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**TAȘCA CORINA**


# STUDY OF REDOX PROCESSES IN THE ANAEROBIC FERMENTATION OF BIOMASS IN THE PRESENCE OF ANTIOXIDANTS

**145.01 - ECOLOGICAL CHEMISTRY**

**Summary of the Doctoral Thesis in Chemical Sciences**


**CHISINAU, 2025**

The research underlying this thesis was conducted at the Institute of Chemistry of Moldova State University and at the Center of Oenology of the Technical University of Moldova. The industrial-scale implementation of the anaerobic fermentation process was carried out at Garma Grup LLC.

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The public defense will take place on **30.10.2025** at **14:00 PM** within the meeting of the Doctoral Committee of the Doctoral School of Natural Sciences, Moldova State University. Venue: Moldova State University, 65A M. Kogălniceanu St., **Block 3, Room 332**, MD-2009, Chişinău, Republic of Moldova.

The doctoral dissertation and the summary may be consulted at the National Library of the Republic of Moldova, the Central Library of Moldova State University (MD-2009, Chişinău, 60 Alexei Mateevici St.), and on the official website of ANACEC (http://www.anacec.md) and on the USM website (http://www.usm.md).

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## Conceptual framework of the research

The agro-industrial sector is a key component of the global economy, providing essential resources for food security and socio-economic development. At the same time, it generates substantial amounts of organic by-products—plant residues, secondary processing products, and residual chemicals—whose improper management can harm soil, water, and air quality, disrupting natural ecosystems. By-products from grape and wine production, as well as stillage from the alcoholic beverage industry, offer significant potential for biochemical valorization due to their high content of fermentable compounds. Globally, these by-products contribute 8–10% of greenhouse gas emissions, emphasizing the need for sustainable technological solutions. In the Republic of Moldova, the prominent role of the agri-food sector and the rapid growth of the food and beverage industry over the past decade have intensified the pressure on by-product valorization systems.

Ecological chemistry offers modern solutions for the conversion of organic by-products into valuable resources through aerobic and anaerobic fermentation, resulting in the production of biogas, natural fertilizers, and bioactive compounds. This approach mitigates environmental impact and supports the circular bioeconomy. Anaerobic fermentation enables energetic valorization of biomass, while aerobic fermentation generates value-added products such as enzymes, organic acids, and secondary metabolites. Both processes depend on substrate composition, microbial balance, and intermediate accumulation. The use of bioactive substances (BAS) with redox and antioxidant properties acts as natural phytocatalysts, accelerating rate-limiting stages, enhancing methane production, reducing inhibitory compounds, and improving biosynthetic yields.

The correlation between theoretical reactivity and kinetic behavior is established through molecular simulations based on frontier orbital descriptors (HOMO, LUMO, $\Delta E$) and the distribution of electrostatic potential. The conceptual framework of the research integrates sustainable biomass conversion, the use of natural phytocatalysts, and the principles of the circular economy. The central objective is the development of advanced fermentation technologies—both aerobic and anaerobic—that are efficient, environmentally compatible, and applicable within the Republic of Moldova as well as in other similar agro-industrial regions. The research is positioned at the intersection of ecological chemistry, biotechnology, and renewable energy, providing innovative solutions for the valorization of agro-industrial by-products and supporting the transition toward a green economy.

**Aim of the research.** The aim of the thesis is to optimize the valorization processes of biomass derived from winemaking and the alcoholic beverage industry through the application of redox phytocatalysts for the acceleration of fermentation.

**Objectives of the research.** To achieve this aim, the research pursued the following objectives:

- characterization of secondary products relevant to aerobic and anaerobic fermentation;
- selection and analysis of BAS with redox functionalities involved in these processes;
- evaluation of the influence of BAS on the kinetics of stillage and grape marc fermentation;
- comparative analysis of aerobic and anaerobic fermentation in the presence of BAS;
- computational modeling of the fermentation mechanism based on HOMO, LUMO, ΔE descriptors and electrostatic potential distribution;
- determination of the relationship between BAS concentration and the anaerobic fermentation capacity of grape marc;
- kinetic modeling of anaerobic fermentation in the presence of bioactive additives;
- industrial-scale testing of the controlled application of BAS, with analysis of the impact on the quantity and quality of the produced biogas.

**Applied Value.** The novelty of the research lies in the application of phytocatalysts to accelerate the conversion of biomass into useful products while minimizing environmental impact, the kinetic analysis of aerobic and anaerobic fermentation of winemaking by-products and stillage from the alcoholic beverage industry, and the investigation of the mechanism and reactivity descriptors of the anaerobic fermentation process in the presence of BAS. The applied contribution consists in the validation of the obtained results through the controlled implementation of BAS (dihydroxyfumaric acid) in anaerobic fermentation processes at industrial scale, including the evaluation of its effects on biogas quality. The proposed solutions contribute to the development of a sustainable system for the management of winemaking by-products and stillage from the alcoholic beverage industry.

**Implementation of scientific results.** The results were experimentally validated in an industrial anaerobic fermentation facility in the Republic of Moldova by comparing a digester treated with BAS and a control batch. The analyzed parameters (biogas volume and composition, fermentation efficiency) demonstrated the advantages of introducing BAS into the process.

**Scientific impact and dissemination of results.** The results of the research were presented and discussed at national and international scientific forums, confirming the scientific and practical relevance of the thesis. They were disseminated within the Technical-Scientific Conferences of

Students, Master's Students, and Doctoral Students organized by the Technical University of Moldova in 2022 and 2023, as well as at prestigious scientific events, including: the International Conference *"Intelligent Valorisation of Agro-Food Industrial Wastes"* (2021, Technical University of Moldova), the 7th International Conference *"Ecological and Environmental Chemistry"* (2022, Moldova State University), the 5th International Conference *"Modern Technologies in the Food Industry"* (2022, Technical University of Moldova), the International Conference *"Smart Life Sciences and Technology for Sustainable Development"* (2023, Technical University of Moldova), and the International Conference *"Geo- and Bioecological Problems of the Middle and Lower Dniester River Basin"* (2024, Eco-TIRAS, Tiraspol).

Additionally, the scientific contributions were presented at national conferences with international participation, such as: *"Prospects and Problems of Integration into the European Research and Education Area"* (2021, "Bogdan Petriceicu Hasdeu" State University of Cahul), *"Innovation: A Driver of Socio-Economic Development"* (2021, B. P. Hasdeu State University of Cahul), *"Life Sciences in the Dialogue of Generations: Connections between Universities, Academia and Business Community"* (2022, Moldova State University), and *"Natural Sciences in the Dialogue of Generations"* (2023, Moldova State University).

The obtained results were valorized through the publication of two chapters in collective monographs, one national and one international, as well as in three scientific articles published in peer-reviewed journals indexed in international databases, thereby confirming the academic relevance of the investigated topic. Two articles published in the *Journal of Engineering Science* (2022 and 2024) addressed the effect of bioactive additives on biomass fermentation and the characteristics of agro-industrial biomass in the context of the circular bioeconomy. Another paper, published in 2025 in the *Journal of Social Sciences* (indexed in DOAJ and Index Copernicus), emphasized the integrated valorization of waste from the alcohol industry through modern biotechnological methods and the use of bioactive substances for optimizing biomass conversion under sustainable conditions.

Furthermore, two contributions were included in collective volumes: one chapter published by the international publisher IGI Global (USA) in the volume *Redox Processes within Environmental and Technological Contexts* (2023), and one chapter in the monograph *Redox Processes with Electron and Proton Transfer*, published by MSU Press, Chișinău (2023). Both addressed fundamental aspects of redox processes in biological and technological systems in the presence of BAS.

# 1. CHARACTERISTICS OF BIOMASS DERIVED FROM AGRO-INDUSTRIAL PROCESSES AND VALORIZATION OPPORTUNITIES WITHIN THE CIRCULAR BIOECONOMY

In recent decades, the expansion of agro-food activities has generated increasing amounts of agricultural by-products, intensifying concerns regarding their environmental impact. Due to their durability, low costs, and accessibility, these by-products are increasingly valorized in technological and industrial applications (Guran, 2018). One of the main problems of the alcoholic beverage industry and the wine-making sector is the accumulation of by-products resulting from alcohol distillation and vinification processes, which has emphasized the importance of sustainable development and the circular bioeconomy based on the recycling and sustainable valorization of agro-industrial resources (Venkata Mohan et al., 2016).

## 1.1 Biomass from ethanol production and the wine industry: characteristics and utilization potential

The distillery industry is among the most polluting branches of the agro-industrial sector, generating liquid effluents with high organic load, acidic pH, elevated temperature, and increased salinity (Venkata Mohan et al., 2016). However, by-products resulting from distillation possess valuable potential for valorization, being important sources of polysaccharides, volatile fatty acids, polyphenols, and other bioactive compounds used in the pharmaceutical, cosmetic, and food industries. Current trends aim at optimizing the extraction of these constituents using modern methods, including advanced solvents, thus contributing to the implementation of a sustainable integrated valorization model while simultaneously reducing the by-products generated (Venkata Mohan et al., 2016).

Stillage, the main by-product obtained from the distillation of fermented mash, is produced in amounts of 10–15 liters for every liter of ethanol, in the absence of recycling systems (Venkata Mohan et al., 2016). Its chemical composition varies significantly depending on the raw material used, presenting high concentrations of organic nitrogen (BON), significant contents of dry matter and ash, as well as appreciable amounts of sugars, proteins, and vitamins (Chaudhary & Arora, 2011; Bookwalter et al., 1984; Bothast, 2005; Guran, 2018; Yu, 2024).

This complex composition explains the growing interest in the valorization of stillage not only as a raw material for biogas production via anaerobic fermentation but also as a source of bioactive compounds with high economic value. Therefore, stillage represents a relevant example of agro-industrial biomass whose efficient management can simultaneously contribute to reducing ecological impact and developing new value chains within the bioeconomy.

## 1.2 Chemical composition and bioactive properties of grape pomace

Grape pomace, a by-product resulting from pressing *Vitis vinifera L.* berries during vinification, consists of skins, seeds, pulp, and stems. Due to the incomplete extraction of bioactive compounds during fermentation, it remains a concentrated source of polyphenols with antioxidant, antimicrobial, and anti-inflammatory activity, characteristics that confer valorization potential in the food, pharmaceutical, and cosmetic industries (Apolinar-Valiente et al., 2015; Prozil et al., 2012).

The elemental composition of pomace highlights a high content of macroelements such as potassium and calcium, alongside essential microelements such as iron, manganese, copper, and zinc, while sodium and chlorine are present in low quantities (Gambier, 2014; Apolinar-Valiente et al., 2015). Pomace also contains significant amounts of amino acids, particularly glutamic acid and aspartic acid, as well as other essential amino acids (Baca-Bocanegra et al., 2021).

The chemical structure and bioactive properties of grape pomace are influenced by grape variety and pedoclimatic conditions (Rondeau et al., 2013). Identified polyphenols include gallic acid, catechin, epicatechin, hydroxytyrosol, tyrosol, cyanidin glycosides, as well as various phenolic and hydroxycinnamic acids (Lafka et al., 2007; Peixoto et al., 2018). Regarding flavonoids, polymeric flavan-3-ols predominate, condensed tannins derived from procyanidins and prodelphinidins, flavones in lower amounts, and glycosylated anthocyanidins responsible for pigmentation of red grapes (Muñoz et al., 2021; Amendola et al., 2010). Total anthocyanin content in *Vitis vinifera* varies between 500 and 5000 mg/kg, influenced by pH and glycosidic structure (Welch et al., 2008).

Studies have demonstrated that pomace extracts exhibit complex biological activity. Antioxidant properties are associated with polyphenols' ability to neutralize free radicals, while antimicrobial effects include inhibition of Gram-positive bacterial strains at concentrations of 850–1000 ppm and Gram-negative strains at 1250–1500 ppm (Jayaprakasha et al., 2001; 2003). Moreover, phenolic compounds in pomace can inhibit enzymes involved in essential bacterial processes, such as glucosyltransferases and F-ATPase, without compromising cellular viability (Mollica et al., 2021).

Therefore, grape pomace emerges as a high-value agro-industrial resource with potential applications in both the recovery of bioactive compounds and biotechnological processes aimed at producing value-added products, in accordance with circular bioeconomy principles.

### 1.3 Aerobic and anaerobic fermentation of agro-industrial biomass: process characteristics and optimization strategies

Fermentation is a complex biochemical process in which organic substrates are transformed under the action of microorganisms under aerobic or anaerobic conditions, depending on oxygen availability (Westergaard & Olsson, 2007). Under anaerobic conditions, main products include volatile fatty acids (VFAs), $CO_2$, $CH_4$, alcohol, and hydrogen, with substrates ranging from carbohydrates to proteins, organic acids, and lipids (Mazzoleni et al., 2015). In biology, the term "fermentation" is predominantly used for anaerobic processes, whereas in environmental engineering and biotechnology, "aerobic" and "anaerobic fermentation" denote microbial processes with or without oxygen, relevant for biomass conversion (Merico et al., 2007; Van Roermund et al., 2022).

Anaerobic digestion (AD) is a major bioconversion process that transforms complex organic matter into biogas and digestate in the absence of oxygen (Xie, 2016). It is widely used in agriculture and industry to valorize plant residues, agro-food by-products, and organic wastes (Deublein & Steinhauser, 2011; Ma et al., 2015). The process includes four stages—hydrolysis, acidogenesis, acetogenesis, and methanogenesis—catalyzed by distinct microbial consortia (Das & Mondal, 2016; Li et al., 2022). Hydrolysis breaks down polymers into monomers via extracellular enzymes; acidogenesis converts monomers into VFAs, alcohol, $CO_2$, and $H_2$; acetogenesis converts long-chain VFAs into acetate, $CO_2$, and $H_2$; methanogenesis, carried out by strictly anaerobic archaea, produces methane from hydrogen, acetate, or methylated compounds (Adekunle & Okolie, 2015; Brummeler, 1985).

Anaerobic digestion efficiency is influenced by pH, temperature, C/N ratio, mixing, absence of oxygen, nutrient supply, and the presence of inhibitors (Das, 2016; Hu et al., 2018). Using wine and alcohol industry by-products for biogas production has attracted significant interest (Ambreen et al., 2018). Enzymatic pretreatment can accelerate hydrolysis and increase methane production, but high costs of commercial enzymes limit applicability, which is why current research aims to produce them through genetic engineering (Ariunbaatar et al., 2014).

The separation of hydrogen and methane production stages in modern biogas plants is a promising strategy for process optimization, requiring detailed knowledge of metabolic pathways and the structure of microbial communities involved. Anaerobic digestion contributes significantly to the global carbon cycle and to the development of a circular bioeconomy through efficient utilization of organic biomass (Asam et al., 2011; Deublein & Steinhauser, 2008).

# 2. MATERIALS AND METHODS

## 2.1 Research materials and characterization of the substances used

In the experimental investigations, biologically active substances (BAS), post-alcohol cereal stillage, and red grape pomace were used, all playing an essential role in the aerobic and anaerobic fermentation processes analyzed in this study.

Powders and plant extracts of escin, tomatine, sclareol, vanillin, catechin, betulin, menthol, and dihydroxyfumaric acid (hereafter referred to as BAS) were obtained during research conducted at the Institute of Chemistry. These substances were selected due to their biological potential—antioxidant, antibacterial, anti-inflammatory, immunomodulatory—with an impact on the microbial biochemical processes involved in fermentation.

Cereal stillage, obtained from the alcoholic distillation process, was supplied by the enterprise “Garma Grup” S.R.L., Fîrlădeni village, Hîncești district, Republic of Moldova. Red grape pomace, derived from Merlot–Cabernet Sauvignon and Cabernet Sauvignon varieties, was collected in 2023 from the microvinification section of the Technical University of Moldova. It was used as a lignocellulosic substrate with high polyphenol content, exhibiting antioxidant and antimicrobial properties with potential applications in anaerobic fermentation and energy valorization of biomass.

## 2.2 Analytical methods

In the experimental investigations, analytical methods recognized internationally and validated through standards or scientific sources were applied for the comprehensive characterization of fermentable substrates and the BAS used. These methods aimed to determine nutrient content, antioxidant potential, and organic loads, as well as to monitor the stages of the fermentation process.

The sugar content was determined using the refractometric method, according to ISO 2173:2003, employing a digital refractometer with a Brix scale to estimate the total level of fermentable sugars in grape must or other reaction media. Amino nitrogen, an essential parameter for ensuring microorganism nutrition during fermentation, was determined using the o-phthaldialdehyde (OPA) colorimetric method. This method, initially described by Church (Church et al., 1983) and standardized through ASBC Wort-12, allows the quantification of readily assimilable nitrogen in the form of free amino acids in extracts and musts. pH determination was carried out using the potentiometric method, according to ISO 10523:2022, employing a pH meter calibrated daily. Total solids content (TSC) was estimated gravimetrically, according to EN 12880:2000, by evaporating the sample in an oven and calculating the residue.

To evaluate the antioxidant activity of phenolic extracts and BAS, the DPPH method proposed by Brand-Williams (Brand-Williams et al., 1995) and the hydrogen peroxide inhibition test (Ruch et al., 1989) were applied. Both tests provided important data regarding the antiradical capacity and redox protection of the studied compounds.

To assess the energy potential of the substrates, the chemical oxygen demand (COD) method, according to ISO 15705:2002, and the biochemical oxygen demand (BOD) method, according to ISO 5815-1:2019, were applied. These methods allow the determination of biodegradability by measuring the oxygen consumption required for the chemical and biological oxidation of organic matter, respectively.

The lignocellulosic composition of pomace and stillage was characterized using the Van Soest method, in the Mertens-modified version (2002), which allows quantification of cellulose, hemicellulose, and lignin content. The total phenolic profile was determined using the Folin–Ciocalteu method (Lamuela-Raventos, 2001), expressing content in gallic acid equivalents. For the identification and quantification of individual phenolic compounds, high-performance liquid chromatography (HPLC-DAD-MS-ESI) was used, according to the European protocol SANTE/11312/2021. This technique provided quantitative data regarding the presence of flavonoids, anthocyanins, and other phenolic compounds in the studied extracts.

Aerobic fermentation was monitored using the indirect volumetric method, capturing $CO_2$ in a 1 N NaOH solution and titrating with 0,1 N oxalic acid, according to authors (Birghilă et al. 2011). This parameter served as an indirect indicator of the intensity of the aerobic fermentation process. In the study of anaerobic fermentation, a batch regime was used (Buffière et al., 2006), monitoring biogas production and calculating the biological methane potential (BMP), expressed in mL $CH_4$/g VS, corrected with the negative control.

Data interpretation was performed using analysis of variance (ANOVA) and Dixon's Q test. Polynomial regression models were also applied to describe kinetic curves and estimate the efficiency of additives under different experimental conditions. To elucidate redox mechanisms, computational modeling based on density functional theory (DFT) was employed using Gaussian 09 software, to simulate electronic structure and electron transfer in the presence of free radicals and peroxide molecules.

# 3. STUDY OF REDOX FERMENTATION PROCESSES OF BIOMASS DERIVED FROM ETHANOL PRODUCTION

## 3.1 Determination of physicochemical indices of the biomass used and selection of biologically active substances for application in fermentation processes

In order to optimize the alcoholic and anaerobic fermentation process in the presence of biologically active substances (BAS), a comparative analysis of the chemical composition of two types of biomass, used as fermentable substrates, was conducted: cereal stillage and grape juice. This characterization allowed the assessment of the fermentative potential, as well as the initial redox and nutritional conditions of the medium.

**Table 3.1 Physicochemical indices of the study media***

| Indicator | Cereal stillage | Grape juice |
|---|---|---|
| Sugar content, g/L | 26,27 ± 0,91 | 124,4 ± 1,6 |
| pH | 3,91 ± 0,07 | 3,77 ± 0,12 |
| Titratable acidity, g/L $H_2SO_4$ | 3,42± 0,24 | 2,74±0,32 |
| Aminic nitrogen content, mg/L | 492,2± 3,6 | 140,8± 2,2 |

* *results obtained within the doctoral thesis*

The comparison of relevant indicators demonstrates that grape juice possesses a high energetic potential, expressed by a sugar concentration more than four times higher than that of cereal stillage, table 3.1. In contrast, cereal stillage exhibits a more pronounced acidity and a slightly more alkaline pH, both characteristics favorable for the progression of anaerobic fermentation. Additionally, cereal stillage is distinguished by a significantly higher content of aminic nitrogen, essential for microbial protein synthesis and cell mass growth during fermentation.

## 3.2 Evaluation of the antioxidant activity of biologically active substances

The antiradical capacity of the BAS was determined using the DPPH method, which is based on the reaction between the stable radical 1,1-diphenyl-2-picrylhydrazyl and hydrogen donors in the analyzed samples. The test was applied to eight selected compounds at two concentrations (50 mg/L and 300 mg/L) in order to highlight the dose–effect relationship in the inhibition of free radicals figure 3.1.

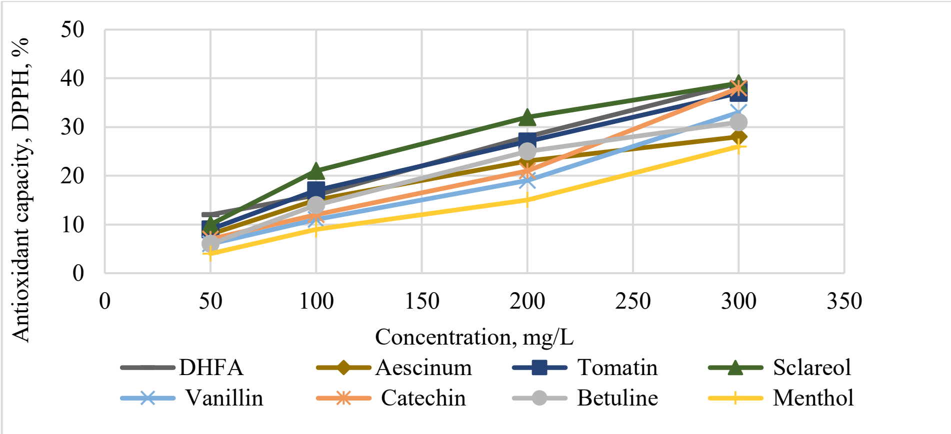



**Figure 3.1 Antioxidant capacity of BA compounds, % DPPH inhibition (**Duca et al., 2022)

The results obtained highlighted a differentiated antioxidant activity among the tested fractions, with the highest inhibition percentages observed for sclareol, DHFA, tomatine, and catechin. In contrast, menthol exhibited the lowest activity, requiring higher concentrations to reach the same level of inhibition (Duca et al., 2022). The DPPH inhibition values were proportional to the applied dose, confirming a direct relationship between concentration and antiradical efficiency.

### 3.3 Analysis of the impact of selected BA compounds on the aerobic fermentation kinetics of cereal distillery by-products

In this stage of the research, the influence of a set of BAS on the aerobic fermentation of cereal distillery by-products was investigated, aiming to optimize the intensity of the fermentation process. The cereal by-product used originated from the distillation of cereals carried out at "Garma Grup" Enterprise in the Republic of Moldova, representing a substrate with biotechnological potential. By monitoring the volume of carbon dioxide ($CO_2$) released during aerobic fermentation, changes in the intensity of the fermentation process under the influence of different BAS compounds applied in controlled doses were analyzed. The experimental approach aimed to identify BAS compounds capable of enhancing the conversion of organic matter through redox mechanisms, with direct implications on the overall efficiency of aerobic fermentation.

The effects of three BAS compounds – betulin, escin, and tomatine – on the aerobic fermentation of cereal distillery by-products were investigated by monitoring the volume of $CO_2$ emitted over 96 hours figure 3.2.

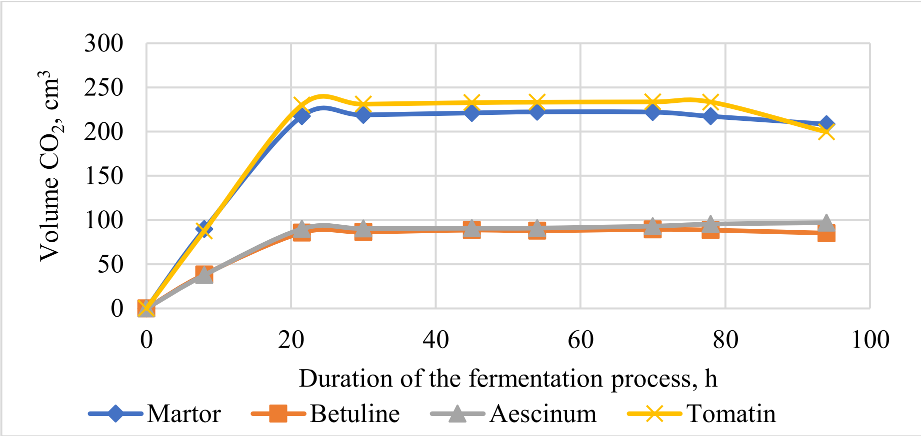
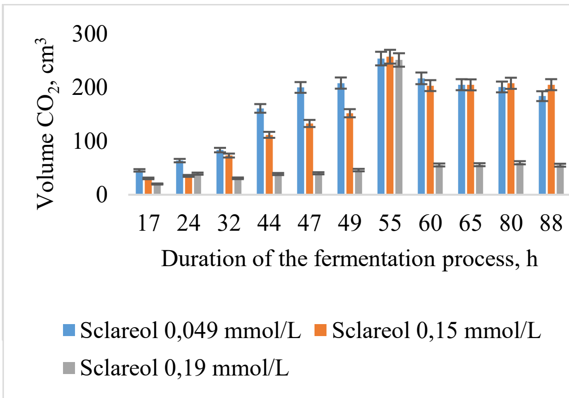



**Figure 3.2 Volume of gas ($CO_2$) released during aerobic fermentation of cereal stillage in the presence of BAS compounds** (Duca et al., 2023)

Tomatine (0,015 mmol/L) induced the most intense fermentation, producing a maximum $CO_2$ volume of 233,5 $cm^3$, approximately 12% higher than the control. In contrast, escin (0,013 mmol/L) and betulin (0,034 mmol/L) significantly inhibited the process, with $CO_2$ emissions reduced by 53% and 59%, respectively (Duca et al., 2023). These results indicate the potential of tomatine to stimulate fermentative activity.

a) 

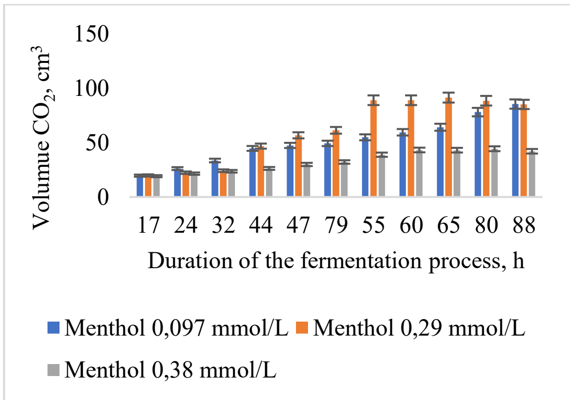

b) 


**Figure 3.3 Volume of gas ($CO_2$) released during aerobic fermentation of cereal distillery grains in the presence of additives: a) sclareol, b) menthol** *(results obtained within the doctoral thesis)*

The influence of the BAS concentrations shown in figure 3.3, specifically sclareol (a) and menthol (b), on the aerobic fermentation of cereal distillery grains demonstrated a non-linear dose–response relationship: sclareol at 0,049 mmol/L generated the highest $CO_2$ volume (253,6 $cm^3$), while at 0,19 mmol/L it significantly inhibited the process, followed by a delayed increase; menthol stimulated fermentation at 0,29 mmol/L, whereas at 0,38 mmol/L it exhibited an inhibitory effect.

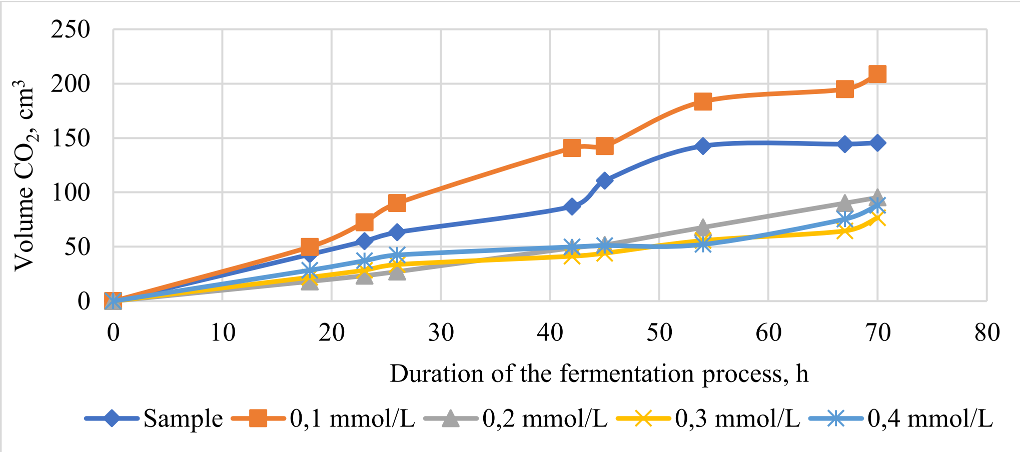



**Figure 3.4 Volume of gas released during aerobic fermentation of cereal distillery grains in the presence of DHFA** ( Duca et al., 2023)

Figure 3.4 illustrates the influence of DHFA, administered at concentrations ranging from 0,1 to 0,4 mmol/L, on the kinetics of aerobic fermentation of cereal stillage, evaluated based on the total volume of $CO_2$ released. The obtained data indicate that only the 0,1 mmol/L concentration exerted a significant stimulatory effect, generating a total $CO_2$ volume of 208,6 $cm^3$, approximately 43% higher compared to the control sample. In contrast, higher concentrations (0,2–0,4 mmol/L) induced a reduction in the intensity of the fermentative process, reflected by $CO_2$ volumes lower than those recorded for the control (Duca et al., 2022; Duca et al., 2023).

The results confirm the influence of naturally derived BAS with antioxidant properties on the aerobic fermentation of cereal stillage under mesophilic conditions. The most effective concentrations of the tested additives are summarized in table 3.2 (Duca et al., 2022; Duca et al., 2023).

**Table 3.2 Comparative efficiency of different types of BAS in the fermentation process of cereal stillage***

| No. | BAS | C, mg/L | Total $CO_2$ volume realeased, $cm^3$ | Fermentation duration, h |
|---|---|---|---|---|
| 1. | DHFA | 0,54±0,02 | 208,62±2,1 | 70 |
| 2. | Tomatine | 0,45±0,01 | 233,46±1,2 | 78 |
| 3. | Sclareol | 0,48±0,01 | 257,09±2,4 | 55 |
| 4. | Vanillin | 0,68±0,02 | 229,64±1,3 | 69 |
| 5. | Catechin | 0,70±0,02 | 180,31±1,6 | 61 |

**results obtained within the doctoral research*

The comparative analysis demonstrates that, among the studied BAS, sclareol (0,48 mgl/L) produced the highest volume of $CO_2$ released within a short fermentation period, confirming a pronounced stimulatory effect on the process. In contrast, catechin generated the lowest gas volume, indicating reduced efficiency at the applied concentration.

### 3.4 Study of the impact of selected BAS on the kinetics of anaerobic fermentation of biomass

The enhancement of biogas production efficiency can be achieved through the use of naturally derived BAS. To this end, the anaerobic fermentation of cereal stillage from the beverage industry was stimulated by adding micro-doses of BAS during the methanogenic phase.

The anaerobic fermentation process of the residual biomass, represented by cereal stillage, was investigated in the presence of selected BAS for biogas production, following the standardized VDI 4630 protocol (Oleszek et al., 2013). Fermentation was carried out under mesophilic conditions at a constant temperature of 37 °C and an approximate pH of 7, using a working volume of 0,8 L. The fermentative mixture contained 3% solid material, and the substrate-to-inoculum (S:I) ratio was set at 1:2 in accordance with methodological requirements.

As an inoculum source, post-fermentation residue from a local biogas facility was employed to ensure a microbial community adapted to the anaerobic process. The bioactive substances were added at a unitary concentration of 3 mg/L of biomass to evaluate their effect on methanogenic process yield; the obtained values are presented in table 3.3 (Duca et al., 2023).

**Table 3.3 Biogas volume and methane content under the influence of BAS***

| BAS | Biogas yield, $dm^3$/kg biomass | Methane, $dm^3$/kg biomass |
|---|---|---|
| Control | 320 | 190 |
| DHFA | 580 | 322 |
| Aescinum | 370 | 205 |
| Tomatin | 355 | 202 |
| Sclareol | 315 | 187 |
| Vanillin | 335 | 212 |
| Catechin | 329 | 198 |
| Betuline | 370 | 225 |
| Menthol | 319 | 186 |

* *results obtained within the doctoral thesis; p<0,05*

The obtained data indicate that the addition of DHFA exerted the most pronounced stimulatory effect on anaerobic fermentation, leading to a substantial increase in biogas volume up to 580 $dm^3$/kg, compared to the control variant (320 $dm^3$/kg). Moreover, DHFA achieved the highest methanogenic yield, reaching 322 $dm^3$/kg of methane, reflecting both intensified microbial activity and efficient conversion of the substrate into the desired energy component.

### 3.5 Computational modeling of the anaerobic fermentation mechanism in the presence of bioactive substances

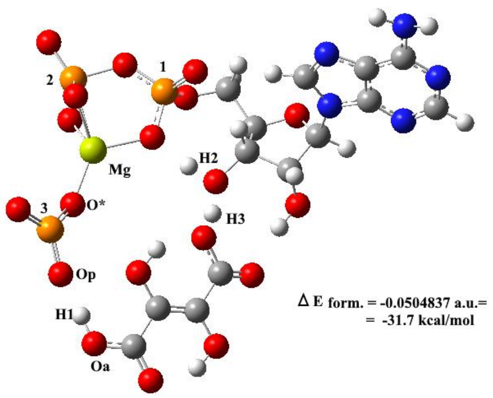



**Figure 3.5 Optimized structure of the complex formed as a result of the reaction between a molecule of dihydroxyfumaric acid and the [MgATP$_{an}$]$^{2-}$ complex (***results obtained within the doctoral thesis)*

Anaerobic fermentation was analyzed from the perspective of the rate-limiting step – glucose phosphorylation catalyzed by hexokinase in the presence of the [MgATPan]$^{2-}$ complex. Quantum-chemical calculations using DFT (B3LYP/6-31G(d)) were employed to investigate various coordination modes of $Mg^{2+}$ with ATP, identifying configurations with superior energetic stability. The results revealed that, in the absence of DHFA, the phosphate group bound to the P3 atom exhibits high lability, being susceptible to premature detachment under the action of intracellular protons.

The introduction of the DHFA molecule into the complex leads to the formation of two intramolecular hydrogen bonds. These bonds stabilize the phosphoryl group and significantly reduce its lability (figure 3.5). The total energy of the [MgATPan–DHFA]$^{2-}$ complex is 31,68 kcal/mol lower than the sum of the initial reactants, confirming a pronounced stabilizing effect. Within this complex, a fragment of the DHFA molecule is almost perfectly integrated between the phosphoryl group and one of the hydroxyl groups of the ribose ring. This fragment establishes two hydrogen bonds: one between the oxygen atom of the phosphoryl group and the H1 hydrogen atom (O---H1—Oa), and the other between the H2 hydrogen atom of DHFA and an oxygen atom from the ribose hydroxyl group. Thus, the structural fragment of dihydroxyfumaric acid incorporated in the [MgATPan–DHFA]$^{2-}$ complex significantly reduces the lability of the P3 phosphoryl group and also protects its oxygen atoms from proton attack in the intracellular milieu.

The catalytic effect of DHFA on the anaerobic fermentation process consists of an increased number of [MgATPan]$^{2-}$ complexes capable of reaching the active site of hexokinase without premature cleavage of the phosphoryl groups during diffusion, thereby participating effectively in the subsequent glucose phosphorylation reaction.

# 4. ANALYSIS OF THE ANAEROBIC FERMENTATION PROCESS OF RED GRAPE MARC

## 4.1 The need for valorization of winemaking by-products

In the Republic of Moldova, grape processing generates annually substantial amounts of winemaking by-products, including marc, seeds, and yeast residues, which can exceed 18–20% of the processed grape mass (Souza da Costa, 2022; Gonçalves, 2024; Lachman et al., 2013; National Office of Vine and Wine, 2021).

Considering the valorization potential of these by-products, red grape marc was selected for detailed characterization of its phenolic composition and evaluation of its applicability in fermentation processes. The marc used in this study was obtained from the microvinification section of the Technical University of Moldova (UTM) and was stored at –18 °C until analysis. The phenolic composition was characterized using HPLC-DAD-MS-ESI, identifying 21 phenolic derivatives: 6 anthocyanins (as glycosides), 11 flavonols, and 3 hydroxycinnamic acids. The total phenolic content ranged from 11,6 to 19,2 mg/g dry matter, with higher values observed in acetone extracts. Epicatechin (3,2–4,5 mg/g d.m.), catechin (1,9–3,3 mg/g d.m.), and procyanidin dimers (1,0–3,0 mg/g d.m.) were quantitatively predominant (table 4.1).

**Table 4.1 Phenolic compound content in red grape marc extracts obtained after fermentation: I – Merlot/Cabernet 60/40 (MCa) and II – Cabernet (Ca)***

| Peak No. | $R_t$ (min) | Phenolic Compound, mg/g d.m. | MCa, ethanol | MCa, acetone | Ca , ethanol | Ca, acetone |
|---|---|---|---|---|---|---|
| 1. | 3,24 | 2-Hydroxybenzoic acid | 0,343 | 0,478 | 0,459 | 0,361 |
| 2. | 11,46 | Procyanidin dimer, isomer I | 1,003 | 0,974 | 1,351 | 1,677 |
| 3. | 12,10 | Malvidin-glucoside/ Peonidin-glucoside | 0,146 | 0,107 | 0,218 | 0,167 |
| 4. | 12,48 | Catechin | 1,929 | 1,964 | 2,562 | 3,308 |
| 5. | 13,07 | Procyanidin dimer, isomer II | 2,164 | 2,286 | 2,494 | 3,034 |
| 6. | 13,57 | Caffeic acid-glucoside | 0,173 | 0,195 | 0,163 | 0,265 |
| 7. | 13,86 | Epicatechin | 3,169 | 3,254 | 3,680 | 4,449 |
| 8. | 14,42 | Malvidin-malonyl-glucoside | 0,106 | 0,085 | 0,137 | 0,161 |
| 9. | 14,74 | Isorhamnetin-glucuronide | 0,422 | 0,443 | 0,788 | 0,863 |
| 10. | 15,85 | Malvidin-diglucoside | 0,074 | 0,070 | 0,080 | 0,083 |
| 11. | 15,90 | Quercetin-rutinoside (Rutin) | 0,275 | 0,541 | 0,451 | 0,860 |
| 12. | 16,28 | Quercetin-glucoside/ Isorhamnetin-rutinoside | 0,168 | 0,329 | 0,217 | 0,479 |

**Continuation of table 4.1**

| | | | | | | |
|---|---|---|---|---|---|---|
| 13. | 17,03 | Malvidin-coumaroyl glucoside Peonidin-coumaroyl glucoside | 0,120 | 0,117 | 0,155 | 0,170 |
| 14. | 17,06 | Quercetin-glucuronide | 0,551 | 0,866 | 0,665 | 1,059 |
| 15. | 18,03 | Coumaroylquinic acid | 0,257 | 0,409 | 0,203 | 0,839 |
| 16. | 21,49 | Quercetin | 0,308 | 0,702 | 0,465 | 0,892 |
| 17. | 23,32 | Isorhamnetin | 0,367 | 0,570 | 0,398 | 0,547 |
| | | ***Total phenolics*** | ***11,574*** | ***13,391*** | ***14,487*** | ***19,214*** |

** results obtained within the doctoral thesis*

The results obtained demonstrate that red grape marc contains significant amounts of phenolic compounds, ranging from 11,6 to 19,2 mg/g dry matter, with more efficient extraction achieved using acetone compared to 60% (v/v) ethanol solution. Detailed analysis indicates the predominance of epicatechin (3,2–4,5 mg/g d.m.), catechin (1,9–3,3 mg/g d.m.), and procyanidin dimers, isomer I (1,0–1,7 mg/g d.m.) and isomer II (2,2–3,0 mg/g d.m.).

Considering the substantial content of phenolic compounds identified in grape marc and other vinification by-products, the radical-scavenging and antioxidant activity of hydroalcoholic extracts was evaluated. The assays were performed at different pH values (acidic pH = 2 and basic pH = 8), corresponding to gastric and intestinal conditions (table 4.2).

**Table 4.2 Radical-scavenging and antioxidant activity of red grape marc extracts in different media***

| Extract | Radical-scavenging activity, % DPPH inhibition | | Antioxidant activity, % hydrogen peroxide inhibition | |
|---|---|---|---|---|
| | Acidic medium, pH=2 | Basic medium, pH=8 | Acidic medium, pH=2 | Basic medium, pH=8 |
| MCa/ethanol | 75,65±1,53 | 70,80±2,52 | 42,64±0,39 | 37,47±0,40 |
| MCa/acetone | 77,03±0,95 | 69,66±1,60 | 46,89±0,38 | 40,74±0,47 |
| Ca/ethanol | 82,25±1,11 | 66,22±1,10 | 49,73±0,28 | 42,51±0,21 |
| Ca/acetone | 89,77±1,30 | 82,65±2,27 | 46,97±0,76 | 43,97±0,26 |

** results obtained within the doctoral thesis*

The radical-scavenging activity determined by the DPPH assay ranged from 77–90% inhibition in acidic medium and 66–90% in basic medium, with higher values associated with acetone extracts. The antioxidant capacity, expressed as hydrogen peroxide inhibition, ranged from 37–50% and did not exhibit significant differences between media. The efficiency is influenced by flavonoid structure, substitutions on aromatic rings, and the degree of polymerization, with epicatechin and B-type procyanidins exhibiting the most pronounced effects (Yeddes et al., 2013; Chedea, 2016).

These results confirm the high potential of red grape marc as a source of natural antioxidants, with possible applicability in biotechnological processes and functional formulations.

### 4.2 Analysis of fermentative capacity and kinetic modeling of anaerobic digestion of grape marc

Whole grape marc and its fractions (skins, seeds) were evaluated as substrates for biogas production in mesophilic anaerobic fermentation (37 °C) from a physicochemical and biochemical perspective (table 4.3).

**Table 4.3 Physicochemical and biochemical characteristics of winery by-products used for anaerobic fermentation***

| Parameter, unit | Grape Marc I | Grape Marc II | Skins from Grape Marc I | Seeds from Grape I |
|---|---|---|---|---|
| pH | 3,88±0,01 | 3,68±0,01 | 3,59±0,01 | 4,56±0,01 |
| Total Solids Content (TS), g/kg | 398±7 | 407±7 | 328±4 | 598±7 |
| Biological Oxygen Demand (BOD), $gO_2$/kg | 597±25 | 622±25 | 387±15 | 980±25 |
| Total Soluble Compounds (polysaccharides, TSC)g/kg CTS | 412±11 | 437±8 | 580±12 | 182±14 |
| Hemicellulose, g/kg TS | 52±3 | 48±2 | 65±3 | 32±2 |
| Cellulose, g/kg TS | 147±7 | 145±5 | 112±12 | 296±14 |
| Lignin, g/kg TS | 142±14 | 135±11 | 112±8 | 181±9 |
| Total Polyphenols, g/kg TS | 18,5±0,5 | 21,0±0,4 | 24,5±0,5 | 3,2±0,3 |
| Total Nitrogen, gN/kg | 6,8±0,1 | 7,5±0,1 | 5,1±0,1 | 12,8±0,1 |
| Total Phosphorus, gP/kg | 1,9±0,1 | 2,1±0,1 | 1,7±0,1 | 2,3±0,1 |

** results obtained within the doctoral thesis*

The obtained data highlighted significant differences among fractions: the skins exhibited the highest content of fermentable compounds (TSC – 580 g/kg TS; polyphenols – 24,5 g/kg TS), suggesting an enhanced methanogenic potential, whereas the seeds showed high levels of cellulose and lignin, associated with increased structural recalcitrance. Whole grape marc presented intermediate values, reflecting the balance between fractions. These characteristics are reflected in the biogas accumulation dynamics (figure 4.1), which revealed clear differences in yield among substrate fractions. Kinetic modeling based on a first-order reaction allowed the determination of the rate constant ($k_T$) and the activation energy ($E_a$).

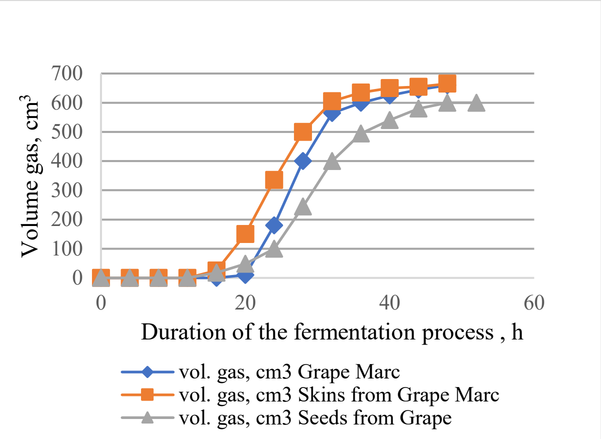



**Figure 4.1 Volume of gas released during the anaerobic fermentation of winery by-products** (*results obtained within the doctoral thesis*)

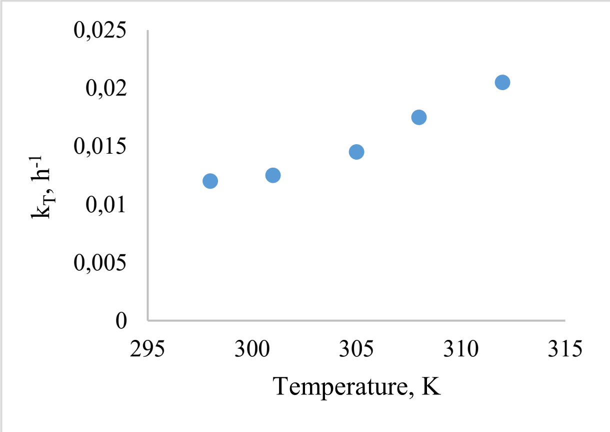



**Figure 4.2 Variation of the rate constant of the anaerobic fermentation process of grape marc at 296–313 K** *(results obtained within the doctoral thesis)*

The results indicated an increase in $k_T$ with temperature, following the Arrhenius equation (figure 4.2), with average calculated values of $E_a$ = 29,76 kJ/mol and A = 1905 $h^{-1}$. These findings confirm that the process follows first-order kinetics and fall within the range reported for the anaerobic fermentation of solid organic wastes (Mahmoud et al., 2004; Ma et al., 2011). To comparatively highlight the experimentally obtained values in correlation with the calculated kinetic parameters, table 4.4 presents the fermentation temperatures and reaction rate constants determined for grape marc.

**Table 4.4 Experimental values of temperature and reaction rate constant ($k_T$), and average calculated values of kinetic parameters ($E_a$ and A)***

| T, K | $k_T$, $h^{-1}$ | $E_a$, kJ/mol | A, $h^{-1}$ |
|---|---|---|---|
| 298 | 0,0120 | 29,76 | 1905 |
| 301 | 0,0125 | | |
| 305 | 0,0145 | | |
| 308 | 0,0175 | | |
| 312 | 0,0205 | | |

* *results obtained within the doctoral thesis*

The calculated activation energy value confirms that the anaerobic fermentation of grape pomace follows a first-order reaction (Mahmoud et al., 2004). This value falls within the range reported for anaerobic fermentation of by-products, between 25 and 346 kJ·$mol^{-1}$ (Ma et al., 2011). The obtained results support the validity of the kinetic model applied to the process.

# 5. INTEGRATED VALORIZATION OF RESIDUES FROM THE ALCOHOL PRODUCTION INDUSTRY

## 5.1 Description of the implementation of scientific results at an industrial scale

At the enterprise SRL Garma Grup (Fîrlădeni village, Hîncești District), which integrates ethyl alcohol production and cattle farming, the main residual streams – cereal stillage and bovine manure – are subjected to anaerobic fermentation in continuously operating reactors (working volume 3200 $m^3$/reactor). The process provides up to 80 000 $m^3$ of biogas daily, used for generating steam required for distillation and for producing renewable electricity, thus contributing to the reduction of conventional resource consumption.

In the applied study, the substrate, consisting of 2324,67 $m^3$ of liquid stillage and 988,33 $m^3$ of bovine manure, was treated with DHFA at a dose of 113,28 g per experimental batch. The main objective of this study was to evaluate the effect of this antioxidant BAS on the efficiency of the anaerobic fermentation process under controlled industrial conditions.

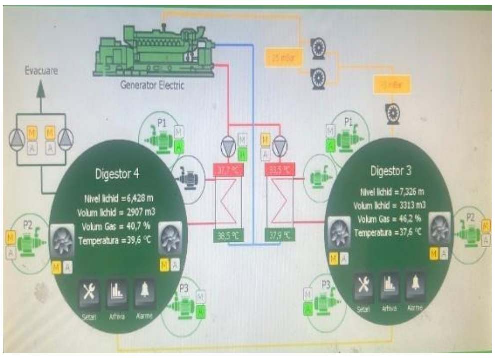



**Figure 5.1 Digital interface for real-time monitoring of the anaerobic fermentation plant at SRL "Garma Grup"**

**Table 5.1 Chemical composition of biogas***

| **Component** | **Unit** | **Control sample (digester 4)** | **SBA-Treated Sample (digester 3)** |
|---|---|---|---|
| Methane ($CH_4$) | % vol | 60,2 | 65,8 |
| Carbon Dixide ($CO_2$) | % vol | 37,5 | 32,1 |
| Residual Oxygen ($O_2$) | % vol | 1,1 | 0,8 |
| Hydrogen Sulfide ($H_2S$) | % vol | 0,25 | 0,18 |

**results obtained within the doctoral thesis*

Digital monitoring of the technological parameters (figure 5.1) revealed significant differences between the BAS-treated digester and the control unit. In the experimental setup, the total biogas volume produced reached 46,2%, compared to 40,7% in the control, while the gas composition was improved. Methane content increased to 65,8% (versus 60,2% in the control), accompanied by reductions in $CO_2$, $O_2$, and $H_2S$ concentrations (table 5.1). These results confirm that the addition of DHFA contributes to optimizing the anaerobic fermentation process by promoting the efficient conversion of organic matter into methane and reducing the formation of undesirable gaseous compounds. Its antioxidant activity can be correlated with the inhibition of sulfate-reducing bacteria, which explains the decreased hydrogen sulfide concentration in the final biogas.

### 5.2 Feasibility study of the implementation of the proposed technology at SRL „Garma Grup”

To validate the practical applicability of the results, the optimized anaerobic digestion technology with DHFA addition was implemented under controlled conditions at SRL „Garma Grup,” according to the official implementation act (Annex 1). The use of 113,28 g DHFA (0,0003 mmol/L) for the anaerobic fermentation of 3 313 $m^3$ of substrate resulted in the production of 80 000 $m^3$ of biogas, with an average methane content of 65%. The total energy generated was estimated at 160 000 kWh, corresponding to an economic value of €48 000, considering an additive cost below €34.

**Table 5.2 Energy efficiency of anaerobic digestion with and without SBA additive**

| Parameter | Biogas volume, $m^3$ | Methane volume, $m^3$ | Methane content (%) | Energy generated (kWh) | Specific Energy yield, (kWh/$m^3$ biogas) | Specific economic yield (€/ $m^3$ biogas) |
|---|---|---|---|---|---|---|
| Control | 60000 | 36000 | 60 | 120000 | 2,0 | 0,2 |
| With SBA | 80000 | 52000 | 65 | 48000 | 3,6 | 0,6 |

* *results obtained within the doctoral thesis*

The results summarized in table 5.2 show that DHFA addition increased the total biogas volume by 33% and the methane potential by more than 44% compared to the control. Following the experimental run, the total energy output increased from 120 000 kWh to 480 000 kWh, and the specific energy yield rose from 2,0 to 3,6 kWh/$m^3$ of biogas. From an economic perspective, the specific yield tripled from 0,2 €/$m^3$ to 0,6 €/$m^3$ of biogas. These findings confirm the stimulation of the anaerobic microbiota activity and improved substrate-to-biogas conversion, validating the feasibility of the technology in an industrial context and within a circular bioeconomy framework (Venkata Mohan et al., 2016; Reena et al., 2018; Eurostat, 2024).

It can also be noted that the DHFA additive contributes to increasing the process’s energy efficiency by reducing the time required to reach maximum biogas production and optimizing the cost–benefit ratio. Furthermore, the higher methane content enables the use of the produced biogas for electricity and heat generation, supporting the transition to renewable energy sources and the reduction of greenhouse gas emissions.

## CONCLUSIONS AND PRACTICAL RECOMMENDATIONS

The study systematically examines the valorization of distillation by-products and wine industry secondary products through anaerobic fermentation using bioactive substances (BAS) with antioxidant properties. The research had a dual objective: obtaining high-quality biogas and integrating the processes into a sustainable system aligned with the principles of circular bioeconomy. The experimental and analytical results obtained confirm the working hypotheses and indicate clear prospects for industrial application.

Based on the conducted research, the following conclusions have been formulated in accordance with the stated objectives:

1. A detailed characterization of distillation by-products and wine industry secondary products highlighted their potential not only as an energy substrate but also as a source of bioactive compounds with catalytic roles. Studies demonstrated that cereal mash and grape pomace provide an optimal balance between fermentable sugars, structural fibers, and polyphenols—conditions essential for efficient fermentation processes.
2. Analysis of the structure and redox properties of BAS revealed significant correlations between the electronic parameters of the molecules (HOMO, LUMO, $\Delta E$) and their influence on fermentation kinetics. The results confirm that integrating experimental and computational methods constitutes a solid approach for developing effective strategies to stimulate the anaerobic process.
3. Comparative studies of aerobic and anaerobic fermentation demonstrated that BAS can be used as selective modulators: some substances (DHFA, aescinium, betuline, tomatin) accelerate aerobic metabolism, increasing $CO_2$ emission, while others promote methanogenesis, enhancing the energy yield of biogas.
4. Investigation of the optimal BAS concentrations in aerobic fermentation revealed a dose-dependent effect, with a maximum efficiency range of 0,1–0,15 mmol/L. This observation indicates the possibility of controlling the process by adjusting the concentration according to substrate type and fermentation conditions.
5. The practical implementation of DHFA in an industrial enterprise demonstrated that biological activation methods for fermentation are feasible and effective, with quantifiable results in biogas production and methane content, providing evidence for technology transfer and large-scale application.

6. Grape pomace was confirmed as a multifunctional substrate, supplying both fermentable components and polyphenols with antioxidant activity, reducing the need for external additives and increasing process sustainability.

7. Mathematical modeling of anaerobic fermentation kinetics allowed for predictive estimation of biomass behavior, facilitating the planning of industrial processes and optimization of operational parameters.

**Practical recommendations**

- Expand research on a broader portfolio of plant-derived BAS to identify efficient and sustainable natural catalysts for anaerobic fermentation.
- Valorize grape pomace and its solid fractions (skins and seeds) as sources of fermentable substrate and natural polyphenols, reducing costs and dependence on chemical additives.
- Optimize BAS concentrations for each type of substrate and fermentation regime, maintaining maximum efficiency without inducing enzymatic inhibition or saturation.
- Extend the application of DHFA to other types of agro-industrial biomass to validate the general applicability of its redox effect.
- Systematically evaluate the resulting digestate as an organic fertilizer to close the agricultural cycle and promote circular economy practices.
- Develop biocatalysts derived from natural resources to optimize costs and enhance the industrial efficiency of anaerobic fermentation.
- Integrate fermentation technologies utilizing BAS within regional agro-industrial systems, contributing to European goals of climate neutrality and energy efficiency.
- Promote collaboration between research institutions and the industrial sector for large-scale implementation of experimental results, including staff training and continuous process monitoring.

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## List of Author's Publications on the Thesis Topic

**1. Monographs and Specialty Books**

**1.2.** Collective Specialty Books

**1**. DUCA, G., STURZA, R., COVALIOVA, O., COVACI, E., ROMANCIUC, L., **TAȘCA, C**. Modification of waste biomass digestion in the presence of additives of bioactive substances. *În: Redox Processes within Environmental and Technological Contexts*. Vol. 2, Cap. 9. SUA: IGI Global, 2023, pp.149–165 ISSN 2326-9162; eISSN 2326-9170. DOI: 10.4018/979-8-3693-0512-6.ch009.

**2**. DUCA, G., COVALIOV, V., COVALIOVA, O., ROMANCIUC, L., **TAȘCA, C**. Studiul proceselor redox în sisteme biochimice în prezența antioxidanților. *În: Procese redox cu transfer de electroni și proton: Monografie.* Chișinău: Editura USM, 2023, pp. 211–237. ISBN 978-9975-62-658-3.

**2. Articles in Scientific Journals**

**2.2**. Articles in Journals Indexed in Other Databases Accepted by ANACEC (with Database Indication)

**3.** DUCA, G., COVALIOVA, O., COVACI, E., ROMANCIUC, L., **TAȘCA, C**. Effect of bioactive additives on biomass fermentation from agro-industrial sector. *Journal of Engineering Science*, 2022, vol. 29, nr. 3, pp. 176–188. ISSN 2587-3474. DOI: 10.52326/jes.utm.2022.29(3).15. *(Indexat în DOAJ, Index Copernicus)*

**4. TAȘCA, C**. Characteristics of biomass resulting from agro-industrial processes and possibilities of its evaluation in the context of the circular bioeconomy. *Journal of Engineering Science*, 2024, vol. 31, nr. 3, pp.156–178. ISSN 2587-3474.
DOI: 10.52326/jes.utm.2024.31(3).12. *(Indexat în DOAJ, Index Copernicus)*

**5. TAȘCA, C.** *Complex valorization of waste from the alcohol production industry.* Journal of Social Sciences, 2025, vol. 8, nr. 2, pp. 17-27. ISSN 2587-3490. DOI: https://doi.org/10.52326/jss.utm.2025.8(2).02.

**3. Articles / Theses in Conference Proceedings and Other Scientific Events**

**6.** COVALIOV, V., COVALIOVA, O., **TAȘCA, C.** Biochemical production of vitamin B12 from the agro-industrial wastes. În: *Proceedings of the International Conference "Intelligent Valorisation of Agro-Food Industrial Wastes"*, 7–8 octombrie 2021, Chișinău. Universitatea Tehnică a Moldovei, 2021, pp. 23. ISBN 978-9975-3464-2-9.

**7. TAȘCA, C.,** COVACI, E., COVALIOVA, O. The influence of biocatalysts on biomass fermentation processes. În: *Proceedings of the International Conference "Intelligent Valorisation of Agro-Food Industrial Wastes"*, 7–8 octombrie 2021, Chișinău. Universitatea Tehnică a Moldovei, 2021, pp. 72. ISBN 978-9975-3464-2-9**.**

**8.** COVALIOVA, O., STURZA, R., COVACI, E., ROMANCIUC, L., **TAȘCA, C.** New additives of bioactive substances in the biochemical digestion processes. În: *Abstract Book of the 7th International Conference "Ecological and Environmental Chemistry"*, 3–4 martie 2022, Chișinău. Centrul Editorial-Poligrafic al USM, 2022, pp. 150–151. ISBN 978-9975-159-07-4. DOI: 10.19261/eec.2022.v1.

**9. TAȘCA, C.** Dinamica procesului de fermentare alcoolică a borhotului de cereale în prezența acidului dehidroxifumaric. În: *Conferința Tehnico-Științifică a Studenților,*

*Masteranzilor și Doctoranzilor*, 29–31 martie 2022, Chișinău. Tehnica-UTM, 2022, Vol. I, pp. 480–483. ISBN 978-9975-45-828-3.

**10. TAȘCA, C.** Studiul cineticii mecanismelor de fermentație anaerobă a biomasei în prezența antioxidanților. În: *Inovația: factor al dezvoltării social-economice*, Conferință științifică națională cu participare internațională, 17 decembrie 2021. Cahul: Universitatea de Stat „Bogdan Petriceicu Hasdeu", 2022, pp. 87–90. ISBN 978-9975-86-234-0.

**11.** DUCA, G., STURZA, R., COVALIOVA, O., COVACI, E., **TAȘCA, C.** The influence of bioactive additives on the process of alcoholic fermentation of waste biomass. În: *Abstract Book of the 5th International Conference "Modern Technologies in the Food Industry"*, 20–22 octombrie 2022, Chișinău. Universitatea Tehnică a Moldovei, 2022, p. 100. ISBN 978-9975-45-851-1.

**12. TAȘCA, C.,** DUCA, G., COVACI, E. The impact of tomatin bac on the process of alcoholic fermentation of cereal biomass. În: *Abstract Book of the 7th International Conference "Ecological and Environmental Chemistry"*, 3–4 martie 2022, Chișinău. Centrul Editorial-Poligrafic al USM, 2022, pp. 186–187. ISBN 978-9975-159-07-4. DOI: 10.19261/eec.2022.v1.

**13. TAȘCA, C.,** DUCA, G., COVACI, E. The influence of tomatin bac on the process of alcoholic fermentation of waste biomass. În: *Life Sciences in the Dialogue of Generations: Connections between Universities, Academia and Business Community*, Conferință științifică națională cu participare internațională, 29–30 septembrie 2022, Chișinău. Universitatea de Stat din Moldova, 2022, p. 197. ISBN 978-9975-159-80-7.

**14. TAȘCA, C.** Efectul SBA asupra fermentării biomasei din sectorul agroindustrial. În: *Conferința Tehnico-Științifică a Studenților, Masteranzilor și Doctoranzilor*, 28–30 martie 2023, Chișinău. Universitatea Tehnică a Moldovei, 2023, Vol. II, pp. 222–226. ISBN 978-9975-45-828-3.

**15. TAȘCA, C.** Study of the kinetics of biomass fermentation processes resulting from the alcohol industry. *În: Smart Life Sciences and Technology for Sustainable Development,* Conferință internațională, 28–30 iunie 2023, Chișinău. Universitatea de Stat din Moldova, 2023, p. 17. ISBN 978-9975-159-84-5.

**16. TAȘCA, C.** Effect of bioactive additives on biomass fermentation from agro-industrial sector. *În: Natural Sciences in the Dialogue of Generations,* Conferință națională cu participare internațională, 14–15 septembrie 2023, Chișinău. Universitatea de Stat din Moldova, 2023, p. 187. ISBN 978-9975-3430-9-1.

**17.** DUCA, G., ROMANCIUC, L., COVALIOVA, O., **TAȘCA, C.** Specifics of the redox processes in natural aquatic systems. În: *Geo- and Bioecological Problems of the Middle and Lower Dniester River Basin*, Conferință științifică cu participare internațională, 16–17 noiembrie 2024, Tiraspol. Tiraspol: Eco-TIRAS, 2024, pp. 78–81. ISBN 978-9975-89-320-6. DOI: 10.70739/gbp2024.18.

# ADNOTARE

La teza cu titlul ***„Studiul proceselor de oxido – reducere în fermentarea anaerobă a biomasei în prezența antioxidanților”*** înaintată de către candidatul – **TAȘCA Corina,** pentru conferirea titlului științific de doctor în științe chimice la specialitatea -145.01 **Chimie Ecologică. Chișinău, 2025**

**Structura tezei:** teza este scrisă în limba română și constă din introducere, cinci capitole, sinteza rezultatelor experimentale, concluzii generale și recomandări, bibliografie 223 de titluri și **1** anexă. Teza conține 118 de pagini cu text de bază, 41 figuri și 29 tabele. Rezultatele obținute sunt publicate în 17 lucrări științifice cu volum total de circa 8 coli de autor.

**Cuvinte-cheie:** substanțe biologic active, fermentație aerobă, fermentație anaerobă, activitate antioxidantă, borhot de cereale rezultat din producerea alcoolului etilic, tescovina de struguri, metanogeneză, sustenabilitate, conversia biochimică a biomasei.

**Scopul lucrării:** constă în optimizarea proceselor de valorificare a biomasei din vinificație și industria băuturilor alcoolice, utilizând fitocatalizatori redox pentru accelerarea proceselor de fermentație.

**Obiectivele cercetării:** Studiul a vizat valorificarea produselor secundare vinicole și a borhotului prin fermentație aerobă și anaerobă, analizând influența substanțelor biologic active cu proprietăți antioxidante asupra cineticii proceselor. Modelarea teoretică, bazată pe descriptorii HOMO, LUMO, ΔE și potențialul electrostatic, a permis elucidarea mecanismelor redox și optimizarea randamentului și calității biogazului.

**Noutatea și originalitatea științifică:** A fost evaluată aplicarea fitocatalizatorilor în accelerarea fermentației biomasei din industria băuturilor, prin analiza cineticii și a mecanismului reacției în prezența substanțelor biologic active.

**Problema științifică principală rezolvată:** A fost evaluată influența antioxidanților biologic activi asupra cineticii fermentației aerobă și anaerobă a produselor secundare vinicole și a borhotului, în vederea optimizării conversiei biomasei în biogaz de calitate. Rezultatele susțin integrarea proceselor într-un sistem sustenabil, conform bioeconomiei circulare, cu aplicabilitate industrială.

**Semnificația teoretică:** Au fost acumulate informații despre reactivitatea substanțelor biologic active în procese de fermentație aerobă și anaerobă. S-a determinat efectul substanțelor biologic active cu proprietăți antioxidante asupra cineticii proceselor de fermentație aerobă și anaerobă a produselor secundare din industria băuturilor

**Valoarea aplicativă:** Contribuția aplicativă constă în validarea rezultatelor obținute prin implementarea controlată a SBA (acidul dihidroxifumaric) în procesele de fermentație anaerobă la scară industrială, inclusiv asupra calității biogazului produs, prin creșterea conținutului de metan. Soluțiile propuse contribuie la dezvoltarea unui sistem sustenabil de gestionare a produselor secundare din industria băuturilor.

**Implementarea rezultatelor științifice:** Conform actului de implementare din 25 aprilie 2025, la întreprinderea SRL „Garma Grup” au fost realizate testări industriale cu aplicarea SBA pe 1 lot experimental de substrat compus din 2325 $m^3$ borhot lichid și 988 $m^3$ dejecții bovine. S-a înregistrat o producție sporită de biogaz și o îmbunătățire a calității acestuia, prin creșterea proporției de metan.

# ANNOTATION

Of the thesis titled *"Study of Redox Processes in Anaerobic Fermentation of Biomass in the Presence of Antioxidants"*, submitted by the PhD candidate **TAȘCA Corina**, for the degree of Doctor of Chemical Sciences, specialty **145.01 Ecological Chemistry**.

Chișinău, 2025

**Thesis structure**: The thesis is written in Romanian and consists of an introduction, five chapters, a synthesis of experimental results, general conclusions and recommendations, a bibliography of 223 titles, and one appendix. The thesis comprises 118 pages of main text, including 41 figures and 29 tables. The results have been published in 17 scientific papers, totaling approximately *8* author sheets.

**Keywords**: bioactive substances, aerobic fermentation, anaerobic fermentation, antioxidant activity, cereal stillage from ethanol production, grape pomace, methanogenesis, sustainability, biochemical conversion of biomass.

**Research aim**: To optimize biomass valorization processes from winemaking and alcoholic beverage industries through the use of redox phytocatalysts for accelerating fermentation processes.

**Research objectives**: The study focused on the valorization of winery by-products and cereal stillage through aerobic and anaerobic fermentation, analyzing the influence of antioxidant-rich bioactive substances on the kinetics of these processes. Theoretical modeling based on HOMO, LUMO, ΔE descriptors, and electrostatic potential allowed the elucidation of redox mechanisms and the optimization of process yield and biogas quality.

**Scientific novelty and originality**: The application of phytocatalysts was evaluated for accelerating fermentation of biomass from the beverage industry by analyzing the kinetics and reaction mechanisms in the presence of bioactive substances.

**Main scientific problem solved**: The study assessed the influence of bioactive antioxidants on the kinetics of aerobic and anaerobic fermentation of winery by-products and cereal stillage to optimize biomass conversion into high-quality biogas. The results support the integration of fermentation processes into a sustainable system aligned with circular bioeconomy principles and industrial applicability.

**Theoretical significance**: The work generated new insights into the reactivity of bioactive substances in aerobic and anaerobic fermentation processes. The effect of antioxidant bioactive substances on fermentation kinetics was determined.

**Applicative value**: The applied contribution lies in the validation of results through the controlled implementation of BAS (dihydroxyfumaric acid) in anaerobic fermentation processes at an industrial scale, with positive effects on the yield and quality of the resulting biogas. The proposed solutions contribute to the development of a sustainable management system for beverage industry by-products.

**Implementation of scientific results**: According to the implementation act dated April 25, 2025, at the company *SRL "Garma Grup"*, industrial-scale testing was carried out using BAS on one experimental lot composed of 2325 $m^3$ liquid stillage and 988 $m^3$ bovine manure. The tests recorded increased biogas production and improved quality, reflected in a higher methane proportion.

# АННОТАЦИЯ

К диссертации на тему *«Исследование окислительно-восстановительных процессов при анаэробном сбраживании биомассы в присутствии антиоксидантов»*, представленной соискателем ученой степени **доктора химических наук** по специальности **145.01 – Экологическая химия** – **ТАШКА КОРИНА**. Кишинэу, 2025

**Структура диссертации**: Диссертация написана на румынском языке и включает введение, пять глав, синтез экспериментальных результатов, общие выводы и рекомендации, библиографию из 223 наименований и одно приложение. Основной текст содержит 118 страниц, включая 41 рисунок и 29 таблиц. Полученные результаты опубликованы в 17 научных работах, общим объемом около 8 авторских листов.

**Ключевые слова**: биологически активные вещества, аэробное сбраживание, анаэробное сбраживание, антиоксидантная активность, барда из этанольного производства, виноградная выжимка, метаногенез, устойчивое развитие, биохимическое преобразование биомассы.

**Цель исследования**: Оптимизация утилизации биомассы из винодельческой и алкогольной промышленности с применением редокс-фитокатализаторов.

**Задачи исследования**: Работа была направлена на утилизацию побочных продуктов винодельческой и спиртовой промышленности методом аэробной и анаэробной ферментации, с анализом влияния биологически активных веществ с антиоксидантными свойствами на кинетику этих процессов. Было проведено теоретическое моделирование с использованием HOMO, LUMO, ΔE и электростатического потенциала для анализа механизма и увеличения выхода метана.

**Научная новизна и оригинальность**: Оценена возможность применения фитокатализаторов для ускорения ферментации биомассы из алкогольной промышленности путем анализа кинетики и механизмов реакции в присутствии биологически активных веществ.

**Решённая научная проблема**: Установлено влияние антиоксидантов биологического происхождения на кинетику аэробного и анаэробного сбраживания побочных продуктов винодельческой промышленности и барды, с целью повышения эффективности преобразования биомассы в высококачественный биогаз. Полученные данные подтверждают возможность интеграции процессов ферментации в устойчивые производственные системы, соответствующие принципам циркулярной биоэкономики и промышленной применимости.

**Теоретическая значимость**: Получены новые данные о реакционной способности биологически активных веществ в процессах аэробной и анаэробной ферментации. Установлено влияние антиоксидантов на кинетику процессов сбраживания.

**Прикладное значение**: Практическая ценность заключается в валидации полученных результатов путем контролируемого внедрения БАВ (дигидроксифумаровая кислота) в процессы анаэробной ферментации на промышленном уровне, что привело к повышению выхода и улучшению качества полученного биогаза. Предложенные решения способствуют созданию устойчивой системы управления побочными продуктами производства алкогольных напитков.

**Внедрение научных результатов**: Согласно акту внедрения от 25 апреля 2025 года, на предприятии *SRL „Garma Grup”* были проведены промышленные испытания с использованием БАВ на одной экспериментальной партии, включающей 2325 $м^3$ жидкой барды и 988 $м^3$ коровьего навоза. Отмечено повышение выхода и качества биогаза благодаря росту содержания метана.

**TAȘCA Corina**

# STUDY OF OXIDATION–REDUCTION PROCESSES IN ANAEROBIC FERMENTATION OF BIOMASS IN THE PRESENCE OF ANTIOXIDANTS

**145.01. Ecological Chemistry**

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