumar, S. (ed.) Rajendran S, Naushad Mu, pp. 243–270. Nanostructured Materials for Energy Related Applications. Springer International Publishing, Cham (2019)
46. Kieush, L., Koveria, A.: Analysis and evaluation of the nanomaterials' impact on the environment. Nanosistemi, Nanomateriali, Nanotehnologii **18**, 141–156 (2020)
47. Kieush, L., Koveria, A., Hrubyak, A., et al.: Corn stalks as ecofriendly sources for carbon nanomaterials. In: 2018 IEEE 8th International Conference Nanomaterials: Application & Properties (NAP), pp 1–4. IEEE, Zatoka, Ukraine (2018)
48. Lackner, M.: Biopolymers. In: Chen, W.-Y., Suzuki, T., Lackner, M. (eds.) Handbook of Climate Change Mitigation and Adaptation, pp. 3211–3230. Springer International Publishing, Cham (2017)
49. Coppola, G., Gaudio, M.T., Lopresto, C.G., et al.: Bioplastic from renewable biomass: a facile solution for a greener environment. Earth Syst. Environ. **5**, 231–251 (2021). https://doi.org/10.1007/s41748-021-00208-7
50. Moshood, T.D., Nawanir, G., Mahmud, F., et al.: Sustainability of biodegradable plastics: new problem or solution to solve the global plastic pollution? Current Res. Green Sustain. Chem. **5**, 100273 (2022). https://doi.org/10.1016/j.crgsc.2022.100273
51. Reshmy, R., Thomas, D., Philip, E., et al.: Bioplastic production from renewable lignocellulosic feedstocks: a review. Rev. Environ. Sci. Biotechnol. **20**, 167–187 (2021). https://doi.org/10.1007/s11157-021-09565-1
52. Mokrzycki, J., Michalak, I., Rutkowski, P.: Biochars obtained from freshwater biomass—green macroalga and hornwort as Cr(III) ions sorbents. Biomass Conv. Bioref. **11**, 301–313 (2021). https://doi.org/10.1007/s13399-020-00649-6
53. Marzeddu, S., Décima, M.A., Camilli, L., et al.: Physical-chemical characterization of different carbon-based sorbents for environmental applications. Materials **15**, 7162 (2022). https://doi.org/10.3390/ma15207162
54. Frolova, L., Kharytonov, M., Klimkina, I., et al.: Adsorption purification of waste water from chromium by ferrite manganese. E3S Web Conf. **168**, 00026 (2020). https://doi.org/10.1051/e3sconf/202016800026
55. Frolova, L., Kharytonov, M., Klimkina, I., et al.: Investigation of the adsorption of ions chromium by mean biochar from coniferous trees. Appl. Nanosci. **12**, 1123–1129 (2022). https://doi.org/10.1007/s13204-021-01995-1

56. Danso, F., Agyare, W.A., Bart-Plange, A.: Benefits and costs of cultivating rice using biochar-inorganic fertilizer combinations. J. Agricult. Food Res. **11**, 100491 (2023). https://doi.org/10.1016/j.jafr.2022.100491
57. Bruun, S., Clauson-Kaas, S., Bobuľská, L., Thomsen, I.K.: Carbon dioxide emissions from biochar in soil: role of clay, microorganisms and carbonates: CO $_2$ emissions from biochar in soil. Eur. J. Soil Sci. **65**, 52–59 (2014). https://doi.org/10.1111/ejss.12073
58. Bai, X., Zhang, S., Shao, J., et al.: Exploring the negative effects of biochars on the germination, growth, and antioxidant system of rice and corn. J. Environ. Chem. Eng. **10**, 107398 (2022). https://doi.org/10.1016/j.jece.2022.107398
59. Adilson de Castro, J., de Medeiros, G.A., de Oliveira, E.M., et al.: The mini blast furnace process: an efficient reactor for green pig iron production using charcoal and hydrogen-rich gas: a study of cases. Metals **10**, 1501 (2020). https://doi.org/10.3390/met10111501
60. Wiklund, C.-M., Pettersson, F., Saxén, H.: Optimization of a steel plant with multiple blast furnaces under biomass injection. Metall. Materi. Trans. B **44**, 447–458 (2013). https://doi.org/10.1007/s11663-012-9790-8
61. Mousa, E., Wang, C., Riesbeck, J., Larsson, M.: Biomass applications in iron and steel industry: an overview of challenges and opportunities. Renew. Sustain. Energy Rev. **65**, 1247–1266 (2016). https://doi.org/10.1016/j.rser.2016.07.061
62. Fick, G., Mirgaux, O., Neau, P., Patisson, F.: Using biomass for pig iron production: a technical, environmental and economical assessment. Waste Biomass Valor **5**, 43–55 (2014). https://doi.org/10.1007/s12649-013-9223-1
63. Suopajärvi, H., Pongrácz, E., Fabritius, T.: Bioreducer use in Finnish blast furnace ironmaking – analysis of CO2 emission reduction potential and mitigation cost. Appl. Energy **124**, 82–93 (2014). https://doi.org/10.1016/j.apenergy.2014.03.008
64. Kieush, L., Koveria, A., Boyko, M., et al.: Influence of biocoke on iron ore sintering performance and strength properties of sinter. Min. Miner. Depos. **16**, 55–63. https://doi.org/10.33271/mining16.02.055
65. Kieush, L., Koveria, A., Boyko, M., et al.: Walnut shells as a potential fuel for iron ore sintering. MSF **1045**, 127–140 (2021). https://doi.org/10.4028/www.scientific.net/MSF.1045.127
66. Kieush, L., Boyko, M., Koveria, A., et al.: Manganese sinter production with wood biomass application. KEM **844**, 124–134 (2020). https://doi.org/10.4028/www.scientific.net/KEM.844.124
67. Kieush, L., Koveria, A., Zhu, Z.Q., et al.: Application of biomass pellets for iron ore sintering. MSF **1045**, 17–31 (2021). https://doi.org/10.4028/www.scientific.net/MSF.1045.17
68. Kieush, L., Boyko, M., Koveria, A., et al.: Utilization of the prepyrolyzed technical hydrolysis lignin as a fuel for iron ore sintering. EEJET **1**, 34–39 (2019). https://doi.org/10.15587/1729-4061.2019.154082
69. Kieush, L., Yaholnyk, M., Boyko, M., et al.: Study of biomass utilisation in the iron ore sintering. Acta Metall. Slovaca **25**, 55 (2019). https://doi.org/10.12776/ams.v1i1.1225
70. Zandi, M., Martinez-Pacheco, M., Fray, T.A.T.: Biomass for iron ore sintering. Miner. Eng. **23**, 1139–1145 (2010). https://doi.org/10.1016/j.mineng.2010.07.010
71. Praes, G.E., de Arruda, J.D., Lemos, L.R., Tavares, R.P.: Assessment of iron ore pellets production using two charcoals with different content of materials volatile replacing partially anthracite fines. J. Market. Res. **8**, 1150–1160 (2019). https://doi.org/10.1016/j.jmrt.2018.09.003
72. Kieush, L., Schenk, J., Koveria, A., et al.: Utilization of renewable carbon in electric arc furnace-based steel production: comparative evaluation of properties of conventional and non-conventional carbon-bearing sources. Metals **13**, 722 (2023). https://doi.org/10.3390/met13040722
73. Bianco, L., Baracchini, G., Cirilli, F., et al.: Sustainable electric arc furnace steel production: GREENEAF. Berg Huettenmaenn Monatsh **158**, 17–23 (2013). https://doi.org/10.1007/s00501-012-0101-0

74. Suer, J., Ahrenhold, F., Traverso, M.: Carbon footprint and energy transformation analysis of steel produced via a direct reduction plant with an integrated electric melting unit. J. Sustain. Metall. **8**, 1532–1545 (2022). https://doi.org/10.1007/s40831-022-00585-x
75. Sommerfeld, M., Friedrich, B.: Replacing fossil carbon in the production of ferroalloys with a focus on bio-based carbon: a review. Minerals **11**, 1286 (2021). https://doi.org/10.3390/min11111286
76. Surup, G.R., Trubetskaya, A., Tangstad, M.: Charcoal as an alternative reductant in ferroalloy production: a review. Processes **8**, 1432 (2020). https://doi.org/10.3390/pr8111432
77. Yuan, P., Shen, B., Duan, D., et al.: Study on the formation of direct reduced iron by using biomass as reductants of carbon containing pellets in RHF process. Energy **141**, 472–482 (2017). https://doi.org/10.1016/j.energy.2017.09.058
78. Han, H., Duan, D., Yuan, P., Li, D.: Biomass reducing agent utilisation in rotary hearth furnace process for DRI production. Ironmak. Steelmak. **42**, 579–584 (2015). https://doi.org/10.1179/1743281215Y.0000000001
79. Buergler, T., Di Donato, A.: Biomass gasification for DRI production. Rev. Met. Paris **106**, 429–433 (2009). https://doi.org/10.1051/metal/2009075
80. Kieush, L., Schenk, J., Pfeiffer, A., et al.: Investigation on the influence of wood pellets on the reactivity of coke with CO2 and its microstructure properties. Fuel **309**, 122151 (2022). https://doi.org/10.1016/j.fuel.2021.122151
81. Rejdak, M., Wojtaszek-Kalaitzidi, M., Gałko, G., et al.: A study on bio-coke production—the influence of bio-components addition on coke-making blend properties. Energies **15**, 6847 (2022). https://doi.org/10.3390/en15186847
82. Yustanti, E., Wardhono, E.Y., Mursito, A.T., Alhamidi, A.: Types and composition of biomass in biocoke synthesis with the coal blending method. Energies **14**, 6570 (2021). https://doi.org/10.3390/en14206570
83. Bazaluk, O., Kieush, L., Koveria, A., et al.: Metallurgical coke production with biomass additives: study of biocoke properties for blast furnace and submerged arc furnace purposes. Materials **15**, 1147 (2022). https://doi.org/10.3390/ma15031147
84. Vassilev, S.V., Baxter, D., Andersen, L.K., Vassileva, C.G.: An overview of the chemical composition of biomass. Fuel **89**, 913–933 (2010). https://doi.org/10.1016/j.fuel.2009.10.022
85. Castro Díaz, M., Zhao, H., Kokonya, S., et al.: The effect of biomass on fluidity development in coking blends using high-temperature SAOS rheometry. Energy Fuels **26**, 1767–1775 (2012). https://doi.org/10.1021/ef2018463
86. El-Tawil, A.A., Björkman, B., Lundgren, M., et al.: Influence of bio-coal properties on carbonization and bio-coke reactivity. Metals **11**, 1752 (2021). https://doi.org/10.3390/met11111752
87. Moghtaderi, B., Meesri, C., Wall, T.F.: Pyrolytic characteristics of blended coal and woody biomass. Fuel **83**, 745–750 (2004). https://doi.org/10.1016/j.fuel.2003.05.003
88. Di Nola, G., de Jong, W., Spliethoff, H.: TG-FTIR characterization of coal and biomass single fuels and blends under slow heating rate conditions: partitioning of the fuel-bound nitrogen. Fuel Process. Technol. **91**, 103–115 (2010). https://doi.org/10.1016/j.fuproc.2009.09.001
89. Lu, K.-M., Lee, W.-J., Chen, W.-H., Lin, T.-C.: Thermogravimetric analysis and kinetics of co-pyrolysis of raw/torrefied wood and coal blends. Appl. Energy **105**, 57–65 (2013). https://doi.org/10.1016/j.apenergy.2012.12.050
90. Vuthaluru, H.B.: Thermal behaviour of coal/biomass blends during co-pyrolysis. Fuel Process. Technol. **85**, 141–155 (2004). https://doi.org/10.1016/S0378-3820(03)00112-7
91. Onenc, S., Retschitzegger, S., Evic, N., et al.: Characteristics and synergistic effects of co-combustion of carbonaceous wastes with coal. Waste Manage. **71**, 192–199 (2018). https://doi.org/10.1016/j.wasman.2017.10.041
92. Zhang, L., Xu, S., Zhao, W., Liu, S.: Co-pyrolysis of biomass and coal in a free fall reactor. Fuel **86**, 353–359 (2007). https://doi.org/10.1016/j.fuel.2006.07.004
93. Panwar, N., Gajera, B., Jain, S., Salvi, B.: Thermogravimetric studies on co-pyrolysis of raw/torrefied biomass and coal blends. Waste Manag Res **38**, 1259–1268 (2020). https://doi.org/10.1177/0734242X19896624

94. Sadhukhan, A.K., Gupta, P., Goyal, T., Saha, R.K.: Modelling of pyrolysis of coal–biomass blends using thermogravimetric analysis. Biores. Technol. **99**, 8022–8026 (2008). https://doi.org/10.1016/j.biortech.2008.03.047
95. Yang, H., Yan, R., Chen, H., et al.: Characteristics of hemicellulose, cellulose and lignin pyrolysis. Fuel **86**, 1781–1788 (2007). https://doi.org/10.1016/j.fuel.2006.12.013
96. ASTM D3172–13; Standard Practice for Proximate Analysis of Coal and Coke. ASTM International: West Conshohocken (2013)
97. Kieush, L., Koveria, A., Schenk, J., et al.: Investigation into the effect of multi-component coal blends on properties of metallurgical coke via petrographic analysis under industrial conditions. Sustainability **14**, 9947 (2022). https://doi.org/10.3390/su14169947
98. ISO/DTS 4699, Hard Coal — Determination of plastometric indices — Manual Sapozhnikov Penetration Plastometer method
99. ISO/TC 27/SC 5 N936 - ISO/NP 4699, Hard Coal - Determination of plastometric indices - Manual Sapozhnikov Penetration Plastometer method
100. ISO 7404–2:2009; Methods for the Petrographic Analysis of Coals—Part 2: Methods of Preparing Coal Samples (2009)
101. ISO 7404–3:2009; Methods for the Petrographic Analysis of Coals—Part 3: Method of Determining Maceral Group Composition (2009)
102. ISO 7404–5:2009; Methods for the Petrographic Analysis of Coals—Part 5: Method of Determining Microscopically the Reflectance of Vitrinite (2009)
103. Haidai, O.A., Pavlychenko, A.V., Koveria, A.S., et al.: Determination of granulometric composition of technogenic raw materials for producing composite fuel. Nauk visn nat hirn univ 52–58 (2022). https://doi.org/10.33271/nvngu/2022-4/052
104. Sumbane-Prinsloo, L., Bunt, J., Piketh, S., et al.: The influence of particle size on the thermal performance of coal and its derived char in a Union stove. Energy Geosci. **2**, 148–159 (2021). https://doi.org/10.1016/j.engeos.2020.08.001
105. Kühn, T., Bunt, J.R., Neomagus, H.W.J.P., et al.: Coal-derived low smoke fuel assessment through coal stove combustion testing. J. Anal. Appl. Pyrol. **126**, 158–168 (2017). https://doi.org/10.1016/j.jaap.2017.06.012
106. ASTM D293/D293M-18; Standard Test Method for the Sieve Analysis of Coke; ASTM International; West Conshohocken
107. GOST 9521–2017; Hard Coals. Method for the Determination of Coking Property (2017)
108. ISO 10143:2019; Carbonaceous Materials for the Production of Aluminium—Calcined Coke for Electrodes—Determination of the Electrical Resistivity of Granules (2019)
109. Rouget, G., Majidi, B., Picard, D., et al.: Electrical resistivity measurement of petroleum coke powder by means of four-probe method. Metall. Materi. Trans. B **48**, 2543–2550 (2017). https://doi.org/10.1007/s11663-017-1022-9
110. Gotor, A.A., Rhazi, L.: Effects of refining process on sunflower oil minor components: a review. OCL **23**, D207 (2016). https://doi.org/10.1051/ocl/2016007
111. Carelli, A.A., Frizzera, L.M., Forbito, P.R., Crapiste, G.H.: Wax composition of sunflower seed oils. J Amer Oil Chem Soc **79**, 763–768 (2002). https://doi.org/10.1007/s11746-002-0556-9
112. Montiano, M.G., Díaz-Faes, E., Barriocanal, C.: Effect of briquette composition and size on the quality of the resulting coke. Fuel Process. Technol. **148**, 155–162 (2016). https://doi.org/10.1016/j.fuproc.2016.02.039
113. Montiano, M.G., Díaz-Faes, E., Barriocanal, C., Alvarez, R.: Influence of biomass on metallurgical coke quality. Fuel **116**, 175–182 (2014). https://doi.org/10.1016/j.fuel.2013.07.070
114. Mochizuki, Y., Naganuma, R., Tsubouchi, N.: Influence of inherently present oxygen-functional groups on coal fluidity and coke strength. Energy Fuels **32**, 1657–1664 (2018). https://doi.org/10.1021/acs.energyfuels.7b03774
115. Tsubouchi, N., Mochizuki, Y., Naganuma, R., et al.: Influence of inherent oxygen species on the fluidity of coal during carbonization. Energy Fuels **30**, 2095–2101 (2016). https://doi.org/10.1021/acs.energyfuels.5b02914