

Biomass as Raw Material for the Production of Biofuels and Chemicals



EDITED BY
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Preface

Plant biomass, a common source of valuable raw materials, has been used by humans as food, fodder for farm animals, fuel, building and furniture material, as well as a natural medicine or fertilizer for centuries. With the development of civilization, accompanied by the emergence of more efficient energy sources, new structural materials, fertilizers and other chemicals used in various spheres of life, its importance has still not diminished. It is still the basic food for humans and animals, a popular energy source currently used not only as a solid fuel but also – after appropriate processing – as a liquid or gaseous biofuel used in means of transport, a valuable material employed in various industries, as well as a source of bioactive chemicals for the production of pharmaceuticals, nutraceuticals, cosmetics or natural agents that improve soil quality.

Today, in addition to the undeniable application values of biomass, special attention is paid to the key role that biomass plays for the Earth's ecosystem, emphasizing its renewable nature, which ensures the circulation of carbon in the global cycle. The growth of biomass is related to the absorption of carbon from the atmosphere *via* photosynthesis. Naturally, the combustion of biomass releases carbon in the form of CO₂, but it can be assumed that the pool of this element in the atmosphere does not increase because it is built up back into the plant tissues. Although treating biomass as a carbon-neutral fuel is an exaggeration, as fossil fuels are also used during the biofuels production, it should be noted that the energetic use of biomass, especially the waste biomass or the mass of hydrobionts such as cyanobacteria, which pose the threat for water ecosystems, certainly contributes to the reduction of the pollutant emissions and provides many other environmental benefits. Such kinds of biomass are especially valuable as a raw material used in biorefineries. The idea of biorefining is gaining more and more popularity around the world. It is based on multidirectional processing of biomass, as a result of which various products are obtained, while maintaining the lowest possible CO₂ emission rate. Biorefining is closely related to another global mainstream concept – the circular economy, in which attention is paid to the fact that by-products generated at various stages of raw material processing are used as substrates in another production process.

Biomass, as a raw material for industry and energy, has a number of advantages including wide availability, renewable nature, and usually low acquisition cost (especially in the case of waste biomass). However, it also has certain disadvantages. Its biodegradable nature can be a problem during transport and storage. Additionally, the use of special preservation methods, such as drying and ensiling, or protection against external factors is sometimes required. On the other hand, in some

types of applications, it is necessary to increase the biodegradability of biomass. The high share of polysaccharides and lignin in lignocellulosic structure limits the efficiency of biomass conversion to the targeted products when the biological processing is realized. Enhancement of biodegradability is achieved through a number of processes based on various mechanisms, ranging from the simple mechanical processing consisting in grinding or crushing to complex and multi-stage chemical or physicochemical methods.

The book shows the exemplary applications of different types of biomass for the production of biofuels and other useful products, such as fertilizers, chemicals, and drugs. Special attention is paid to the practical directions of using the biomass of hydrobionts and microorganisms of activated sludge. Considering different applications of the biomass-derived products, the environmental, economic and energetic aspects were taken into account.

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Waldemar Wójcik was born in Poland in 1949. He is the Director of the Institute of Electronics and Information Technology, former long-time dean of the Faculty of Electrical Engineering and Computer Science at Lublin University of Technology, and Doctor Honoris Causa of five universities in Ukraine and Kazakhstan. He obtained his Ph.D. in 1985 at the Lublin University of Technology, and D.Sc. in 2002 at the National University Lviv Polytechnic, Ukraine. In 2009, he obtained the title of professor granted by the President of Poland. In his research, he mainly deals with process control, optoelectronics, digital data analysis and also heat processes or solid-state physics. He pays particular attention to the use of optoelectronic technology in the monitoring and diagnostics of thermal processes. He is a member of Optoelectronics Section of the Committee of Electronics and Telecommunications of the Polish Academy of Sciences and Metrology Section of the Committee of Metrology and Scientific Equipment of the Polish Academy of Sciences. He is also a member of European Academy of Science and Arts (Austria); Academy of Applied Radioelectronics of Russia, Ukraine and Belarus; the International Informatization Academy of Kazakhstan; and many other scientific organizations of Poland as well as Europe and Asia. In total, he has published 56 books and over 400 papers, and authored several patents. He is also a member of the editorial board of numerous international and national scientific and technical journals.

Małgorzata Pawłowska, Ph.D., is a researcher and lecturer at the Faculty of Environmental Engineering of Lublin University of Technology. In 2013–2019, she was the Head of the Department of Alternative Fuels Engineering at the Institute of Renewable Energy Sources Engineering. Currently, she heads the Department of Biomass and Waste Conversion into Biofuels. She received her M.Sc. in philosophy of nature and protection of the environment at the Catholic University of Lublin in 1993. In 1999, she received her Ph.D. in Agrophysics at the Institute of Agrophysics of the Polish Academy of Sciences, and in 2010, she obtained a postdoctoral degree in the technical sciences in the field of environmental engineering at the Wrocław University of Technology. In 2018, she was awarded the title of Professor of Technical Sciences. Her scientific interests focus mainly on the issues related to the reduction of the concentrations of greenhouse gases in the atmosphere, energy recovery of organic waste, and the

possibility of using the waste from the energy sector in the reclamation of degraded land. A measurable outcomes of her research is the authorship or co-authorship of 105 papers, including 40 articles in scientific journals, 4 monographs, 24 chapters in monographs, co-edition of 5 monographs, co-authorship of 15 patents and dozens of patent applications. She has participated in the implementation of nine research projects concerning, first of all, the prevention of pollutant emissions from landfills and the implementation of sustainable waste management.

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Assessment of Ecology-Economic Efficiency in Providing Thermal Stabilization of Biogas Installations

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3.1 INTRODUCTION

One of the ways of environmental-friendly and rational use of fuel and energy resources is the investment in the renewable energy sources, such as construction of solar, wind, and bioelectric power plants. In Ukraine, such investments were about 3.7 million euros in 2019. The implementation of bioconversion helps dispose of organic waste in biogas installations, prevents the contamination of the biosphere with harmful substances, and allows obtaining an alternative source of energy – biogas. The process of methane formation requires energy consumption for thermal stabilization of anaerobic fermentation in biogas installations (Suresh et al. 2013, Weiland 2003). In terms of scientific research, the energy-saving mechanisms for providing thermal stabilization in biogas energy installations are insufficiently substantiated.

It is possible to increase the energy efficiency and environment friendliness of bioconversion by rational selection of alternative renewable heat sources for fermentation processes of thermal stabilization. Such alternative sources are solar energy, low-potential thermal energy of soil and water as well as utilization of thermal emissions of bioconversion systems (Zabarnyi & Shurchkov 2002). Ukraine plans to give up the coal energy by 2050. The share of renewable energy sources is predicted to make up 70%.

The analysis of the literature shows that the theoretical and experimental studies of animal waste bioconversion mechanisms and kinetics of the technological process were conducted by G. Ratushnyak, E. Larushkin, S. Yakushko, M. Drukovani, and O. Zuev (Rotshtein 1999, Noyola et al. 2006, Rotshtein et al. 2008). An expert system for an intelligent support of energy-saving management of bioconversion technological process is also considered in the works of E. Larushkin and A. Rotshtein (Rotshtein 1999, Rotshtein et al. 2008). There are no examples in the literature of the calculations related to the ecological and economic efficiency of bioconversion (Drukovani et al. 2006, Noyola et al. 2006, Rotshtein et al. 2008). The purpose of the research was to create a theoretical background and develop a scientifically proven system of making effective decisions for choosing an innovative bioconversion project.

In order to achieve this goal, the research should solve the following tasks (Geletukha & Martseniuk 1999, Ratushnyak & Anokhina 2013, Zhelikh et al. 2013):

- Develop a classification of factors affecting ecological and economic indicators of the mechanisms for ensuring thermal stabilization in biogas plants (Zadeh 1975, Zuev 2009).
- Develop a hierarchical system of mathematical models related to multifactor analysis regarding the ecological economic efficiency of the mechanism ensuring the process of thermal stabilization based on fuzzy logic, which takes into account the influence of quantity and quality factors (Redko et al. 2016, Kukharchuk et al. 2017).

3.2 METHODOLOGY

The classification of the factors affecting ecological and economic indicators of mechanisms ensuring thermal stabilization in biogas plants was developed. The inference tree (Figure 3.1) is based on classified factors; it defines a system of nested statements and establishes hierarchical links between them. It characterizes the impact of a set of influencing factors. It can be represented as a fixed ratio:

$$Y = f(X, Z), \quad (3.1)$$

where

X is a linguistic variable which describes environmental factors;

Y is a linguistic variable which describes economic factors.

The linguistic variable X that describes environmental factors can be represented by the expression:

$$X = f(x_1, x_2, x_3) \quad (3.2)$$

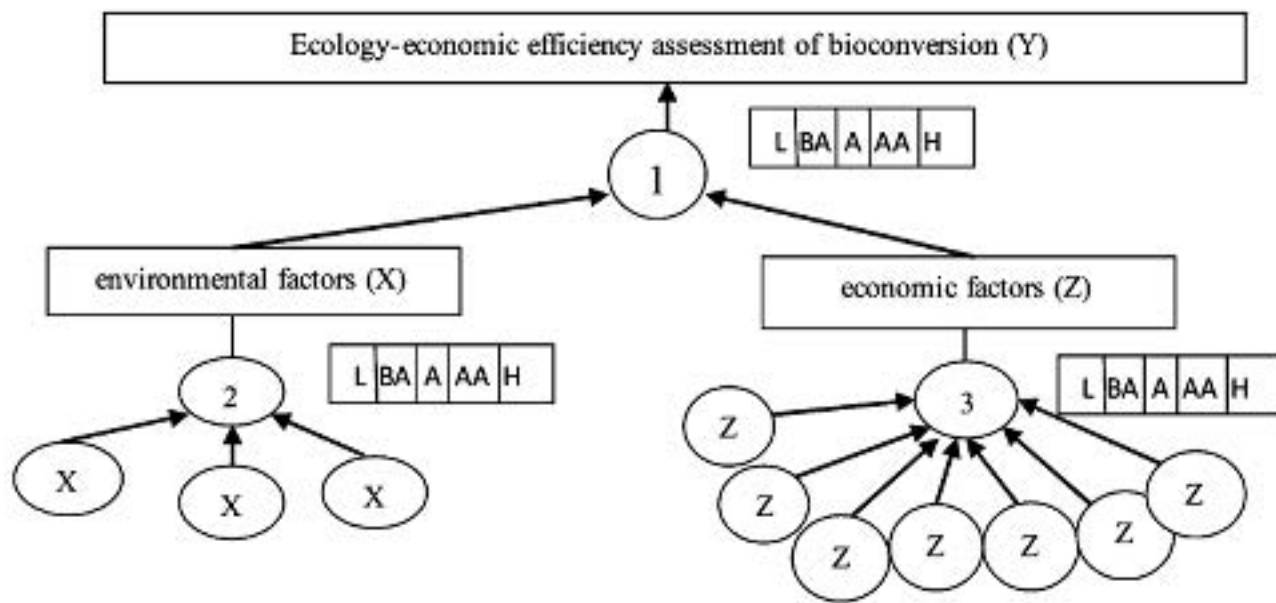


Figure 3.1 The tree of inference which concerns hierarchical relationships of factors that influence environmental and economic assessments of a bioconversion project.

where

- x_1 is the linguistic variable “CO₂ emissions”,
- x_2 is the linguistic variable “organic waste disposal”,
- x_3 is the linguistic variable “environmental pollution”.

The linguistic variable Z , which describes environmental factors, can be represented by the expression:

$$Z = f(z_1, z_2, z_3, z_4, z_5, z_6, z_7), \quad (3.3)$$

where

- z_1 – the linguistic variable “term of recoupment”;
- z_2 – the linguistic variable “Net Present Value”;
- z_3 – the linguistic variable “Internal Rate of Return”;
- z_4 – the linguistic variable “Profitability Index”;
- z_5 – the linguistic variable “duration of operation”;
- z_6 – the linguistic variable “profit”;
- z_7 – the linguistic variable “operating costs”.

Simulation of the system-level intellectual support of project variant selection can be done by using the following terms:

$$\begin{aligned} T(Y) &= \langle \text{Low, Below Average, Average, Above Average, High} \rangle \\ T(X) &= \langle \text{Low, Below Average, Average, Above Average, High} \rangle \\ T(Z) &= \langle \text{Low, Below Average, Average, Above Average, High} \rangle \end{aligned}$$

The fuzzy inference technique helps calculate the predicted number by means of a fuzzy set using the “IF - THAT” linguistic expression system. It combines the fuzzy

terms of output and input variables by using operations I and OR, which correspond to operations min and max (Zadeh 1975, Rotshtein et al. 1997, Rotshtein 1999).

Linguistic statements correspond to a system of fuzzy logical equations, which characterize the surface of belonging to the variables (X, Z) of the corresponding term:

$$\mu_L(Y) = \mu_L(X) \wedge \mu_L(Z) \vee \mu_{BA}(X) \wedge \mu_L(Z) \vee \mu_L(X) \wedge \mu_{BA}(Z) \quad (3.4)$$

$$\mu_{BA}(Y) = \mu_{BA}(X) \wedge \mu_{BA}(Z) \vee \mu_{BA}(X) \wedge \mu_A(Z) \vee \mu_A(X) \wedge \mu_{BA}(Z) \quad (3.5)$$

$$\mu_A(Y) = \mu_A(X) \wedge \mu_A(Z) \vee \mu_L(X) \wedge \mu_{AA}(Z) \vee \mu_{AA}(X) \wedge \mu_L(Z) \quad (3.6)$$

$$\mu_{AA}(Y) = \mu_{AA}(X) \wedge \mu_{AA}(Z) \vee \mu_{AA}(X) \wedge \mu_A(Z) \vee \mu_A(X) \wedge \mu_{AA}(Z) \quad (3.7)$$

$$\mu_H(Y) = \mu_H(X) \wedge \mu_H(Z) \vee \mu_{AA}(X) \wedge \mu_H(Z) \vee \mu_H(X) \wedge \mu_{AA}(Z) \quad (3.8)$$

The assessment of linguistic variables levels related to environmental factors (X) is done by the amount of CO₂ emissions (x_1), the level of organic waste utilization (x_2) and the level of environmental pollution (x_3) using the following system of term sets:

$$T(x_1) = \langle \text{Low, Average, High} \rangle$$

$$T(x_2) = \langle \text{Low, Average, High} \rangle$$

$$T(x_3) = \langle \text{Low, Average, High} \rangle$$

The system of fuzzy logical equations which characterizes the surface of belonging to the variables (x_1, x_2, x_3) of the corresponding term can be shown as the linguistic statement:

$$\begin{aligned} \mu_L(X) = & \mu_H(x_1) \wedge \mu_L(x_2) \wedge \mu_H(x_3) \vee \mu_H(x_1) \wedge \mu_L(x_2) \wedge \mu_A(x_3) \vee \mu_A(x_1) \\ & \mu_L(x_2) \wedge \mu_H(x_3) \end{aligned} \quad (3.9)$$

$$\begin{aligned} \mu_{BA}(X) = & \mu_A(x_1) \wedge \mu_H(x_2) \wedge \mu_H(x_3) \vee \mu_A(x_1) \wedge \mu_L(x_2) \wedge \mu_A(x_3) \vee \mu_H(x_1) \cdot \\ & \mu_L(x_2) \wedge \mu_A(x_3) \end{aligned} \quad (3.10)$$

$$\begin{aligned} \mu_A(X) = & \mu_A(x_1) \wedge \mu_A(x_2) \wedge \mu_A(x_3) \vee \mu_H(x_1) \wedge \mu_L(x_2) \wedge \mu_A(x_3) \vee \mu_L(x_1) \cdot \\ & \mu_H(x_2) \wedge \mu_A(x_3) \end{aligned} \quad (3.11)$$

$$\begin{aligned} \mu_{AA}(X) = & \mu_A(x_1) \wedge \mu_A(x_2) \wedge \mu_L(x_3) \vee \mu_A(x_1) \wedge \mu_H(x_2) \wedge \mu_A(x_3) \vee \mu_L(x_1) \\ & \mu_H(x_2) \wedge \mu_A(x_3) \end{aligned} \quad (3.12)$$

$$\begin{aligned} \mu_H(X) = & \mu_L(x_1) \wedge \mu_H(x_2) \wedge \mu_L(x_3) \vee \mu_L(x_1) \wedge \mu_H(x_2) \wedge \mu_L(x_3) \vee \mu_A(x_1) \\ & \mu_H(x_2) \wedge \mu_L(x_3) \end{aligned} \quad (3.13)$$

The assessment of the levels of linguistic variables linking economic factors (Z) with payback period (z_1), with Net Present Value (z_2), with Internal Rate of Return (z_3), with Profitability Index (z_4), with duration (z_5), with profit (z_6), and with operating costs (z_7) is performed by using a system of term sets:

$$T(z_1) = \langle \text{Small}(S), \text{Average}, \text{Long}(\text{Ln}) \rangle$$

$$T(z_2) = \langle \text{Low}, \text{Average}, \text{High} \rangle$$

$$T(z_3) = \langle \text{Low}, \text{Average}, \text{High} \rangle$$

$$T(z_4) = \langle \text{Low}, \text{Average}, \text{High} \rangle$$

$$T(z_5) = \langle \text{Small}(S), \text{Average}, \text{Long}(\text{Ln}) \rangle$$

$$T(z_6) = \langle \text{Low}, \text{Average}, \text{High} \rangle$$

$$T(z_7) = \langle \text{Low}, \text{Average}, \text{High} \rangle$$

The system of fuzzy logical equations which characterizes the surface of belonging to the variables ($z_1, z_2, z_3, z_4, z_5, z_6, z_7$) of the corresponding term can be shown as the linguistic statement:

$$\begin{aligned} \mu_L(Z) = & \mu_{Ln}(z_1) \wedge \mu_L(z_2) \wedge \mu_S(z_3) \wedge \mu_L(z_4) \wedge \mu_L(z_5) \wedge \mu_L(z_6) \wedge \mu_L(z_7) \vee \\ & \mu_A(z_1) \wedge \mu_L(z_2) \wedge \mu_L(z_3) \wedge \mu_L(z_4) \wedge \mu_S(z_5) \wedge \mu_L(z_6) \wedge \mu_L(z_7) \vee \\ & \mu_{Ln}(z_1) \wedge \mu_A(z_2) \wedge \mu_L(z_3) \wedge \mu_L(z_4) \wedge \mu_S(z_5) \wedge \mu_L(z_6) \wedge \mu_L(z_7) \end{aligned} \quad (3.14)$$

$$\begin{aligned} \mu_{BA}(Z) = & \mu_{Ln}(z_1) \wedge \mu_A(z_2) \wedge \mu_A(z_3) \wedge \mu_L(z_4) \wedge \mu_S(z_5) \wedge \mu_L(z_6) \wedge \mu_H(z_7) \vee \\ & \mu_{Ln}(z_1) \wedge \mu_L(z_2) \wedge \mu_L(z_3) \wedge \mu_L(z_4) \wedge \mu_S(z_5) \wedge \mu_L(z_6) \wedge \mu_H(z_7) \vee \\ & \mu_A(z_1) \wedge \mu_L(z_2) \wedge \mu_A(z_3) \wedge \mu_L(z_4) \wedge \mu_S(z_5) \wedge \mu_L(z_6) \wedge \mu_H(z_7) \end{aligned} \quad (3.15)$$

$$\begin{aligned} \mu_A(Z) = & \mu_A(z_1) \wedge \mu_A(z_2) \wedge \mu_A(z_3) \wedge \mu_A(z_4) \wedge \mu_A(z_5) \wedge \mu_A(z_6) \wedge \mu_A(z_7) \vee \\ & \mu_A(z_1) \wedge \mu_L(z_2) \wedge \mu_A(z_3) \wedge \mu_A(z_4) \wedge \mu_S(z_5) \wedge \mu_L(z_6) \wedge \mu_A(z_7) \vee \\ & \mu_{Ln}(z_1) \wedge \mu_L(z_2) \wedge \mu_A(z_3) \wedge \mu_L(z_4) \wedge \mu_S(z_5) \wedge \mu_L(z_6) \wedge \mu_H(z_7) \end{aligned} \quad (3.16)$$

$$\begin{aligned} \mu_A(z_1) \wedge \mu_A(z_2) \wedge \mu_A(z_3) \wedge \mu_H(z_4) \wedge \mu_A(z_5) \wedge \mu_A(z_6) \wedge \mu_L(z_7) \vee \\ \mu_S(z_1) \wedge \mu_H(z_2) \wedge \mu_A(z_3) \wedge \mu_A(z_4) \wedge \mu_A(z_5) \wedge \mu_A(z_6) \wedge \mu_L(z_7) \end{aligned} \quad (3.17)$$

$$\begin{aligned} \mu_H(X) = & \mu_S(z_1) \wedge \mu_H(z_2) \wedge \mu_H(z_3) \wedge \mu_H(z_4) \wedge \mu_{Ln}(z_5) \wedge \mu_H(z_6) \wedge \mu_L(z_7) \vee \\ & \mu_S(z_1) \wedge \mu_A(z_2) \wedge \mu_A(z_3) \wedge \mu_H(z_4) \wedge \mu_{Ln}(z_5) \wedge \mu_H(z_6) \wedge \mu_L(z_7) \vee \\ & \mu_S(z_1) \wedge \mu_H(z_2) \wedge \mu_H(z_3) \wedge \mu_H(z_4) \wedge \mu_{Ln}(z_5) \wedge \mu_A(z_6) \wedge \mu_L(z_7) \end{aligned} \quad (3.18)$$

The fuzzy logic confirmation technique allows observing an indicator predicted as fuzzy sets. Fuzzy sets estimate the environmental and economic performance of a project variant for the fixed vector of influencing factors. In order to move from the obtained fuzzy sets to quantity assessment, a dephasing procedure must be performed. It consists in the transformation of fuzzy information into a distinct form. Among various methods of defuzzification, the most common is finding the "center of gravity" of a flat figure, which is limited by the function of fuzzy set membership and horizontal coordinate. The fuzzy inference model, together with the dephasification procedure, provides an opportunity to monitor the changes in the baseline – the environmental and economic efficiency of the project.

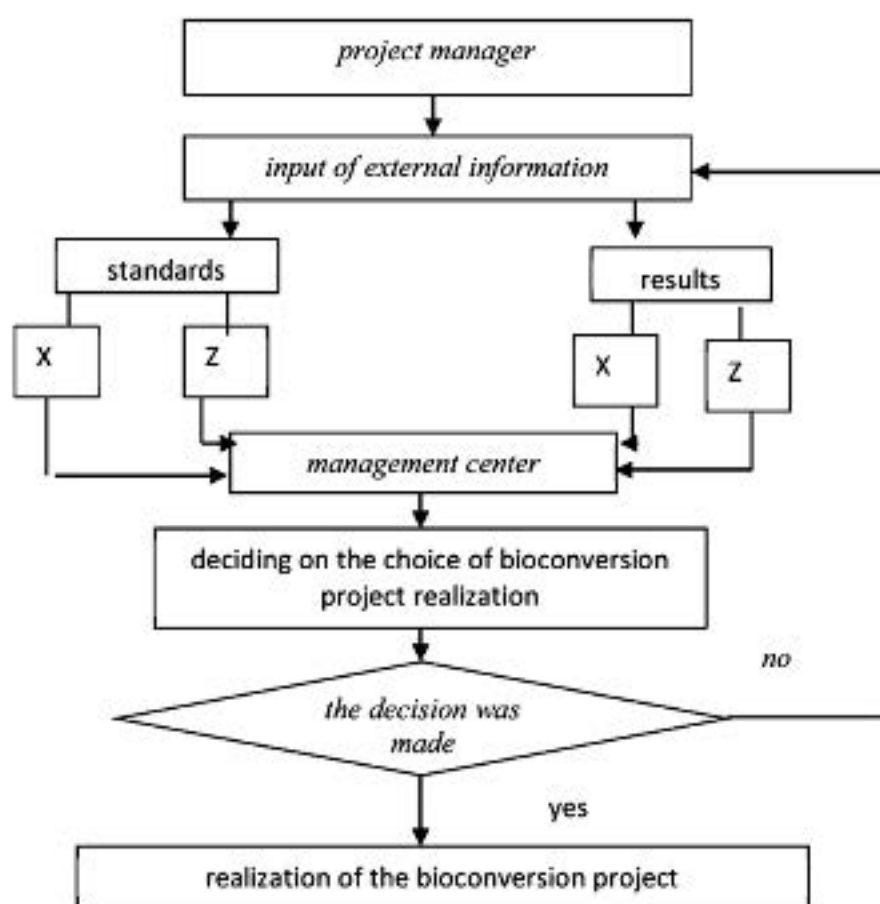


Figure 3.2 Structural and logical model of managing ecological and economic feasibility of an innovative bioconversion project.

In order to assess the economic efficiency of the mechanisms for providing thermal stabilization process in biogas installations at the conceptual phase of the life cycle of an investment project, a structural logical model for minimizing the bioconversion products cost by managing renewable energy sources has been offered (Figure 3.2). This model allows taking into account required variable data about the dynamic parameters of the thermal stabilization process in the production of biogas as ecological energy source.

3.3 CONCLUSIONS

- Formalization and hierarchical classification of the quantity and quality factors were completed, which are important and significantly help determine innovative appeal of a bioconversion project variant.
- Models of managing the assessment of bioconversion ecological-economic efficiency based on fuzzy logic at ecological and economic levels were developed.
- For the first time, a structural and logical model for managing ecological and economic feasibility of an innovative bioconversion project was created.

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Efficiency Assessment Functioning of Vibration Machines for Biomass Processing

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6.1 INTRODUCTION

The use of new energy-saving technologies has led to a significant development of the designs of vibrating machines and their widespread use, in particular for processing biomass. During their operation, the question of the efficiency and reliability of using this type of machine is quite relevant, due to the presence and possibility of using the reserves of its operation. The machines of this type must meet the requirements of quality and reliability in order to fulfill their official purpose.

The reliability and performance characteristics of vibrating machines are important technical and economic indicators related to the operation of systems for processing biomass. The increase of these characteristics opens the direction for the scientifically sound designation of reliability indicators, the achievement of these indicators in an economically optimal way. Improving the reliability and durability of vibrating machines has a serious reserve for saving money, materials, energy, and labor. To a large extent, the reliability and durability of a vibrating machine depend on extreme overloads. The qualification choice of materials and the correct calculations, taking into account the presence of a priori statistical information about the load at

the design stage, are the main sources of improving reliability without significantly raising the cost of the machine. Therefore, this research topic is relevant.

There are numerous known published monographs, textbooks, and periodic sources on the subject. The issues of ensuring the reliability of machines at the stages of design and operation are disclosed in the textbook (Sharov et al. 2015; Chernovol et al. 2010). An interconnected set of tasks is considered here: friction, aging, and wear. The causes of changes in the technical condition of machines and the physics of their failures were revealed. In the monograph (Iskovych-Lototsky et al. 2018), the approach for assessing the reliability of the effectiveness of ensuring the conditions of failure-free automated process was presented.

There are both fundamental and periodic sources where the results of the operation of vibratory-press equipment are published (Iskovych-Lototsky et al. 2017; Zhu et al. 2017). However, there are virtually no publications evaluating the efficiency and reliability of the operation of vibrating machines. In this regard, the topic of the article is relevant.

A research was conducted in order to propose and develop a system for evaluating the effectiveness and reliability of quantitative characteristics that is probabilistic-statistical in nature.

6.2 THE MAIN RESULTS OF THE STUDY

The problem of improving the reliability and efficiency of machines and structures constitutes an important technical and economic task, the solution of which opens the way for the science-based designation of the reliability indicators, achievement of these indicators in an economically optimal way. Improving the reliability and durability of machines represents a serious reserve for saving money, materials, energy, and labor costs. To a large extent, the reliability and durability of machines depend on current loads and actions. The correct choice of materials and the correction of calculations, taking into account a priori statistical information about the load at the design stage, are the main sources of improving reliability without significantly raising the cost of the machine.

The problem of the efficiency and reliability of using vibrating machines is associated with the presence and possibility of using the reserves of operation of the machine.

Therefore, to assess the effectiveness and reliability, it is necessary to introduce the quantitative characteristics that are probabilistic in nature. Since they can be determined not only experimentally but also by theoretical analysis, it is advisable to consider them from a statistical and probabilistic point of view.

As the quantitative characteristics of failure-free operation, the probability of the absence of failures, the frequency of failures, the failure rate, and the mean time between failures were used.

These questions are quite important in the direction of increasing the efficiency of technical diagnostics of the operation of vibrating machines (Sharov et al. 2015; Adamchuk et al. 2017; Vedmitskyi et al. 2017).

The probability of the absence of failures $P(t)$ is the probability that – under certain operating conditions – within the specified duration of operation, failure does not occur, and the probability of failure $Q(t)$ is the probability that – under the same

conditions – a failure occurs during the specified time. The mill of serviceability (absence of failures) and malfunctions (presence of failures) of the system is incompatible and opposite events. The sum of the probabilities of such events, as is known from probability theory, is equal to unity. That is, the probability of failure and the probability of failure are related by:

$$P(t) + Q(t) = 1 \quad (6.1)$$

as defined

$$\left. \begin{aligned} P(t) &= R(T \geq t); \\ Q(t) &= R(T \leq t); \end{aligned} \right\} \quad (6.2)$$

where

R is the probability symbol of an arbitrary event,

T is the operating time of the system to failure,

t is the operating time of the system for which we determine the reliability.

By the definition of probability theory (Sharov et al. 2015), the probability distribution function $F(x)$ of a random variable is the probability that the quantity will take a value less than some quantity x , that is,

$$F(x) = R(\xi < x) \quad (6.3)$$

It follows that the function of the probability of failure $Q(t)$ is similar to the distribution function of the operating time of the system to failure.

In a statistical assessment, the empirical probability of the absence of failures is defined as the relationship:

$$P_e(t) = \frac{N_0 - n(t)}{N_B} = \frac{N_0}{N_0} - \frac{n(t)}{N_0} = 1 - \frac{n(t)}{N_0}, \quad (6.4)$$

and the empirical probability of failure as a relationship

$$Q_e(t) = n(t)/N_0 \quad (6.5)$$

where

N_0 is the number of nodes of the hydraulic pulse drive,

$n(t)$ is the number of hydroimpulse drive units that failed during time t .

The values of the empirical probabilities of the absence of failure and failures obtained by a statistical method always differ from theoretical ones (Chernovol et al. 2010). With an increase in the number of tested nodes $Pe(t)$ and $Qe(t)$, they asymptotically approach $P(t)$ and $Q(t)$. The same can be said about other quantitative characteristics of reliability. The initial conditions of the functions $P(t)$ and $Q(t)$ are defined in this way,

at $t=0$ the hydro-pulse drive retains its original characteristics and meets the requirements presented to it, that is:

$$P(0)=1; \quad Q(0)=0. \quad (6.6)$$

Like any continuous function, the failure probability $Q(t)$ can be differentiated for all values of the argument. In probability theory, the derivative of the distribution function is called the distribution density:

$$f(x) = dF(x)/dx, \quad (6.7)$$

where

$f(x)$ is the probability density of a random variable ξ .

In the reliability theory, this density of the distribution of the system's operating time k for failures is called the failure rate $a(t)$ (Chernovol et al. 2010; Kukharchuk, Kazyv et al. 2017). We carry out the following transformations:

$$Q(t) = 1 - P(t). \quad (6.8)$$

Let us find the differential of the left and right sides of the dependence (6.8):

$$dQ(t)/dt = a(t) = \frac{d}{dt}[1 - P(t)] = -dP(t)/dt. \quad (6.9)$$

Integrating the left and right sides of equality (6.9), we obtain:

$$Q(t) = \int_0^t a(t) dt \quad (6.10)$$

$$P(t) = 1 - \int_0^t a(t) dt. \quad (6.11)$$

By definition, the failure rate is the ratio of the number of nodes that failed per unit time to the number of all nodes that are tested, provided that they are not restored and are not replaced by serviceable ones

$$a_e(t) = n(\Delta t)/N_0 \Delta t, \quad (6.12)$$

Here, $n(\Delta t)$ – the number of nodes that failed in the time interval Δt .

A typical time dependence of the failure rate is shown in Figure 6.1.

Three gaps are highlighted on the curve. Gap 1 is caused by a large number of failures at the beginning of operation of the hydro-pulse drive due to gross defects of its elements, errors of the operating personnel. The initial period is different for various hydroimpulse occasions. It can be reduced, or completely removed, using the methods of training and testing.

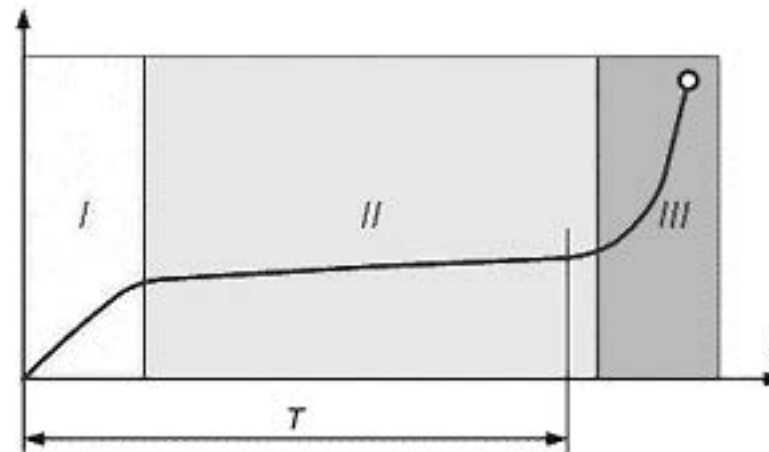


Figure 6.1 Typical failure rate λ versus time t .

Gap 2 characterizes the normal operation of the hydraulic drive. The failures in this period are mostly unexpected in nature, their average frequency decreases.

The aging period is caused by the wear of the hydro-pulse drive, when, due to the aging of the elements (nodes), the failure rate gradually increases (Kukharchuk, Hraniak et al. 2016; Kukharchuk, Bogachuk et al. 2017).

If the failure rate makes it possible to assess the reliability of the hydro-pulse drive for the desired period of time without taking into account the time of the previous operation, then the failure rate accounts for this effect. The distribution density, which takes into account the previous value of a random variable, is called the conditional density. Thus, the failure rate is the conditional density of the distribution of the failure time, which represents the instantaneous failure rate of the system at time t , provided that there are no failures up to this point.

The failure rate is defined as the ratio of the number of nodes of the hydraulic pulse drive that failed per unit time to the average number of nodes that worked correctly in a given period of time, provided that the nodes that failed to be restored and not replaced by serviceable ones

$$\lambda_e(t) = n(\Delta t) / N_{cep} \Delta t, \quad (6.13)$$

where

$N_{cep} = (N_i + N_{i+1}) / 2 = N_0 - n(\Delta t)$ is the average number of serviceable nodes at the beginning and end of the time interval Δt .

The probability representation of intensity was obtained using the main theorems of probability theory (Sharov et al. 2015). The proposed approach is new, which has its own elements of the novelty of the relation between the reliability theory and probability theory and mathematical statistics.

From expression (6.13), we replace $n(\Delta t)$ with the values obtained from formula (6.12), and N_{cep} – with its value from expression (6.4), we obtain:

$$\lambda(t) = a(t) / P(t) = - \frac{dp(t)}{dt} / P(t). \quad (6.14)$$

In accordance with this, we finally define one more way $P(t)$, $Q(t)$, $a(t)$:

$$P(t) = \exp\left(-\int_0^t \lambda(t) dt\right), \quad (6.15)$$

$$Q(t) = (1 - \exp(-\lambda(t)dt)), \quad (6.16)$$

$$a(t) = \lambda(t) \exp\left(-\int \lambda(t) dt\right). \quad (6.17)$$

The obtained expressions (6.15), (6.16), and (6.17) establish the relationship between the probability of no failure, the probability of failure and the failure rate of the nodes of the hydraulic pulse drive. The result of this approach is the determination of mathematical expectation T , variance $D(t)$, and standard deviation $\sigma(t)$ as compound probability theory (Sharov et al. 2015). We will use the failure rate $\lambda(t)$, failure probability $P(t)$, failure probability $Q(t)$ as part of a reliability theory (Chernovol et al. 2010; Vedmitskyi et al. 2017).

Let us define the mathematical expectation T . From the point of view of probability theory, this is the mathematical expectation of the average value of a point estimate \bar{t}_i of the average time, as the average operating time of the i -th node. Here, the indicators are reliability characteristics calculated using the tools of the mathematical apparatus of probability theory and mathematical statistics. Thus, the mean failure time T is the mathematical expectation of the operating time of the corresponding hydraulic pulse drive unit to failure.

In probability theory, the mathematical expectation of a random continuous variable ξ is called an integral of the form $\int xf(x)dx$. Turning to the theory of reliability, we can write:

$$T = \int_{-\infty}^{+\infty} ta(t) dt. \quad (6.18)$$

Substituting the value $a(t)$ with (6.17) in expression (6.18), integrating by parts and taking into account that $P(0) = 1$, $P(\infty) = 0$, and time cannot be negative, we obtain:

$$T = \int_{-\infty}^{+\infty} tP'(t) dt = -tP(t) \Big|_0^{\infty} + \int_0^{\infty} dt = \int_0^{\infty} P(t) dt. \quad (6.19)$$

Given the formula (6.17), we get:

$$T = \int_0^{\infty} \exp\left(-\int_0^t \lambda(t) dt\right) dt \quad (6.20)$$

Expression (6.19) shows that the average time of absence of failures T is completely determined by the probability of the absence of failures $P(t)$ and represents the area that limits the curve $P(t)$ and the coordinate axes.

In order to determine the average time of absence of failures with statistical empirical data, we use the formula of a small sample of the form:

$$T_e = \sum_{i=1}^N t_i / N_0, \quad (6.21)$$

where

t_i is the operating time of the i -th hydropulse drive unit before a failure occurs.

This quantitative characteristic is important, as it allows in some cases to visually judge the reliability of hydraulic pulse drive units.

When assessing reliability using the average time of absence of failure, it is necessary to know the variance of the time of occurrence of failure $D(t)$, which characterizes the discrepancy of the studied value. We define it as the mathematical expectation of the squared deviation of a random variable t from the mathematical expectation of this random variable (T):

$$D(t) = \int_0^{\infty} (t - T)^2 a(t) dt. \quad (6.22)$$

Moreover, we note that it is necessary to minimize. We will develop this direction in further studies. For example, in classical sources, it is indicated that $D(t) = 1$.

At the variance level $D(t)$, the root-mean-square deviation of the no-failure time is important. The standard deviation is:

$$\sigma(t) = \sqrt{D(t)}. \quad (6.23)$$

It is quite complete and simple to determine all quantitative characteristics of reliability from the law of distribution of the operating time of nodes to failure. Time is a random continuous quantity; therefore, arbitrary continuous distributions that are used in probability theory can be used as theoretical distribution laws.

6.3 CONCLUSIONS

The assessment of the efficiency and reliability of the operation of hydraulic pulse drives was conducted to evaluate the effectiveness and reliability of the introduced quantitative characteristics that are probabilistic in nature. They can be determined not only experimentally but also by theoretical analysis, where they are examined from the statistical and probabilistic points of view.

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Mathematical Model of Synthesis of Biodiesel from Technical Animal Fats

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18.1 INTRODUCTION

The high price of biodiesel (over double the price of diesel) mostly results from the price of the feedstock, which makes up to 75% of the overall production costs (Ade-wale, Dumont, J. & Ngadi 2015). However, biodiesel can be made from other feed stocks, including beef tallow, pork lard, yellow grease, and waste tannery fats (Chai et al. 2014, Farooq, Ramli, & Subbarao 2013, Hawrot-Paw, Wijatkowski, & Mikiciuk 2015), which are unpleasant wastes and are consequently incinerated. The incineration

is charged, which makes the tannery waste economically profitable in the biodiesel production. The acid value of flashings (the main waste fat produced by tanneries) usually exceeds 2 mg KOH/g.

Therefore, their direct processing via alkali-catalyzed transesterification is not suitable since the inorganic alkali catalyst (KOH, NaOH) is spent on free fatty acids (FFA) neutralization. Moreover, the salts formed during this reaction prevent easy separation of the methyl ester and glycerin phase; also, simultaneously formed water decreases the transesterification yield (Issariyakul & Dalai 2014, Mohammadshirazi et al. 2014). There are several methods capable to overcome this problem. Probably, the most investigated way is an acid catalyzed transesterification of FFA used at an industrial scale (Mushtruk et al. 2017), in contrast to the majority of other techniques (e.g. enzymatic transesterification and transesterification (Nielsen et al. 2016), fat treatment in supercritical methanol (Sajith, Sobhan, & Peterson 2010)).

The acid-catalyzed transesterification method uses a strong inorganic acid (like sulfuric acid) for transesterification of the FFA to methyl esters. The transesterification reduces the FFA content to a level at which an alkali catalyst may be employed for subsequent transesterification of glycerols (Sukhenko et al. 2017). In Sukhenko et al. (2018), a scale-up of the two-step transesterification technology is used, in which sulfuric acid was employed as a transesterification catalyst and the refined fat was transesterification with an inorganic alkali.

The main drawback of the described techniques is the necessity of acid neutralization prior to alkali transesterification, which leads to a formation of large amounts of salts in the reaction system (Xiong, Guo, & Xie 2015). These salts must be removed from the final biodiesel (and also glycerin), which may be the limiting factor during the product purification (Kolyanovska et al. 2019).

Thus, much effort is made to develop suitable solid transesterification catalysts (e.g. Xiong, Guo, & Xie 2015), which are easily separable from the reaction mixture after successful transesterification. Despite the fact that some of these solid catalysts are available commercially, the solid catalyst efficiency and its possible fouling are still an issue, namely in the case of transesterification under mild reaction conditions, that is, at atmospheric pressure and temperatures around 60°C (Xiong, Guo, & Xie 2015).

Modeling has become one of the most powerful means of making engineering decisions in modern technical re-equipment of production. With its application and introduction, there are undeniable advantages in reducing the terms of experimental research and saving resources in science and technology. Mathematical modeling of processes in the overwhelming majority of cases may rule out the need for pilot installations to test technical and technological solutions, or to carry out labor-intensive and expensive experiments (Adewale, Dumont, & Ngadi 2015).

There are many ways of performing mathematical modeling of technological processes. Its most important purpose is determined by the way of establishing the possibility of simulating the process with the help of physical, mathematical, chemical, and other models, separately or in combination with the laws, mechanisms, and connections between the influencing factors, in order to calculate the parameters of the model as accurately as possible (Chai et al. 2014).

The aim and objectives of research are to construct a mathematical model of the process of transesterification of technical animal fats in biodiesel.

18.2 LITERATURE REVIEW AND PROBLEM STATEMENT

The basics of the theory and results of experimental studies of technological processes, machines, and equipment for the production and use of diesel and other types of biodiesel in the agro industrial complex of Ukraine are presented in detail in the scientific works of M. Virevsky, V. Voytova, Ya. Gukova, V. Dubrovina, B. Kochirky, S. Kovalishina, V. Kravchuka, M. Linnaeus, V. Mironenka, S. Pastushenko, G. Ratushniaka, V. Semenova, Yu. Sukhenka, G. Topilina, and V. Yasenetsky et al. (Issariyakul & Dalai 2014, Mohammadshirazi et al. 2014, Mushtruk et al. 2017).

However, little attention is paid to the study of the processes of mathematical modeling for the production of biodiesel, which reduces the cost and increases the yield and quality of the final product (biodiesel), although the volume of raw materials is rather high. Therefore, the relevance of the chosen direction of research is beyond doubt.

18.3 MATERIALS AND METHODS OF RESEARCH

Technical animal fats – triglycerides (TG) – consist of three chains of fatty acids, which are joined by molecules of glycerol.

When passing the reaction of transesterification with methyl (ethyl) alcohol, triglycerides are converted to methyl (ethyl) esters of fatty acids (biodiesel). Catalysts are used for intensification of the process (often sodium hydroxide or potassium). Hydroxides break the bonds in the triglyceride molecules and provide their reaction with methanol or ethanol to form esters that are biodiesel. Other catalysts may also be used (Farooq, Ramli, & Subbarao 2013, Issariyakul & Dalai 2014, Sukhenko et al. 2017).

At the end of the re-transesterification, the triglyceride molecules are converted into three molecules of methyl ether and one molecule of glycerol.

This reaction takes place in three stages (Figure 18.1). First, a chain of fatty acids is separated from the triglyceride (TG) and is joined to methanol (A), forming a molecule of methyl ether (ME) and diglyceride (DG). Afterwards, the second chain of fatty acid is separated from diglycerides and binds to the methanol molecule to form a molecule of methyl ether and monoglycerides (MG). Then, in monoglycerides, glycerol is replaced with methyl alcohol to form methyl ester and glycerol. This step completes the reaction (Hawrot-Paw, Wijatkowski, & Mikiciuk 2015).

Initially, the reaction proceeds very quickly, but over time, the pace of conversion slows down. Some triglycerides become diglycerides with the release of methyl esters of fatty acids (biodiesel). Diglycerides are more slowly converted into monoglycerides, which are then more slowly converted into methyl esters, and there is a complete loss of free glycerin in the precipitate. The rate of reaction decreases gradually, and it never ends completely. At the end of the process, the amount of glycosides is negligible and limited to the strict limits set by the standard for biodiesel fuels (Issariyakul & Dalai 2014).

Each of the stages of the transesterification reaction can take place in the forward and reverse direction with an individual rate, which depends on the reaction rate constant k_n .

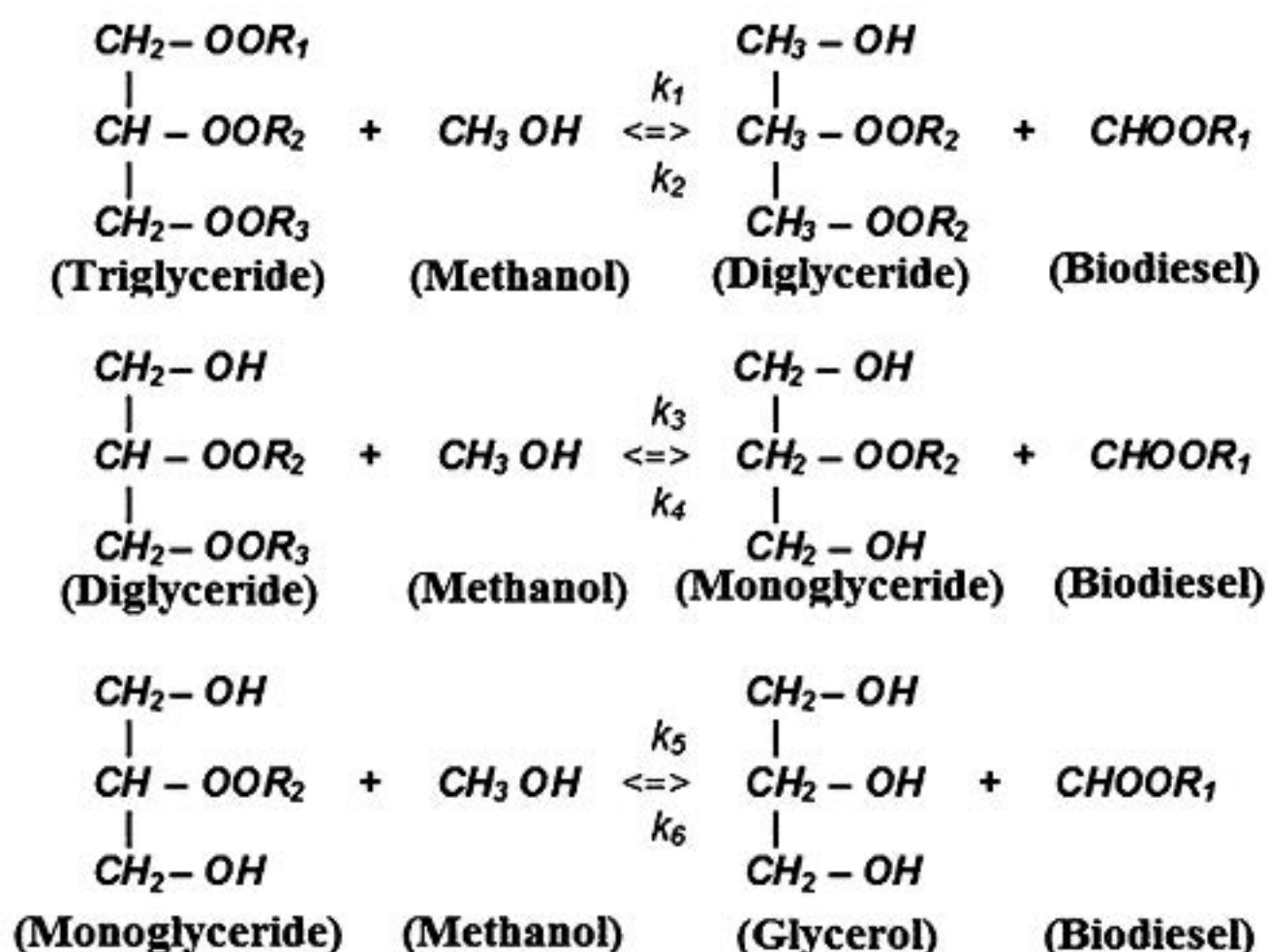


Figure 18.1 Scheme of phased transesterification of triglycerides.

In order to determine the rate of occurrence and disappearance of the components of the reacting mixture, the following system of differential equations that collectively simulates the process of transesterification of triglycerides of fat can be used:

$$\frac{d[\text{TG}]}{dt} = -k_1[\text{TG}] + k_2[\text{DG}][\text{E}] \quad (18.1)$$

$$\frac{d[\text{DG}]}{dt} = -k_3[\text{DG}][\text{A}] + k_4[\text{MG}][\text{E}] + k_1[\text{TG}][\text{A}] - k_2[\text{DG}][\text{E}]; \quad (18.2)$$

$$\frac{d[\text{MG}]}{dt} = -k_5[\text{GL}][\text{E}] + k_6[\text{GL}][\text{E}] + k_3[\text{DG}][\text{A}] - k_4[\text{MG}][\text{E}]; \quad (18.3)$$

$$\frac{d[\text{GL}]}{dt} = k_5[\text{MG}][\text{A}] - k_6[\text{GL}][\text{E}]; \quad (18.4)$$

$$\begin{aligned} \frac{d[\text{E}]}{dt} = & k_1[\text{TG}][\text{A}] - k_2[\text{DG}][\text{E}] + k_3[\text{DG}][\text{A}] - k_4[\text{MG}][\text{E}] \\ & + k_5[\text{MG}][\text{A}] - k_6[\text{GL}][\text{E}]; \end{aligned} \quad (18.5)$$

$$\frac{d[A]}{dt} = -k_1[TG][A] - k_2[DG][E] + k_3[DG][A] - k_4[MG][E] + k_5[MG][A] - k_6[GL][E]; \quad (18.6)$$

$$\frac{d[A]}{dt} = -\frac{d[E]}{dt}, \quad (18.7)$$

where the expressions in brackets indicate the molar concentrations of the following components:

[TG] – triglycerides,
 [DG] – diglycerides,
 [MG] – monoglycerides,
 [GL] – glycerol,
 [A] – alcohol,
 [E] – methyl ether,

$k_1, k_2, k_3, k_4, k_5, k_6$ – reaction constants in the directions indicated in Figure 18.1.

To solve this model system of differential equations, a numerical method using the Microsoft Excel software was used. The values of the reaction constants are taken from the literature (Hawrot-Paw, Wijatkowski, & Mikiciuk 2015) and are given in Table 18.1.

At a fixed temperature, the reaction is possible if the interacting molecules have a certain amount of excess energy. Arrhenius called this excess energy the activation energy, and the molecules activated themselves. By Arrhenius, the constant of the reaction rate k and the activation energy E_a are related by the Arrhenius equation (Mohammadshirazi et al. 2014, Polishchuk et al. 2018, Polishchuk et al. 2019):

$$k = A \cdot e^{-E_a/RT}, \quad (18.8)$$

where,

E_a – value of the activation energy,
 A – pre-exponential coefficient,
 R – universal gas constant (8.31 J/mol·K),
 T – absolute temperature, K.

Thus, at constant temperature, the reaction rate determines the level of activation energy E_a . The more E_a , the lower the number of active molecules and the slower the reaction proceeds. With decreasing E_a , the velocity increases, and at $E_a = 0$, the reaction proceeds instantaneously.

Table 18.1 Concentrations of reactions at a temperature of 50°C (mol% min)⁻¹ for animal fat

Constants	k_1	k_2	k_3	k_4	k_5	k_6
Size	0.05	0.11	0.215	1.228	0.242	0.007

Table 18.2 Activation energy, calcium (mole·K)⁻¹

Activation energy	E_1	E_2	E_3	E_4	E_5	E_6
Size	13,145	9,932	19,860	14,639	6,421	9,588

The quantity E_a characterizes the nature of the reactants and is determined experimentally with the dependence $k=f(T)$. By writing equation (18.8) in logarithmic form (18.9) and solving it for constants at two temperatures (18.10), we find E_a (Hawrot-Paw, Wijatkowski, & Mikiciuk 2015).

$$\ln \frac{k_1}{k_2} = \frac{(T_2 - T_1)}{RT_2 \cdot T_1} E_a \quad (18.9)$$

$$E_a = \frac{RT_1 T_2 \ln \left(\frac{k_{T_2}}{k_{T_1}} \right)}{T_1 - T_2} \quad (18.10)$$

The results of the calculations of the activation energy in the reactions corresponding to the constants (see Table 18.1) are given in Table 18.2.

The output system of differential equations (18.1–18.7) can be transformed into the following system of discrete equations:

$$\frac{TG^{P+1} - TG^P}{\Delta t} = -k_1 TG^P A^P + k_2 DG^P E^P; \quad (18.11)$$

$$\frac{DG^{P+1} - DG^P}{\Delta t} = k_1 TG^P A^P - k_2 DG^P E^P - k_3 DG^P A^P + k_4 MG^P E^P; \quad (18.12)$$

$$\frac{MG^{P+1} - MG^P}{\Delta t} = k_3 DG^P A^P - k_4 MG^P E^P - k_5 MG^P A^P + k_6 GL^P E^P; \quad (18.13)$$

$$\frac{GL^{P+1} - GL^P}{\Delta t} = k_5 MG^P A^P + k_6 GL^P E^P; \quad (18.14)$$

$$\begin{aligned} \frac{E^{P+1} - E^P}{\Delta t} = & -k_1 TG^P A^P - k_2 DG^P E^P + k_3 DG^P A^P - k_4 MG^P E^P \\ & + k_5 MG^P A^P - k_6 GL^P E^P; \end{aligned} \quad (18.15)$$

$$\begin{aligned} \frac{A^{P+1} - A^P}{\Delta t} = & -k_1 TG^P A^P + k_2 DG^P E^P - k_3 DG^P A^P + k_4 MG^P E^P \\ & - k_5 MG^P A^P + k_6 GL^P E^P, \end{aligned} \quad (18.16)$$

where

- p – the interval (dimensionless),
- E – the concentration of methyl ether, mole,
- Δt – step by time, seconds.

The current time t is determined by the formula:

$$t = p \cdot \Delta t; \quad (18.17)$$

The system of discrete equations (18.11–18.16) can be rewritten as follows:

$$TG^{P+1} = (1 - k_1 \Delta t A^P) TG^P + k_2 \Delta t DG^P E^P; \quad (18.18)$$

$$DG^{P+1} = (1 - k_2 \Delta t E^P - k_3 \Delta t A^P) DG^P + k_1 \Delta t TG^P A^P + k_4 \Delta t MG^P E^P; \quad (18.19)$$

$$MG^{P+1} = (1 - k_4 \Delta t E^P - k_3 \Delta t A^P) MG^P + k_1 \Delta t DG^P A^P + k_6 \Delta t GL^P E^P; \quad (18.20)$$

$$GL^{P+1} = (1 - k_6 \Delta t E^P) GL^P + k_5 \Delta t MG^P A^P; \quad (18.21)$$

$$E^{P+1} = (1 - k_2 \Delta t DG^P - k_4 \Delta t MG^P - k_6 \Delta t GL^P) E^P + (k_1 \Delta t TG^P + k_3 \Delta t DG^P + k_5 \Delta t ML^P) A^P; \quad (18.22)$$

$$A^{P+1} = (1 - k_1 \Delta t TG^P - k_3 \Delta t DG^P - k_5 \Delta t ML^P) A^P + (k_2 \Delta t DG^P + k_4 \Delta t MG^P + k_6 \Delta t GL^P) E^P; \quad (18.23)$$

This system of discrete equations has a solution provided that all the coefficients of the equations are equal to or less than one.

18.4 RESEARCH RESULTS

In order to calculate the developed model, the initial concentration of the reacting mixture in the ratio of 6 moles of methanol per mole of triglycerides was taken. The results of the calculations performed using the Microsoft Excel spreadsheet show (Table 18.3) that the reaction is fast during the first 2,500 seconds (0.69 hours), and then the rate of biofuel production is significantly slowed down, which correlates with the data of work (Mushtruk et al. 2017, Kozlov et al. 2019).

Figure 18.2a and b shows the effect of temperature on the yield of methyl ether. Obviously, an increase in temperature above 60°C practically does not affect the output of biodiesel.

The experimental studies on the degree of transformation of animal fats into biodiesel in time and their comparison with the data obtained theoretically using the mathematical model allowed confirming that the theoretical results fall into the confidence interval with the probability of 0.95 (Ogorodnikov, Zyska, & Sundetov 2018).

The analysis of the discrete system of equations generated by equations 18.18–18.23 enables to predict (see Figure 18.2a and b) an increase in the yield of

Table 18.3 Change in the concentration of components in the transesterification reaction over time at a temperature of 65°C

Reaction time, seconds	Components of the reacting mixture				
	Triglycerides	Diglycerides	Mono-glycerides	Glycerol	Methyl ether
0.000	1.000	0.000	0.000	0.000	0.000
50.000	0.784	0.136	0.054	0.025	0.321
100.000	0.629	0.175	0.088	0.108	0.675
150.000	0.519	0.190	0.089	0.201	0.972
200.000	0.440	0.194	0.081	0.284	1.209
250.000	0.383	0.191	0.072	0.354	1.397
300.000	0.340	0.184	0.064	0.413	1.549
350.000	0.307	0.174	0.057	0.462	1.673
400.000	0.282	0.165	0.051	0.503	1.775
450.000	0.261	0.155	0.046	0.538	1.861
500.000	0.244	0.146	0.042	0.568	1.934
550.000	0.230	0.138	0.038	0.594	1.997
600.000	0.218	0.131	0.035	0.617	2.051
800.000	0.182	0.109	0.028	0.681	2.208
1,000.000	0.160	0.095	0.024	0.721	2.306
1,500.000	0.131	0.079	0.019	0.771	2.431
2,000.000	0.119	0.073	0.018	0.790	2.480
2,500.000	0.082	0.065	0.024	0.827	2.597
3,000.000	0.082	0.065	0.024	0.827	2.597
3,600.000	0.082	0.065	0.024	0.827	2.597

methyl ester from 2.56 to 2.58 mol (from 86.7% to 87.4%) with an increase in the reaction temperature from 55°C to 60°C. The time to achieve equilibrium in the reaction (1,200...2,000 seconds) is also significant, as it greatly influences the choice of structural parameters for the reactor for the production of methyl esters. With an increase in temperature to 70°C (Figure 18.2c), there is a decrease in the yield of methyl ether to 2.51 mol (up to 85%).

Figure 18.2a and b shows the effect of temperature on the yield of methyl ether. Obviously, an increase in temperature above 60°C practically does not affect the output of biodiesel.

The experimental studies on the degree of transformation of animal fats into biodiesel in time and their comparison with the data obtained theoretically using the mathematical model allowed confirming that the theoretical results fall into the confidence interval with the probability of 0.95 (Ogorodnikov, Zyska, & Sundetov 2018).

The analysis of the discrete system of equations generated by equations 18.18–18.23 enables to predict (see Figure 18.2a and b) an increase in the yield of methyl ester from 2.56 to 2.58 mol (from 86.7% to 87.4%) with an increase in the reaction temperature from 55°C to 60°C. The time to achieve equilibrium in the reaction (1,200...2,000 seconds) is also significant, as it greatly influences the choice of structural parameters for the reactor for the production of methyl esters. With an increase in temperature to 70°C (Figure 18.2c), there is a decrease in the yield of methyl ether to 2.51 mol (up to 85%).

After finding the most favorable conditions for the process, the most rational ones that will be used for designing the equipment will be selected.

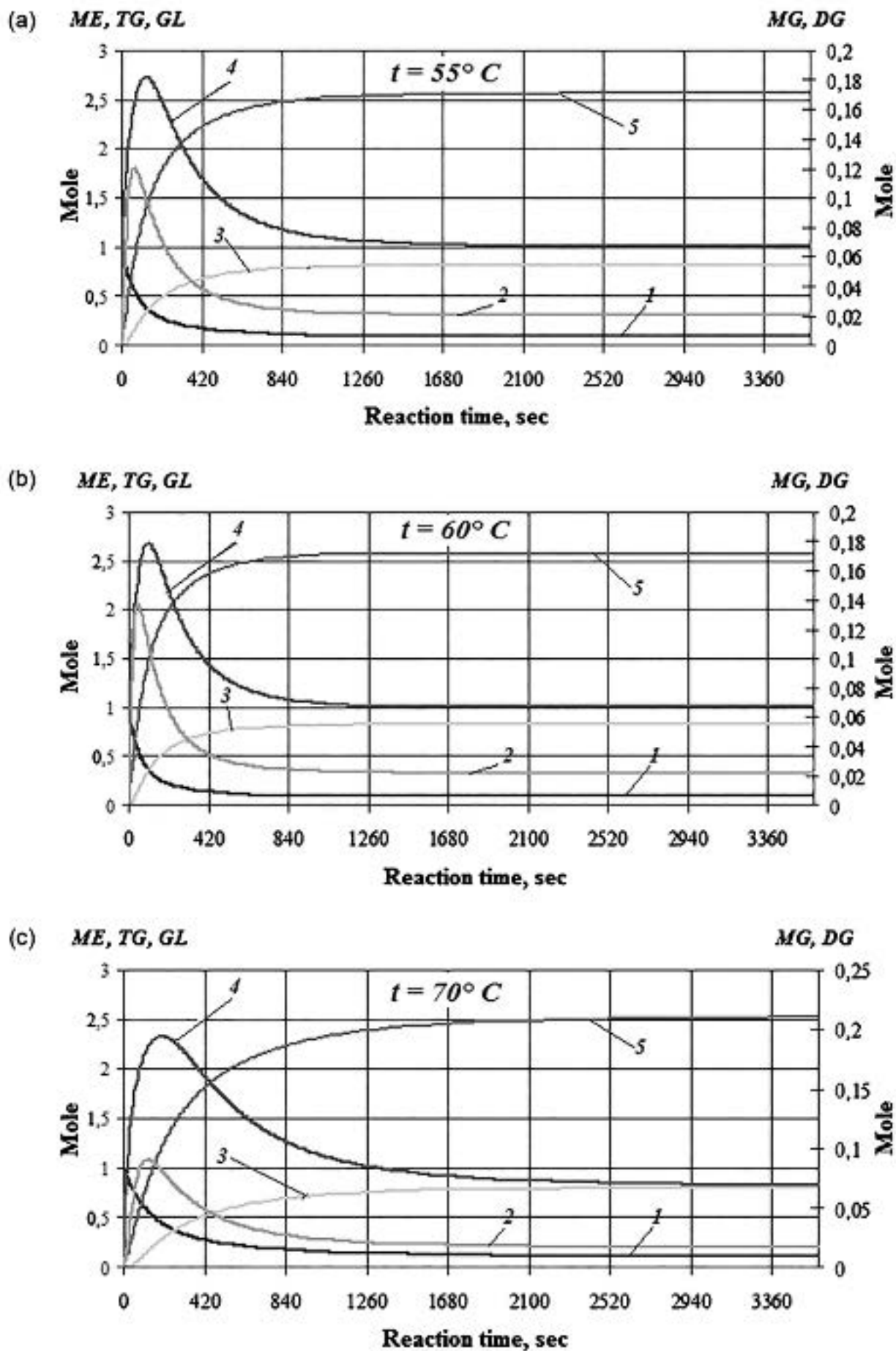


Figure 18.2 (a–c) Effect of temperature on the yield of methyl ether: 1 – triglycerides, 2 – monoglycerides, 3 – glycerol, 4 – diglycerides, and 5 – methyl ether.

Table 18.4 Properties of substances loaded into the reactor

Substance	Moles	Weight, kg	Density, kg/l	Volume, l	Concentration, mol/l
TG	3,545.2	3,604.2	0.96	3,441.9	0.2045
ME	482,163	1,544.9	0.79	1,955.5	2.7811
B	139,576	5,088.9	1.16	4,886.9	8.05
H ₂ SO ₄	85,089.6	6,646.2	0.88	7,552.5	4.908
Σ	276,428	16,584		17,336	

Table 18.5 Output of the main components of the reaction after 4 hours

Substance	TG	MT	B	ME	DG	MG	GL
Initial concentration (mol/l)	0.21	2.78	8.1	0	0	0	0
Final concentration (mol/l)	0.11	2.53	8.1	0.26	0.01	0.01	0.1

After modeling the equations of the molar balance, we turn to their solution using the Matlab software package (the algorithm of the solution presented in Nielsen et al. (2016)). As the initial conditions for the solution of equations, we take the balance of masses. Table 18.4 shows the number of moles, mass, density, and volume in which each of the substances is loaded into the reactor and their initial concentrations. Table 18.5 shows comparison of the main components of the reaction after 4 hours with their initial concentration.

Having analyzed Figure 18.3, it can be concluded that all components of the reaction stabilize after 30 minutes. The transformation of TG reaches 45.52%, indicating that these are not the best conditions for the reactor to work. Such indicators do not meet the technical task, under which the conversion of triglycerides should be equal to 77%.

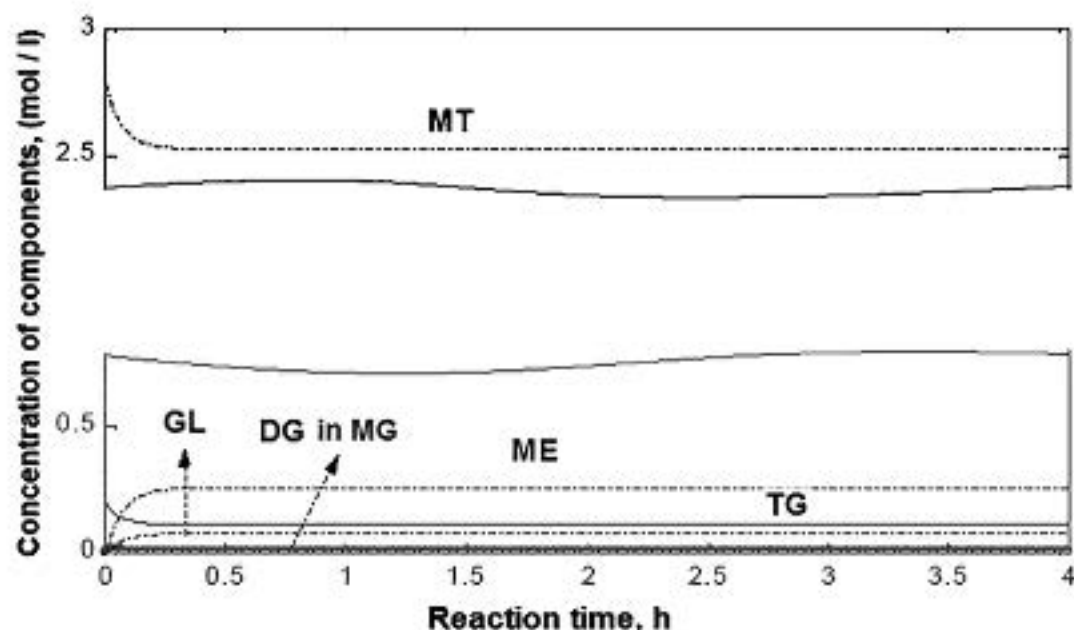


Figure 18.3 Output of the main components of the esterification reaction after 4 hours of process.

Since the conditions we have adopted from the literary sources do not meet our industrial production requirements, we analyze the various concentrations of triglycerides, alcohol, and acids, while analyzing the kinetics of reactions and the variations of transformations for animal fats into biodiesel.

18.4.1 Change in TG Concentration

In order to better analyze the change in the concentration of TG and ME, we neglect the change in the concentration of alcohol, and the reaction time will be reduced to 2 hours: $[TG]/2 = 0.10225$ (Figures 18.4 and 18.5).

As can be seen from the graphs, the transformation of triglycerides increases with low concentrations and higher.

18.4.2 Change in the concentration of methanol [ME]: $[ME]/2 = 1.3905$

Having analyzed the graphs in Figures 18.6 and 18.7, it can be concluded that the ether output is proportional to the concentration of methanol, and it increases along with concentrations and vice versa.

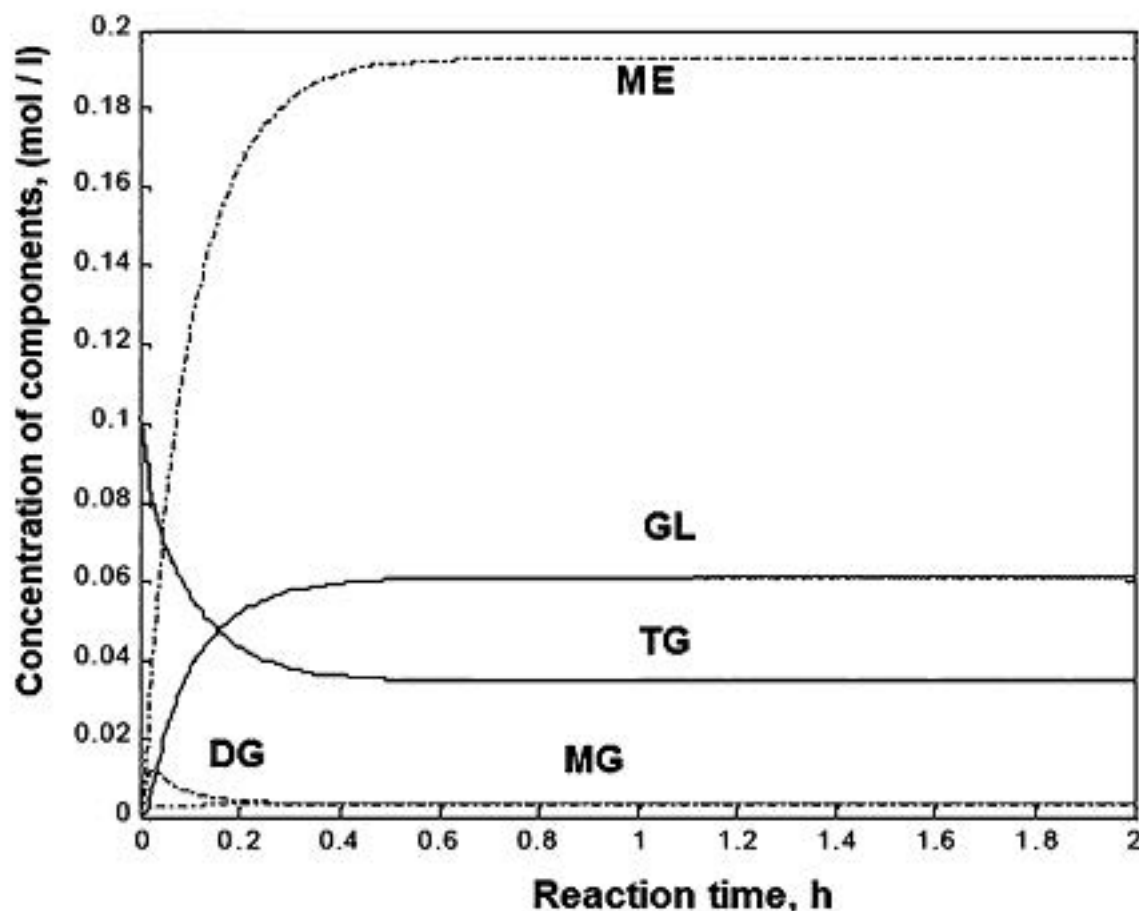


Figure 18.4 Output of the main components of the reaction after 2 hours of the process of changing the concentration of triglycerides: $X = 66.42\%$, $[TG] = 0.03433$, $[ME] = 0.1931$, $[TG] \cdot 2 = 0.409$, where: X – the output of biodiesel.

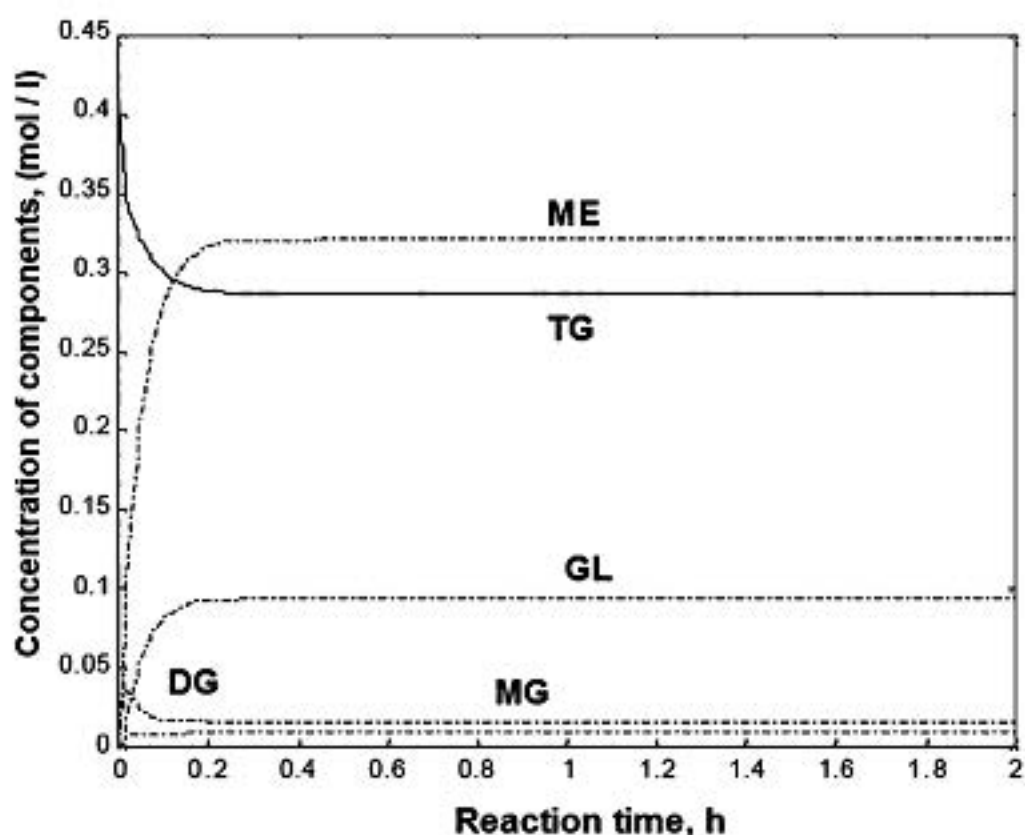


Figure 18.5 Output of the main components of the reaction after 2 hours of the process of changing the concentration of triglycerides: $X = 29.7\%$, $[TG] = 0.2875$, $[ME] = 0.3213$, where: X – the output of biodiesel.

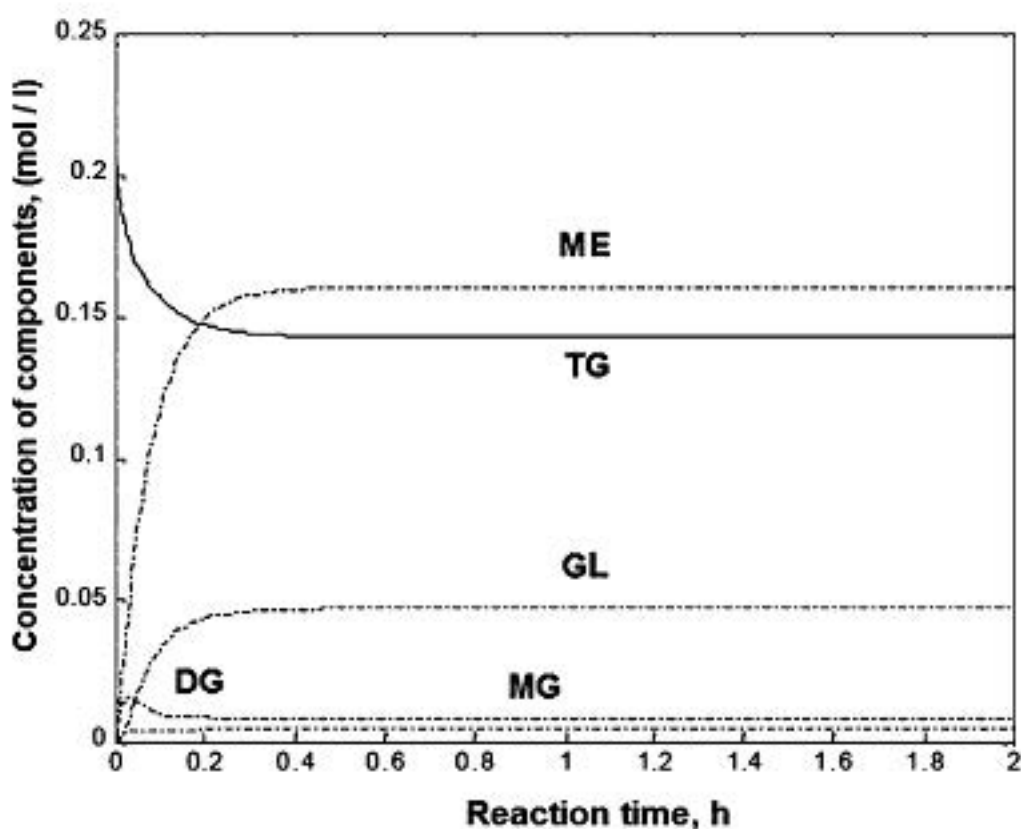


Figure 18.6 Exit of the main components of the reaction after 2 hours of the process of changing the concentration of methanol.

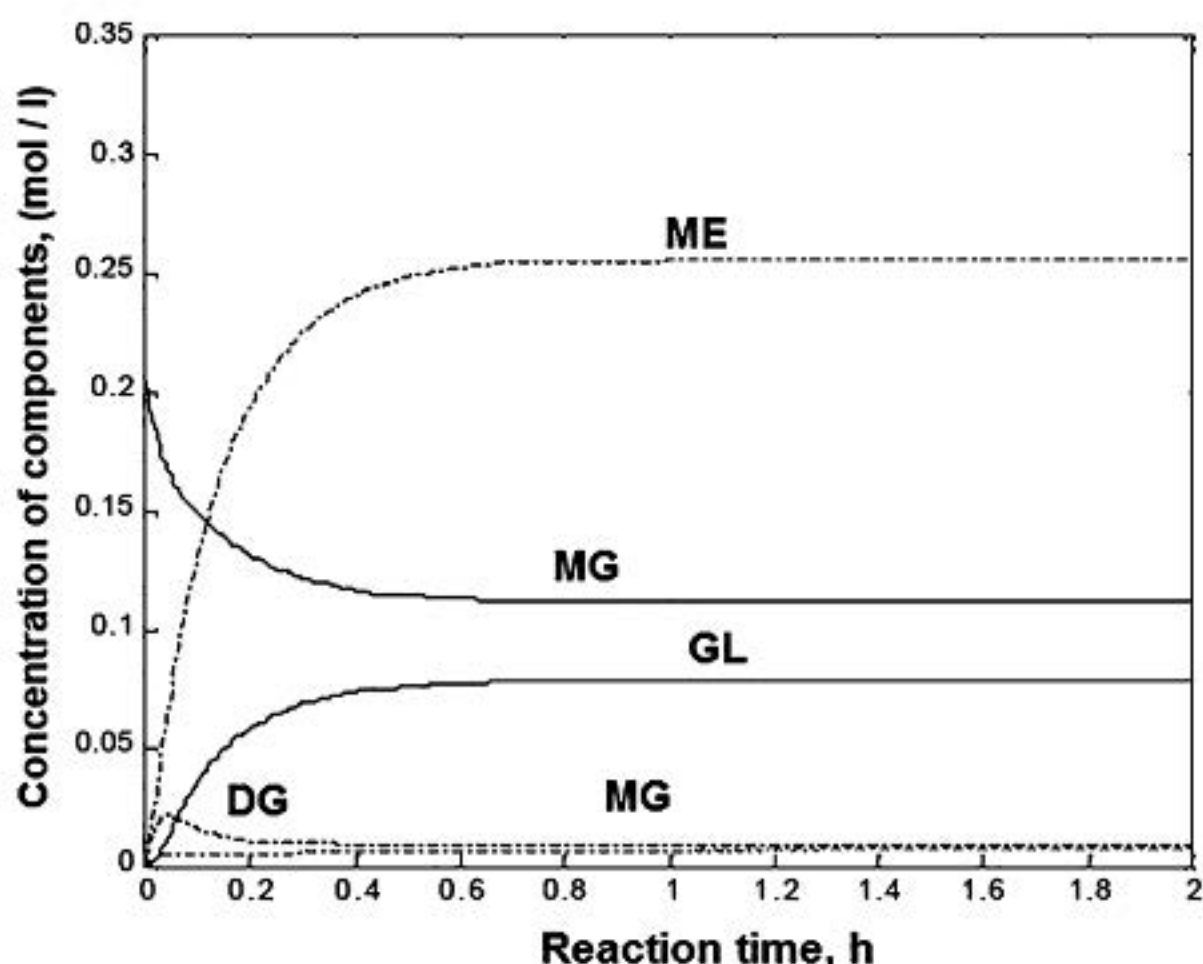


Figure 18.7 Output of the main components of the reaction after 2 hours of the process of changing the concentration of methanol: $X = 66.42\%$, $[TG] = 0.06866$, $[ME] = 0.3862$, where: X – the output of biodiesel.

18.4.3 Change in Catalyst Concentration $[H_2SO_4]$: $[H_2SO_4]/2 = 4.025$

If the catalyst concentration changes, the reaction rate does not; in some cases, it is possible to use a higher concentration of the catalyst, but one should not forget that an increase in its concentrations may lead to a decrease in the yield of biodiesel (Figures 18.8 and 18.9). How will the reaction occur when the catalyst concentration is reduced to one-tenth of percentage as shown in Figure 18.10.

If the catalyst concentration changes, the reaction rate does not; in some cases, it is possible to use a higher concentration of the catalyst, but one should not forget that an increase in its concentrations may lead to a decrease in the yield of biodiesel. How will the reaction occur when the catalyst concentration is reduced to one-tenth of percentage as shown in Figure 18.10.

After analyzing the graphs, it can be seen that a significant decrease in the level of components of the reaction leads to an increase in the time they are in the reactor. It can be concluded that the reaction is better at low concentrations of the catalyst and high concentrations of triglycerides and methanol, but the concentration of the catalyst affects the residence time of the mixture in the reactor. In order to have a better idea of the change in the concentrations of the main components of the reaction, the curves of methanol and rice acid concentrations were excluded.

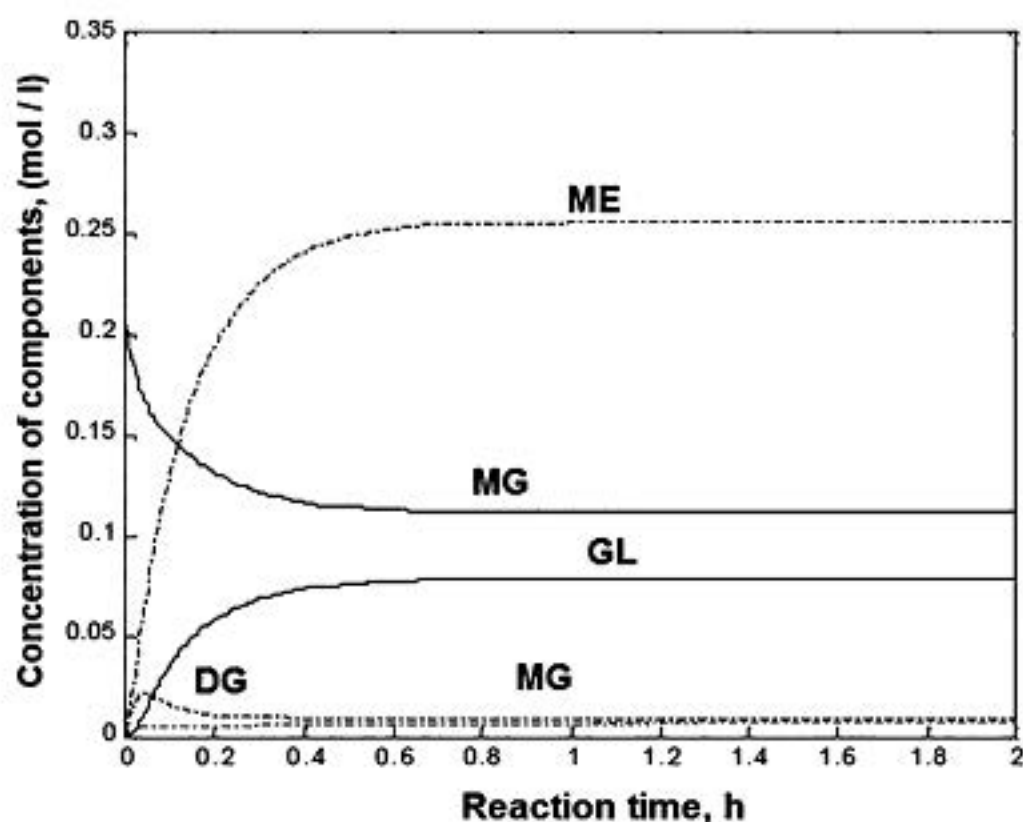


Figure 18.8 Output of the main components of the reaction after 2 hours of process with the change in catalyst concentration: $X = 45.52\%$, $[TG] = 0.1114$, $[ME] = 0.2562$, $[H_2SO_4] \cdot 2 = 16.1$, where: X – the output of biodiesel.

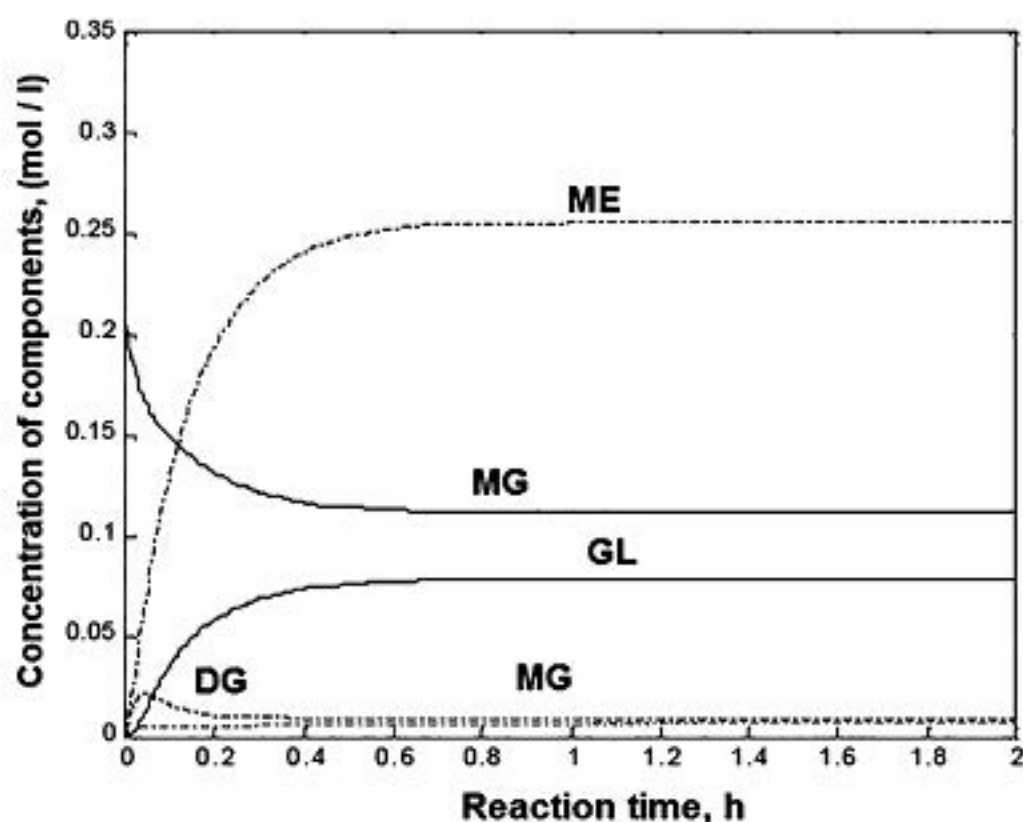


Figure 18.9 Output of the main components of the reaction after 2 hours of the process of changing the catalyst concentration: $X = 45.52\%$, $[TG] = 0.1114$, $[ME] = 0.2562$, where X – the output of biodiesel $[H_2SO_4]/10 = 0.805$.

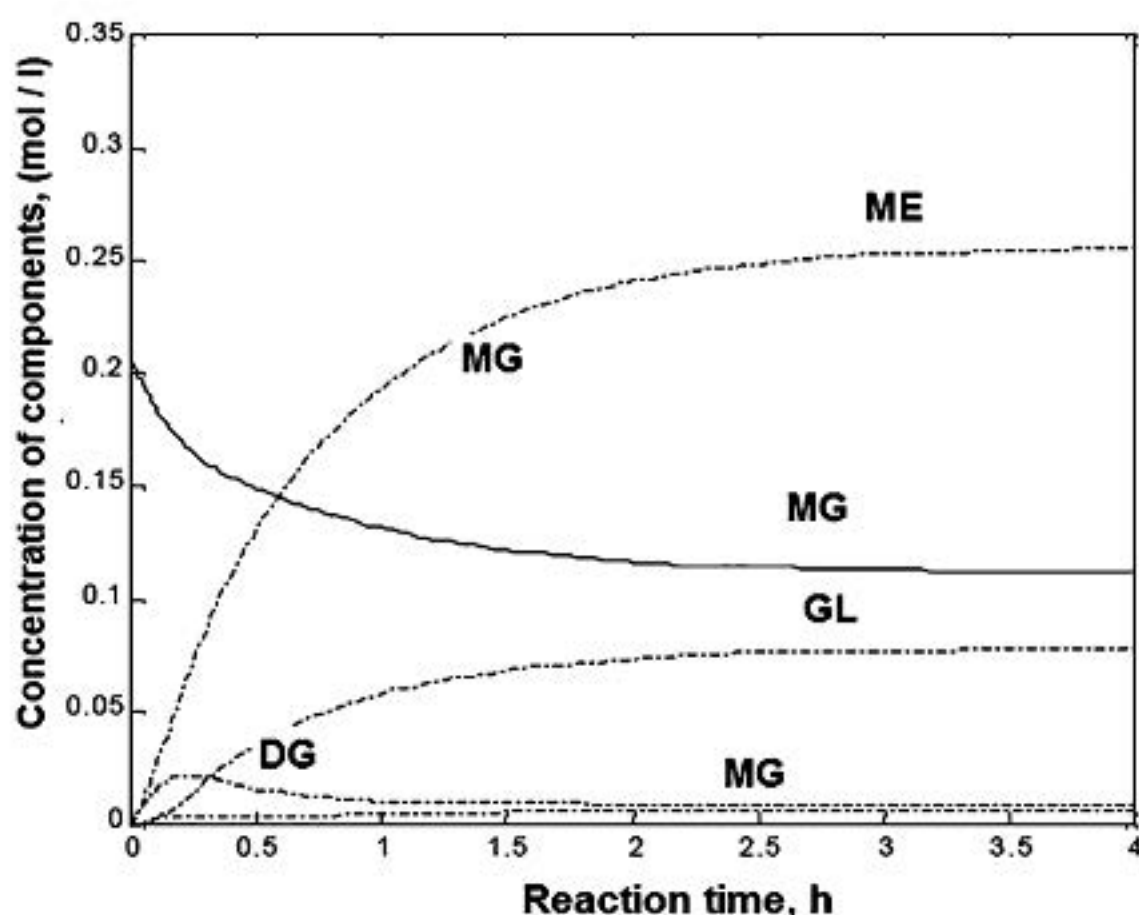


Figure 18.10 Output of the main components of the reaction after 2 hours of process of changing the catalyst concentration: $X = 45.37\%$, $[TG] = 0.1117$, $[ME] = 0.2554$, where: X – the output of biodiesel.

Apparently (Figure 18.11), the concentration of methyl ester is rapidly increasing, because it has a higher rate of conversion, the concentration of triglycerides is reduced, but not as fast as diglycerides, the rate of conversion of which increases, and then decreases when converted to monoglycerides and methyl ether. The concentration of monoglycerides increases until the equilibrium of the reaction is achieved. The rate of their conversion is higher than diglycerides conversion rate.

18.5 CONCLUSIONS

1. The developed mathematical model of the reaction of transformation of fats into biodiesel allows using the Microsoft Excel spreadsheet editor with sufficient accuracy to calculate the basic parameters of the reaction of re-esterification.
2. The reaction rate and the completeness of the conversion of components into biodiesel primarily depend on the temperature and composition of the reactant mixture.
3. Increasing the temperature to 65°C accelerates the reaction of transesterification triglycerides, and increases the yield of biofuels, but more than heating reagents to a temperature higher than the boiling point of alcohol (for methanol $\sim 65^{\circ}\text{C}$ at atmospheric pressure) causes a decrease in the yield of methyl ether.
4. Graphical dependences of the output of the main components of the reaction are constructed when the concentrations of triglycerides, diglycerides, monoglycerides, methanol, catalyst, etc. are changed components of the reaction.

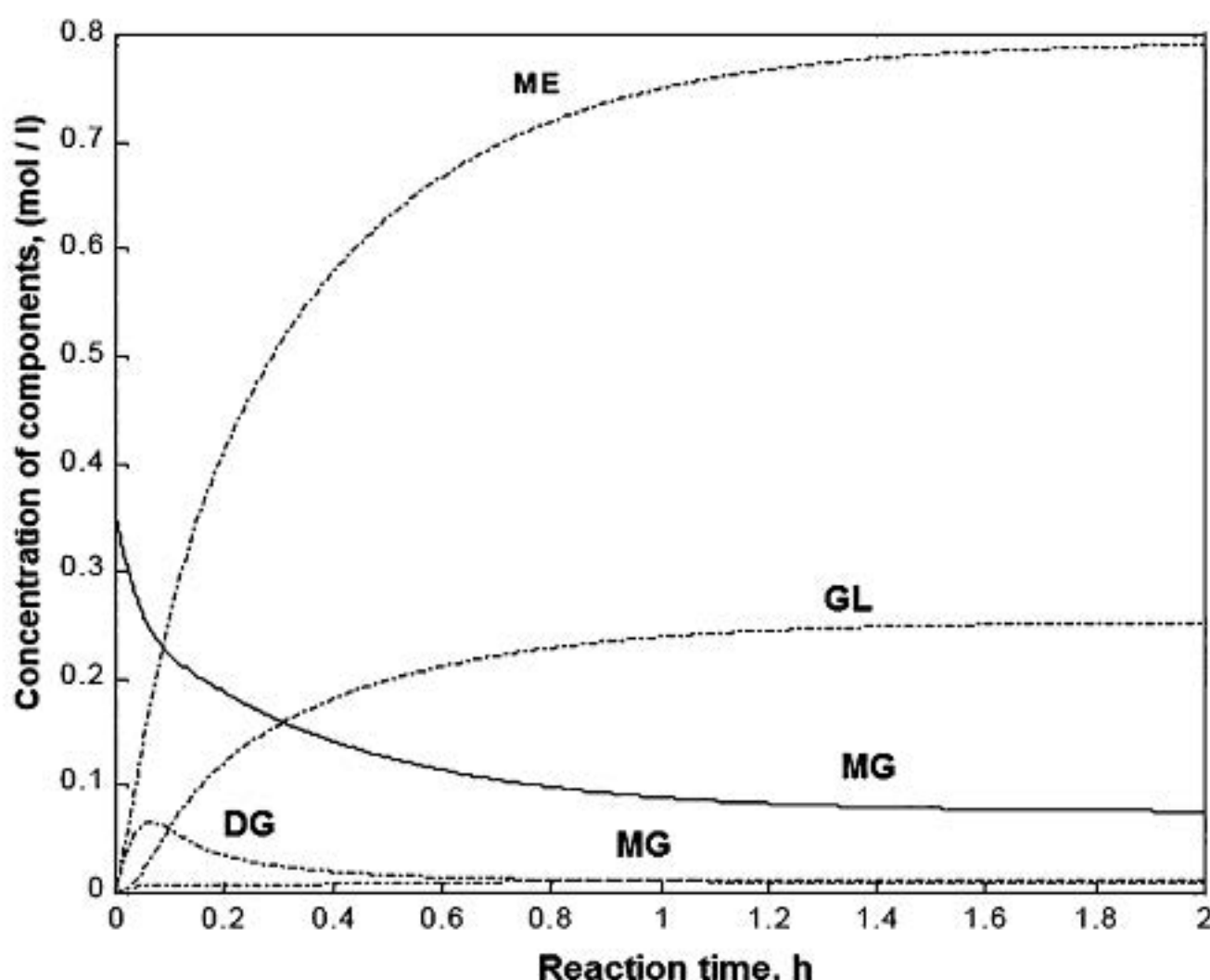


Figure 18.11 Exit of the main components of the reaction after 2 hours of process.

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