UNIVERSITY „POLITEHNICA" of BUCHAREST
FACULTY OF APPLIED CHEMISTRY AND MATERIALS SCIENCE
DEPARTMENT OF BIORESOURCES AND POLYMER SCIENCE

DOCTORAL THESIS

Tehnici neconvenționale pentru intensificarea sintezei de biocombustibili lichizi

Unconventional techniques for intensifying the synthesis of liquid biofuels

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Thesis summary

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OBIECTIVELE CERCETARII

For the first topic addressed in the elaboration of the thesis, the effect of microwaves on the metabolic activity of *Saccharomyces cerevisiae* cells in the process of alcoholic fermentation of glucose, were proposed as main objectives: the realization of an experimental laboratory installation, allowing a good control of the temperature and microwave dose during the studies carried out; the identification of a microwave exposure field for which to obtain a intensification of the fermentation process; tracking the effect of microwaves on the viability, morphology and structural integrity of yeast cells. It was also proposed to model the fermentation reactor to confirm the degree of homogeneity in the environment and the lack of temperature gradients that could have a negative impact on the conduct of fermentation studies. In order to carry out the fermentation studies, two configurations were proposed, the initial one obtained by modifying a microwave oven by adding a magnetron control system, and the second configuration, on which most of the experimental studies were carried out, in which the magnetron was replaced by a solid-state generator, the two installations being presented schematically within the experimental study chapter of the first part of the doctoral thesis.

The second topic addressed in this thesis, the synthesis of inferior alcohol esters with vegetable oils by unconventional methods, had as main objective the realization of a detailed comparative study of the methods for process intensification which can be applied for the transesterification reaction in the synthesis of biodiesel, from the point of view of both the methyl ester content and the specific energy consumptions in continuous processes at short reaction times. A secondary objective was the potential for the use of ultrasound to intensify the synthesis of ethyl esters, and to obtain FAEE products of high purity, which can be used as alternative solvents. The equipment used to carry out these studies consisted of: the Vibracell VCX750 ultrasonic processor, an ultrasonic processor based on an advanced technology, in which the output power can be varied, both the output power and the energy can be monitored; MMM Clamp-on, a multi-frequency sonic and ultrasonic vibrations technology, which offers the possibility of obtaining high-efficiency active powers for a wide band of sonic and ultrasonic vibrations, this power being able to be supplied to metal containers with walls of different thicknesses. This MMM technology allows the creation of an evenly and homogeneously distributed acoustic activity in the system, while avoiding the formation of long-lasting stationary waves, so that the sample volume is completely mixed.

PART I – INTENSIFICATION OF THE MICROWAVE FERMENTATION PROCESS

INTRODUCTION

As early as the 18th century, researchers were intrigued by the interaction between electromagnetic fields and biochemical processes inside living cells. Particular attention was paid to the spectrum belonging to microwaves, a significant number of studies noticing a possible impact of microwaves on the structure of the chromosomes and on the functionality of the cell, but also on its tolerance to mutagenic factors. Belyaev studied the impact of microwaves on chromosome DNA, while Hellar and Teixeira demonstrated that low-intensity microwaves can mutate in mammalian and insect cells [1-3]. Studies in the 1960s and 1970s showed that proteins, RNA and DNA absorb radiation between 65 – 75 GHz, microwaves being able to interfere with the self-repairing capacity of cells [4].

The effects of applying a magnetic field to living cells cannot be fully explained by any of the mechanisms formulated so far. The most common mechanism by which one tries to explain the biological effects of electromagnetic waves, involves the effect of transporting ions through channels in the cell membrane. It should be kept in mind, however, that ions do not move freely through a liquid, but move through a body. One of the most recognizable effects of the magnetic field is on the Brownian motion of ions and the triggering of ion transfer through membrane channels. Thus, exposure to a magnetic field affects the receptors in the cell and activates the transport chain of Ca^{2+} ions and triggers cell growth [5].

In most fermentation processes, reactions involved in the oxidation of simple sugars under anaerobic conditions include two stages: the oxidation of glucose and the metabolism of pyruvate. Glucose metabolism is carried out by glycolysis, similar to the process of aerobic or anaerobic respiration. The absence of oxygen, which can perform the role of an external electron acceptor, and the lack of ability to use inorganic alternatives such as sulphates and nitrates, leads to the need to regenerate the electron-carrying molecule NAD^+ by donating electrons to organic intermediates. In the fermentation of glucose by the yeast *Saccharomyces cerevisiae*, glycolysis is carried out through e^- transfer to NAD^+. Pyruvate decomposes into acetaldehyde and carbon dioxide, and for the regeneration of NAD^+, acetaldehyde is reduced to ethanol by accepting 2 e^- [6]. A significant amount of ethanol is needed to meet global needs, but the production of ethanol using free-state yeasts is inefficient due to the high cost of reuse

of yeast, the risk of contamination and susceptibility to changes that may occur in the fermentation medium [7].

A large part of the studies that followed the proliferation of *S. cerevisiae* in a magnetic field, have reached the same results, namely an inhibitory effect on cell development or no effect on cells; Ruiz-Gomez et al. applied a field between 0.35 – 2.5 mT and 50 Hz [8]; Nakasono et al., in an intensity field below 300 mT, at 50 Hz, for 24 h [9]; Ikehata et al. examined 5900 genes at a field strength of up to 14 T [10]; Binninger and Ungvichian, in the field of 20 μT at 60 Hz did not identify any effect on the cell division [11]; Iwasaka et al., tracked cell proliferation up to a field strength of 14 T [12]. The lack of a positive effect on cell development can be associated with the fact that proliferation studies were conducted by applying the magnetic field in the stationary stage, at which stage the cells acquired stress resistance mechanisms.

Assisting bioprocesses by applying magnetic or electromagnetic fields is an area of interest due to the potential to increase the performance of classical processes, both in the production of biofuels and in the food and cosmetic industries. The main research trends in the processes that use the activation of cells by applying an electromagnetic field are: carrying the cell growth stage or the fermentation stage in vessels totally exposed to electromagnetic fields; batch fermentation processes, in which the mixture is circulated through an external vessel, for constant exposure. The expectations in regards to assisting classical bioprocesses of bioethanol production through exposure to electromagnetic fields are to favor or limit the growth rate or metabolic processes of exposed microorganisms [5].

3.1 Fermentation studies without dry yeast cell growth period

I. The influence of SAR on the biological activity of *Saccharomyces cerevisiae* in the fermentation process

As part of the study on the impact of microwaves on the metabolic activity of yeast cells and productivity in bioethanol during glucose fermentation, the optimal microwave exposure range was identified in a first step by varying the specific absorption dose. Fermentation experiments were carried out simultaneously in the multimode applicator and in the thermostated water bath under the following reaction conditions: glucose concentration 120 g/L, reaction temperature 35°C, SAR 9.6, 15.7, 25 respectively 41.5 $W \cdot kg^{-1}$.

The experimental data obtained, suggest that exposure to microwaves has a beneficial effect on the process of glucose fermentation by *Saccharomyces cerevisiae*, obtaining higher concentrations of ethanol for all the cases studied compared to the average value obtained in the conventional process. The highest concentrations of ethanol correspond to the range 15.7 – 25 W. kg^{-1}, outside this range, there is a less significant increase than in the conventional process. This can be easily seen in Figure 24, in which the productivity in ethanol is represented for the cases studied after 10 h of fermentation.

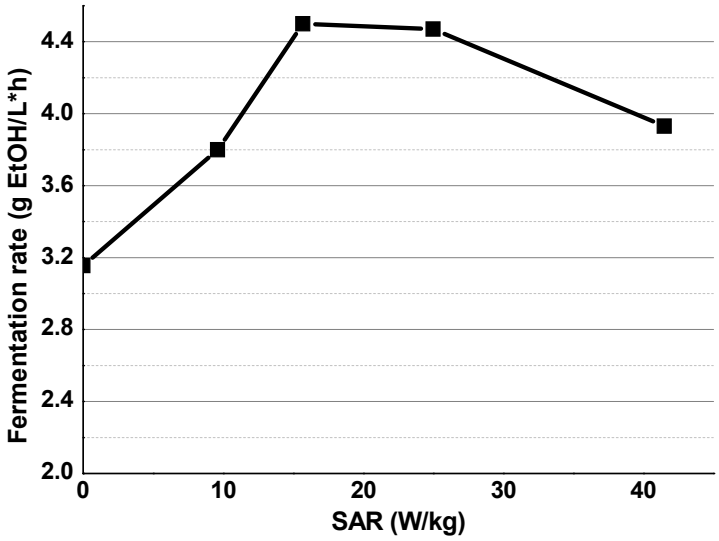


Figure 24. Influence of SAR on fermentation rate (120 g/L glucose, 35°C, 1.6 g yeast/100 mL)

Based on these results, we opted to perform the other experiments using a SAR value of 25 W· kg^{-1}, for which smaller variations in reflected power were observed, and thus a better reproducibility.

At the end of the fermentation process, the yeast was centrifuged and freeze-dried in order to perform SEM analyses, as to track the impact of microwaves on the morpho-structural characteristics of the cells. By comparing the images in figures 25-26 of the samples of *Saccharomyces cerevisiae* following 10 h of fermentation of a glucose solution of 120 g/L with an amount of 1.6 g of dry yeast/ 100 mL solution, without a growth period, at different SAR values it can be observed that the exposure to microwaves did not lead to any disturbances of the life cycle, in all the cases presented, young cells or at different stages of development can

be distinguished. The dimensions of the cells are within the same range in all the cases studied, with diameters of up to 4 μm, regardless of the microwave dose to which they were exposed.

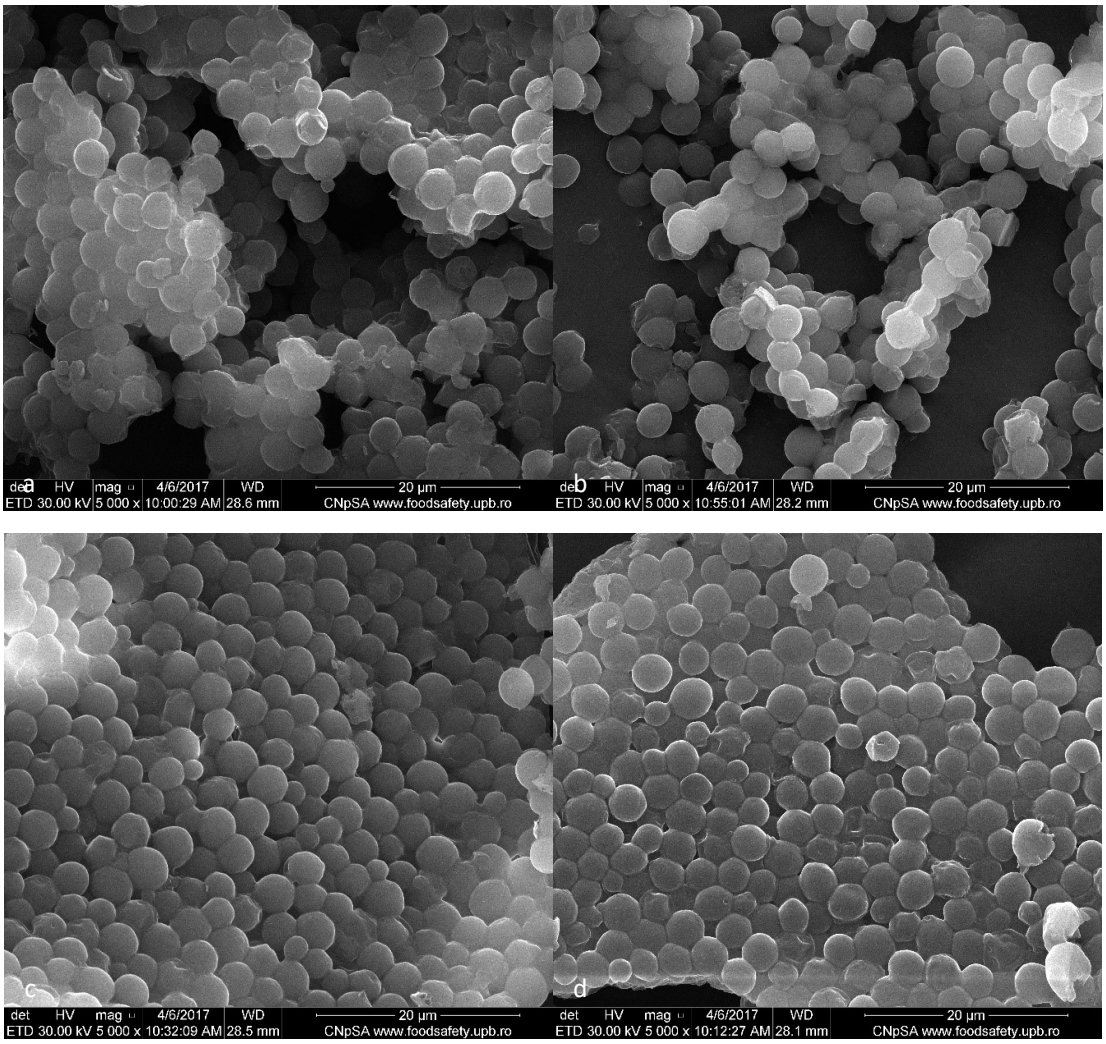


Figure 25. Samples of Saccharomyces cerevisiae at magnification 5000x, following 10 h of fermentation (1.6 g yeast / 100 mL glucose solution 120g/L, without growth period):
a – the classic process, b – microwaves (SAR = 9.5 W/kg),
c – microwaves (SAR = 25W/kg), d – microwaves (SAR 38.9 = W/kg)

In all cases studied, with and without a growth period and in the presence or absence of microwaves, dead or deformed cells can be identified. Correlating the information conferred by SEM with the results obtained in determining the cellular viability by microscopy, we can consider that in the field of SAR studied the effect of microwaves is not destructive, while the effect of microwaves on transmembrane mass transfer or on the permeability of the cell membrane is visible from the perspective of intensification of the fermentation process and productivity in ethanol.

II. Influence of the concentration of substrate on the biological activity of *Saccharomyces cerevisiae* in the fermentation process

Figure 27 shows the influence of substrate concentration on the biological activity of yeast cells in the glucose fermentation reaction at a specific absorption rate of 25 $W \cdot kg^{-1}$ compared to the reaction carried out under conventional conditions. Increase in glucose concentration from 90 to 120 $g \cdot L^{-1}$ led to an increase in the concentration of ethanol. Further doubling of the glucose concentration to 240 $g \cdot L^{-1}$ led to a decrease in the concentration of ethanol, which can be explained by the manifestation of the phenomenon of inhibition of yeast cells through the substrate.

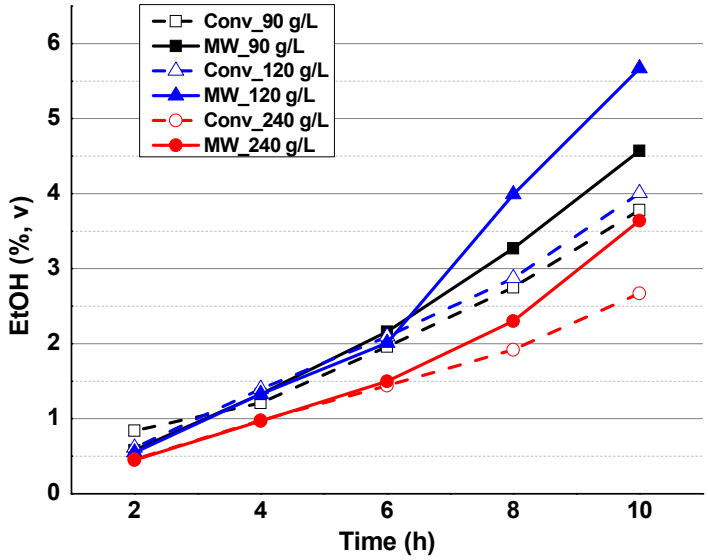


Figure 27. Influence of glucose concentration on the concentration of ethanol (25 $W \cdot kg^{-1}$; 35°C, 1.6 g yeast/100 mL)

3.2 Fermentation studies with dry yeast cell growth period

Growing yeast cells produce ethyl alcohol at a rate about 33 times higher than cells at rest. To increase productivity, part of the substrate should be consumed for the development of new cells. Maintaining cell in the growth phase for a longer time, a greater amount of carbohydrates is converted with high efficiency into alcohol. The reason behind the higher conversion rate of growing cells compared to those at rest may be that cells do not process sugars unless they need energy, so cells at rest will absorb and process sugars only for maintenance [6]. As energy production, ethanol and cell growth are correlated, efforts in

optimizing the fermentation process will have to be focused on keeping yeast in conditions that do not lead to low growth or death. For these reasons, it was proposed to conduct experiments in which young yeast cells are present in a higher share, cells that can be obtained as a result of cell multiplications over time. For this we worked with lower initial yeast concentrations, 0.16 g respectively 0.32 g dry yeast / 100 mL nutrient solution, which were increased under stirring on the thermostated water bath at 25 ° C for 1 h, respectively 16 h, in glucose solution with nutrients, equivalent to 10% of the total volume used in the fermentation process. The other working parameters were: glucose concentration of 60 $g \cdot L^{-1}$, fermentation temperature 35 °C, SAR 25 $W \cdot kg^{-1}$.

From Figure 28, it can be seen that mature cells reach sizes of the order of 3 to 4 μm, but depending on the stage of development of the cells they may have smaller sizes, young cells have a diameter of the order of 1 μm. From the point of view of the sphericity of the cell, no significant differences occur between the cells subjected to the conventional process and those exposed to microwaves, we can thus conclude that the stress exerted by microwave irradiation did not lead to significant deformation of the cells or the destruction of cell membranes. As expected in the case of yeast samples grown for 16 h at 25°C, young cells or cells with chickens can be observed in a higher proportion than in the case of samples without growth period, shown in the pictures below.

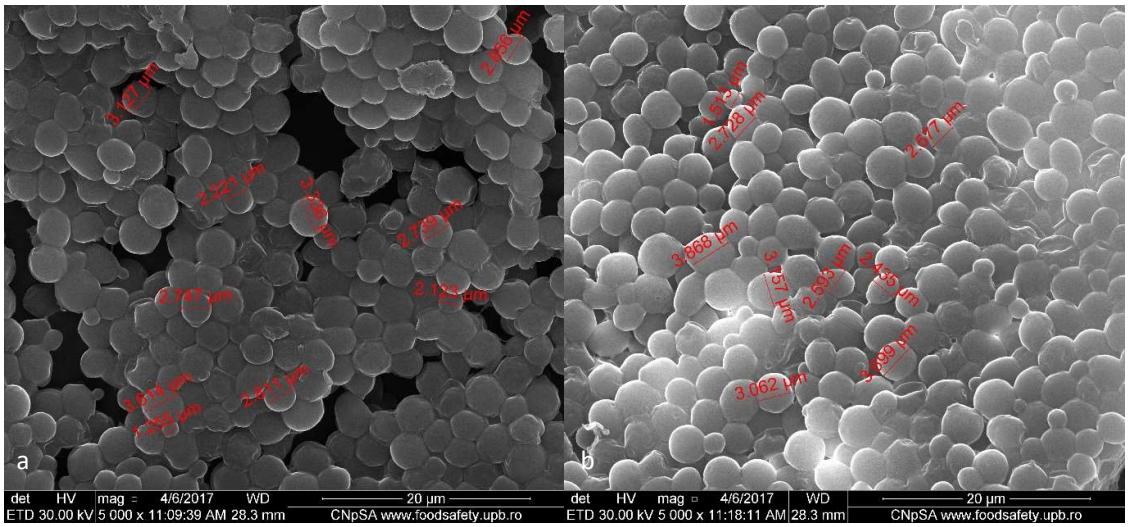


Figure 28. Samples of *Saccharomyces cerevisiae* at magnification 5000x, following 10 h of fermentation (0.32 g yeast/100 mL glucose solution 60g/L, with growth period of 16 h) a – the classic process, b – exposed to microwaves to a SAR of 25W kg^{-1}

3.3 Comparison of cell viability

The evolution of cell density during the fermentation process, determined by optical microscopy, showed that microwave exposure of cells of *Saccharomyces cerevisiae* had no negative impact on cell development. Although a significant increase in fermentation rate has been observed in samples exposed to microwaves compared to control samples, Figure 32 shows that no significant differences in cell density occur as a result of exposure to microwaves.

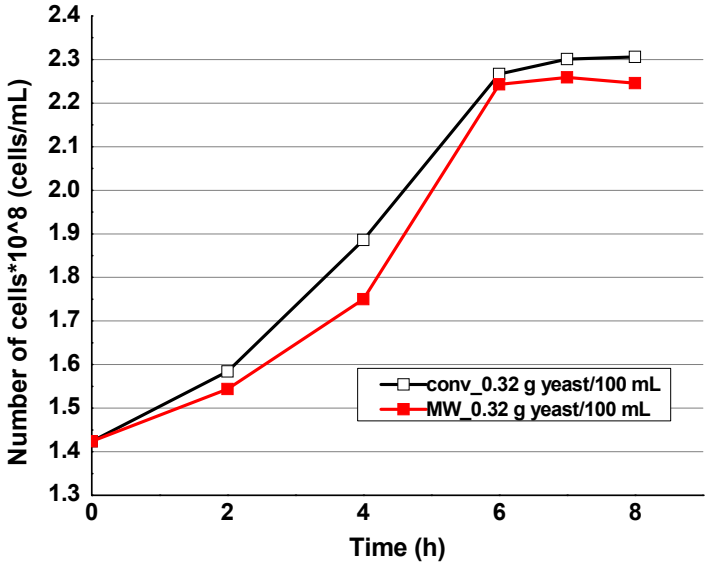


Figure 32. The evolution of the number of yeast cells over time (SAR 25 W· kg^{-1}; glucose concentration 60 g/L; 0.32 g yeast/100 mL nutrient glucose solution; temperature of 35 °C; growth period 16 h)

Based on optical microscopy, the cellular viability was determined, summarily presented in Table 6. During all the experiments carried out, it was confirmed that the exposure to microwaves in the field under study did not significantly affect cell viability, which is very close to the values obtained in the conventional process carried out under similar conditions of temperature, substrate concentration and initial concentration of dry yeast.

Table 6. Cell viability comparison after 6 and 8 h of fermentation respectively

Sample viability, [%]	Conventional	Microwaves
At 6 h of fermentation without growth	62.75	63.46
At 8 h of fermentation without growth	60.16	61.58
At 6 h of fermentation with 16 h of growth	68.44	70.95
At 8 h of fermentation with 16 h of growth	64.36	68.49

3.4 Thermal or non-thermal effect of microwaves. Influence of temperature on the biological activity of *Saccharomyces cerevisiae* in the fermentation process

In carrying out studies on the intensification of the microwave fermentation process, we have encountered the hypothesis that the superior results obtained in the case of irradiated samples, would be as a result of the thermal effects resulting from the application of microwaves, especially the different selective heating of the fermentation medium and yeast cells. In order to eliminate this hypothesis, additional studies have been carried out, at higher temperature values, and theoretical calculations have also been performed to determine whether selective heating is a significant factor in the performance of cells of *Saccharomyces cerevisiae* under the influence of microwaves.

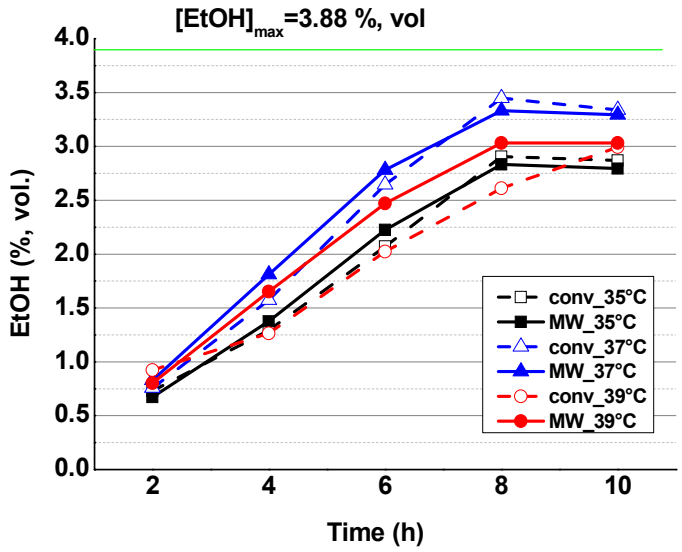


Figure 35. Influence of temperature on the concentration of ethanol (SAR 19.3 $W \cdot kg^{-1}$; glucose concentration 60 g/L; 1.6 g yeast/100 mL nutrient glucose solution, without a growth period)

The results obtained in conventional and microwave-assisted fermentation processes carried out at different reaction temperatures in the range of 35-39°C, are shown in figure 35, the data obtained show that the best results are obtained at 37 °C. For microwave-assisted processes, the concentration of ethanol is higher than that obtained in conventional processes, especially in the first part of the process (0 - 6 hours), towards the end of the process, when the concentration of ethanol is approaching its maximum, the values obtained in conventional and microwave-assisted processes have become similar. The most interesting result is the one obtained at 37°C. In this case, if the selective heating of yeast cells and implicitly the increase

in cell temperature were the driving force, then the results obtained in the microwave-assisted process would have been lower and closer to the ethanol concentrations obtained at 39°C in the conventional process. Instead, these results show that the microwave-assisted process at 37°C produces higher concentrations of ethanol than that of conventional processes at both the same temperature and 39°C. Moreover, the largest difference between the concentrations of ethanol obtained in the microwave assisted process compared to conventional processes occurs at 39°C, where heat stress is the most significant, the conventional process is carried out at the lowest speed.

4. PARTIAL CONCLUSIONS

- A plant has been developed that allows glucose fermentation in the presence of MW, with better control of both SAR and temperature in the environment. In all the experiments carried out, a positive effect of exposure to MW on the metabolic activity of yeast is observed, with concentrations of ethanol obtained by MW-assisted fermentation being higher than those in conventional processes.
- An optimal SAR range was determined, between 15 and 25 $W \cdot kg^{-1}$, providing a significant effect on the fermentation of glucose by Saccharomyces cerevisiae, with an increase in fermentation rates of up to 20%.
- Based on observations made through electron and optical microscopy on the growth and viability of cells, we have noticed that microwave irradiation favours the ethanol production of cells, and less the growth of cells.
- Experiments on the influence of temperature, supported by theoretical calculations, excluded selective heating as the main reason for the beneficial effect of microwaves on metabolic activity in the production of bioethanol.

PART II – SYNTHESIS OF ESTERS OF INFERIOR ALCOHOLS BY TRANSESTERIFICATION OF VEGETABLE OILS BY UNCONVENTIONAL METHODS

INTRODUCTION

Ultrasound is a form of mechanical energy that manifests itself in the form of waves that propagate at frequencies above the perception limit of the human ear, which is why the high amplitudes generally required for the processing of products in the food industry or in non-destructive material tests, can be generated without producing a painful stimulus on humans.

The air molecules dissolved in the solution diffuse and form bubbles that grow in areas of low pressure and are compressed in high pressure zones. These cycles continue until the external pressure becomes too high and the bubble collapses occur. As it compresses, the particles of material inside the bubble having high energy, emit light in the range of 200 to 800 nm for a very short period of up to 100 ps (1 ps = 10^{-12}s). This phenomenon is called sonoluminescence and has been used to determine the conditions in the bubble, concluding that during cavitation temperatures up to 5000 K and pressures of up to 1000 atm are reached. In the central region, called the hot spot, collisions occur between particles that generate energy with a value of up to 13 eV. Cases of ionization and plasma formation inside the bubble were recorded, depending on the solvents and compounds existing in the system.

Hydrodynamic cavitation can be generated by speeding a liquid through a narrow section such as a flow control valve, or through a plate or venturi device. When the liquid passes through a smaller section, its speed and kinetic energy increase, while the pressure decreases. When the pressure reaches the value of the liquid's vapor pressure at the operating temperature, bubbles are generated that will collapse as the pressure increases, but part of the energy will be lost as a permanent pressure drop. The great turbulence created will be present downstream, and the intensity of this turbulence depends on the pressure drop, which in turn depends on the geometry of the construction and the parameters of fluid flow. A proper design of the installation can lead to the generation of a phenomenon of cavitation similar to the acoustically generated cavitation, which allows the development of technological processes in similar conditions [13].

The reaction of transesterification with inferior alcohols of various oils has gained a lot of attention due to its use in the biodiesel industry. Catalytic transesterification can be divided into two main processes: chemical catalysis and biocatalysis. Chemical catalysis can be either heterogeneous or homogeneous. As for biocatalysis, enzymes are the main catalysts. The transesterification process can also be carried out without catalyst when supercritical conditions are used, where the pressure and temperature are above the critical point of the alcohol used. The commercial process currently used to obtain biodiesel, in homogeneous basic catalysis, is constrained by high operating costs, high energy consumption and long downtime [14].

The resistance to mass transfer exerted in the case of immiscible mixtures such as alcohol and oil during the transesterification reaction can be reduced by using ultrasound, which offers an innovative, efficient and attractive solution. By applying ultrasound in the transesterification reaction one can reduce the reaction time, energy consumption and increase the reaction speed compared to the conventional process [15]. In the conventional process of obtaining methyl esters by reacting methanol oils, the reaction occurs at the interface between the two immiscible phases, namely oil and methanol. In order to improve the reaction speed and conversion of the product, the interfacial area between these two immiscible phases must be maximized. Although conventional mechanical agitation can improve the surface area and mass transfer characteristics of the process, the development of ultrasound-assisted technologies has led to improved chemical reactions [16]. These technologies allow the use of ultrasound as a new, efficient, mixing tool in the production of esters from various raw materials [17]. Ultrasonication has already demonstrated the potential for use in a large number of applications, its use in the production of methyl esters being timely and justified by existing research work [18]. In general, the use of ultrasound leads to the emergence of physical and chemical effects on heterogeneous reaction systems through cavitation bubbles. Physical effects are related to the emulsification of immiscible liquids as a result of microturbulence generated by the movement of cavitation bubbles, while the chemical effect is associated with the appearance of free radicals during the collapse of bubbles. The increase in the interfacial surface between immiscible reactants leads to an increase in the reaction speed in a similar manner as in the case of the use of mechanical agitators, while the free radicals that form can induce or accelerate chemical reactions [19].

The papers published so far on the introduction of unconventional processes in the transesterification reaction have not allowed to solve the problems related to the transition from laboratory scale or pilot plant to industrial scale, which is why at present the transesterification

reaction in conventional basic catalysis remains the most widespread method of obtaining biodiesel. Numerous published studies have highlighted the benefits of using both microwaves and ultrasound, but the vast majority of these works take into account the effect of different process parameters (ratio of reactants, catalyst concentration) in the case of the implementation of one of the two unconventional techniques (microwaves or ultrasound). The field of combined use of microwaves and ultrasound for the intensification of chemical and biochemical reactions is a relatively new and poorly documented one.

3. RESULTS AND DISCUSSIONS

3.1 Biodiesel obtained by hydrocavitation

For the study of hydrocavitation, a piece of equipment, Figure 40, was used, consisting of an engine with a power of 2.2 kW, on the central axis of which a rotor provided with small indentations is mounted, and at a very short distance from it, a stator with a similar construction is mounted, both elements being shown in Figure 41. During operation, the shear forces exerted on the liquid in the space between the rotor and the stator, lead to the formation of bubbles and the appearance of the phenomenon of cavitation.

Figure 40. Hydrocavitation generator

The installation is also equipped with a centrifugal pump that can be connected to the hydrocavitation generator for the circulation of a larger volume of liquid or if a shorter residence time is desired in the reactor.

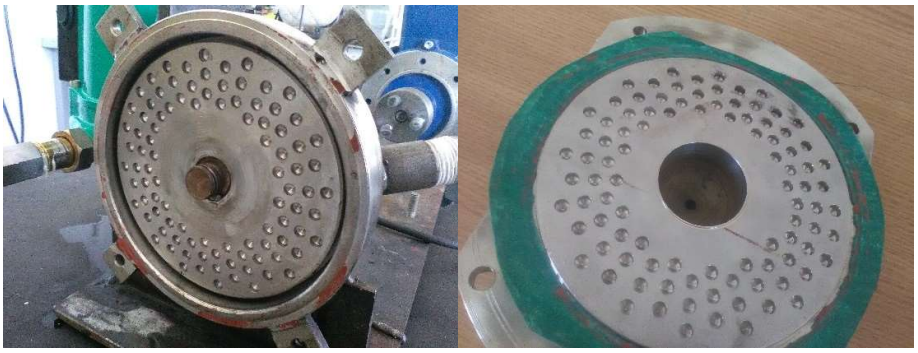


Figure 41. Rotor (left), respectively the stator (right) of the hydrocavitation generator

For a better understanding of this type of equipment, but also of the phenomenon of hydrodynamic cavitation in the context of the synthesis of methyl esters, a series of preliminary tests in different constructions were carried out, necessary to identify the limitations of this type of equipment.

IV. A single pass through the hydrocavitation reactor, with cooling jacket

A final construction was studied for the synthesis of hydrocavitation-assisted methyl esters, in which a cooling jacket was welded on the stator of the hydrocavitation reactor, in order to increase the heat transfer surface, according to figure 48. For this experimental set, it was chosen to use sodium hydroxide dissolved in methanol, as a catalyst, at different concentrations, and also parallel experiments were carried out in the conventional continuous flow process at short reaction times.

Figure 48. Hydrocavitation reactor installation in the construction of a single-pass and cooling jacket

In the hydrocavitation reactor used in these studies, the presence of two effects that contribute to the intensification of the transesterification process was observed, namely the effect of hydrodynamic cavitation and the effect of mixing. At lower temperature values, hydrodynamic cavitation manifests as the driving force, but as the temperature rises, the effect of cavitation diminishes, and the set-up becomes the equivalent of a conventional continuous-flow reactor, but with more efficient mixing of reactants.

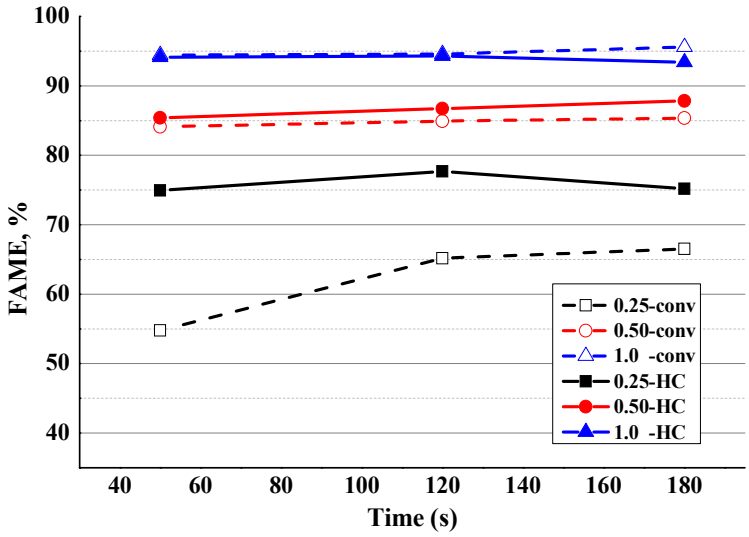


Figure 49. Influence of catalyst concentration and reaction time in the hydrocavitation assisted process

In the case of shorter reaction times, 50 and 120 seconds, high conversion values were obtained in this construction, results shown in Figure 49, but as the reaction time increases to 180 seconds, the reactor's performance does not improve, the temperature reaching 50°C in this case, and leading to a decrease in the effect of cavitation and to the possible favoring of side effects with the formation of soaps.

3.2 Biodiesel obtained by acoustic cavitation

For the study of intensifying the transesterification reaction with the help of acoustic cavitation, two types of equipment were used.

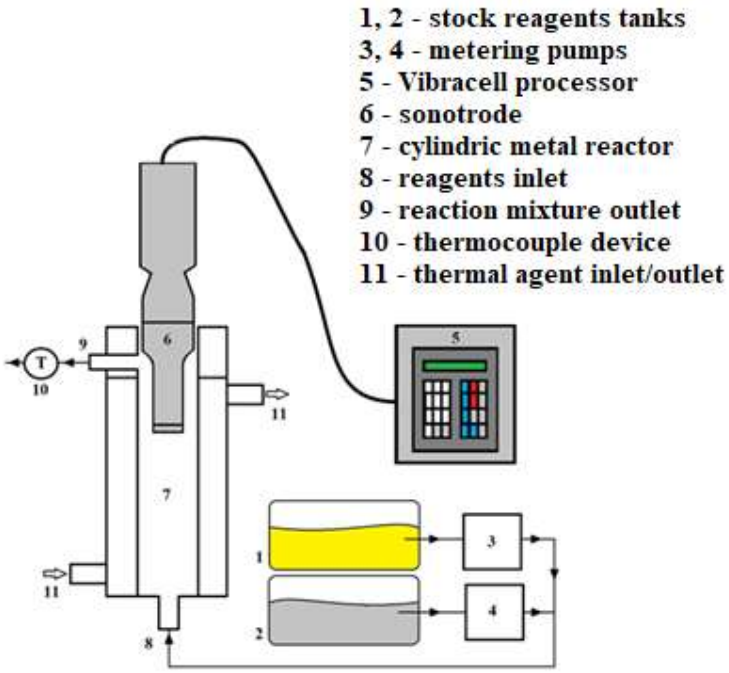
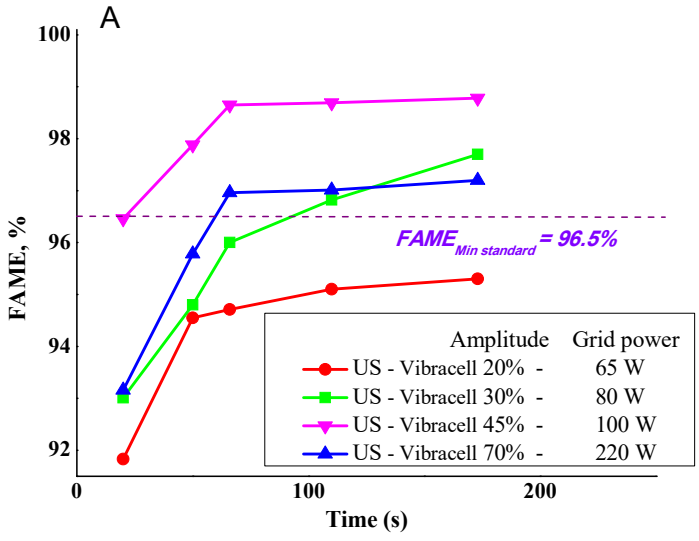


Figure 50. Schematic representation of experimental setup used for continuous ultrasound assisted biodiesel production, using the sonotrode system

The first set of experiments was carried out in a cylindrical metal reactor, equipped with a cooling jacket, and with outlets/inlets for reactants/products, in which the ultrasound probe of a Vibracell 750 processor is inserted, at the top of the reactor, according to figure 50. the reactants are pumped into the reactor through the inlet at the bottom of the metal reactor, while the reactants leave the enclosure through a side outlet, the position of which allows to obtain a reaction volume of 60 mL.



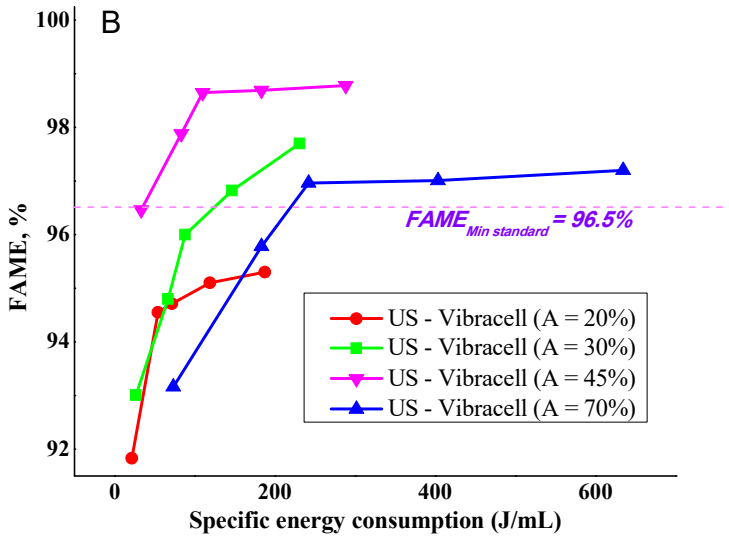


Figure 51. Influence of US power amplitude on the concentration of esters as a function of time (A) and specific energy consumption (B), NaOH catalyst concentration 1%, Vibracell system

The system with a sonotrode, led to obtaining the best results at an amplitude of 45%, according to Figure 51, corresponding to an ultrasound power of 70 W, with a network consumption of about 100 W. Experiments performed at an amplitude value of 70%, even at shorter reaction times, did not lead to better results, which suggests the existence of an optimal field of ultrasonic power specific to the geometry of the metal reactor used. The formation of cavitation bubbles near the tip of the sonotrode, can negatively affect the transfer of ultrasound energy to the reaction medium and implicitly lead to the reduction of process efficiency.

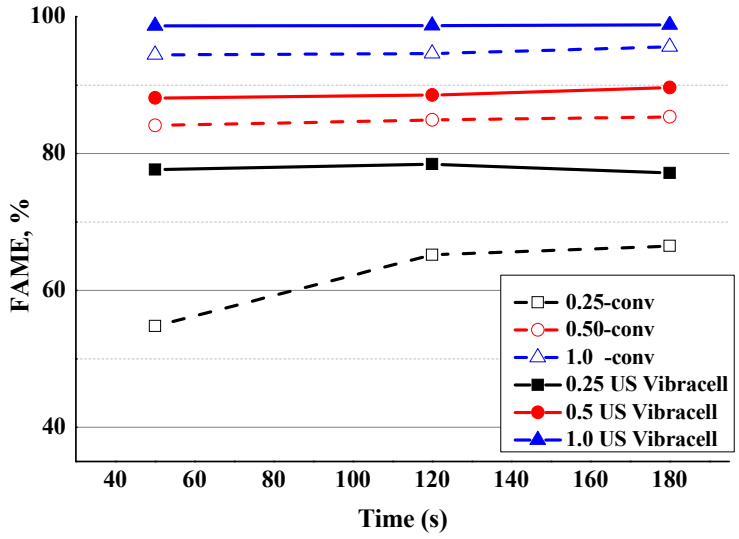


Figure 52. Influence of catalyst concentration, system with sonotrode, amplitude of 45%

The beneficial effect of acoustic cavitation in the system with a Vibracell processor, although it is more pronounced in the case of using a lower catalyst concentration, according to Figure 52, is visible even in cases where higher concentrations of catalyst are used.

The other type of equipment used, MMM Clamp-on type (AMMM – 400 W, frequency 20 kHz – 100 kHz, developed by MPI), consists of a glass tube with a volume of 40 mL, surrounded by a metal pipe, being shown in figure 53. The reactants pass through the inside of the glass tube, and through the space between the two elements, the thermal agent circulates, which also fulfills the role of coupling liquid for the transfer of ultrasonic energy to the reaction mixture. In this type of equipment, ultrasound is generated along the entire length of the metal pipe, but the mixing of the reactants proved to be insufficient, which is why a pre-mixer provided with a magnetic stirrer, is connected to the system before entering the Clamp-on. The reactants are continuously pumped through the pre-mixer at room temperature, and reach the reaction temperature of 40°C inside the reactor. Experiments were conducted at two amplitude values, 30 and 60%.

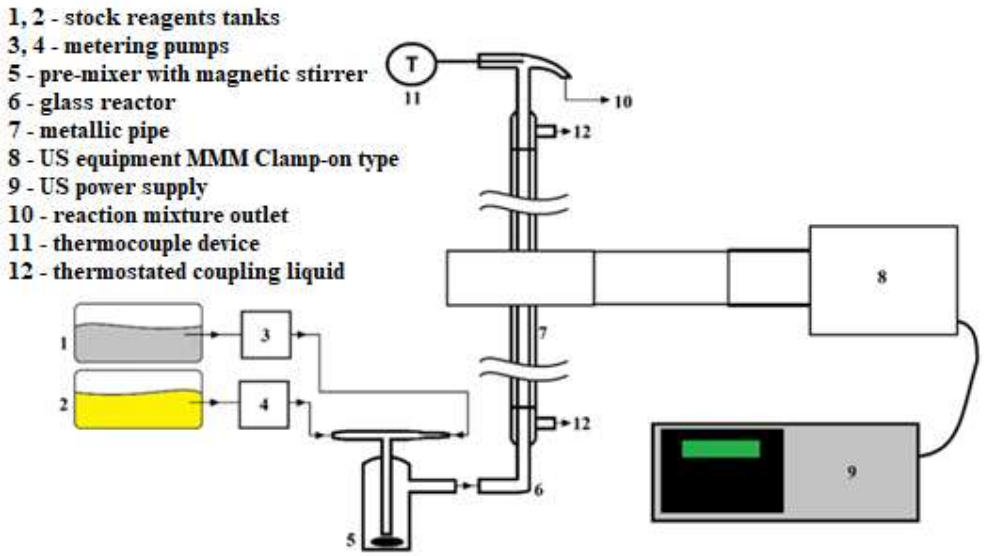


Figure 53. Sketch of the experimental plant for the production of biodiesel in continuous mode in the presence of ultrasound, MMM Clamp-on system

For the Clamp-on equipment, it is necessary to use a higher catalyst concentration to ensure the minimum ester content, but an amplitude value of 30 % and a reaction time of about 70 seconds proved to be sufficient to exceed the minimum required value, with a specific energy consumption lower than when using an amplitude of 60 %, as can be seen from Figure 54.

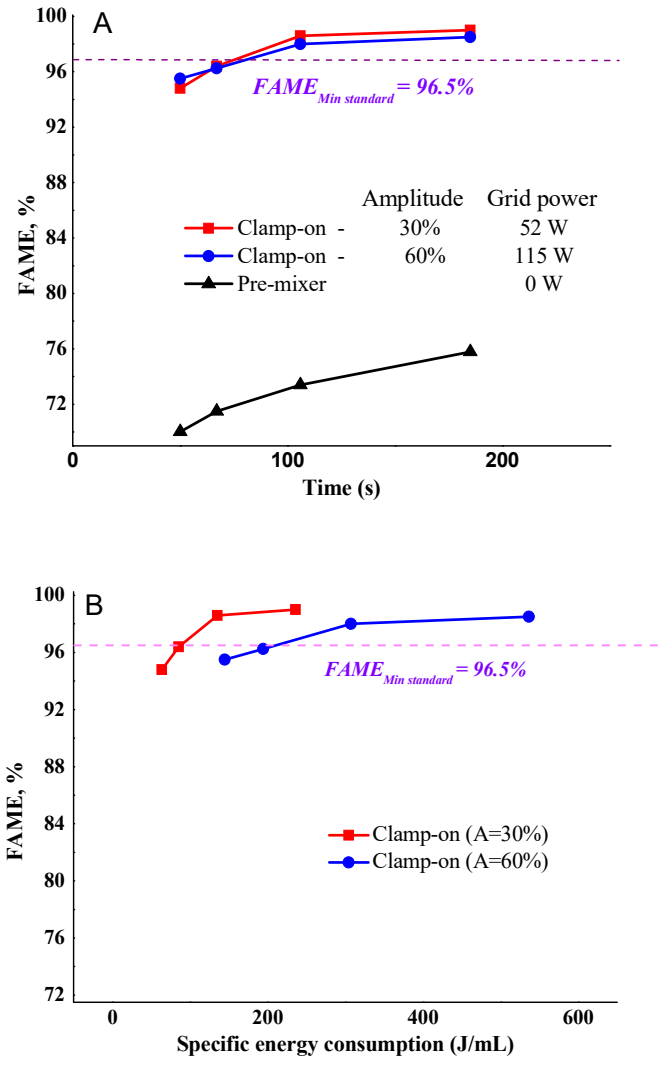


Figure 54. Influence of the amplitude of ultrasonic power on the concentration of esters as a function of time (A) and specific energy consumption (B), catalyst concentration 1%, MMM Clamp-on system

The propagation mode of ultrasound in the Clamp-on equipment, with the generation of radial vibrations along the length of the reactor, is not enough to ensure the mixing of immiscible liquids, which is why the pre-mixer was added, but its performance is not due exclusively to the pre-mixer, the conversion to FAME being about 76% after 180 seconds in the pre-mixer according to figure 54. The results obtained for an amplitude of 30 % by varying the catalyst concentration are shown in figure 55, in all the cases studied being obtained higher concentrations than in the conventional process.

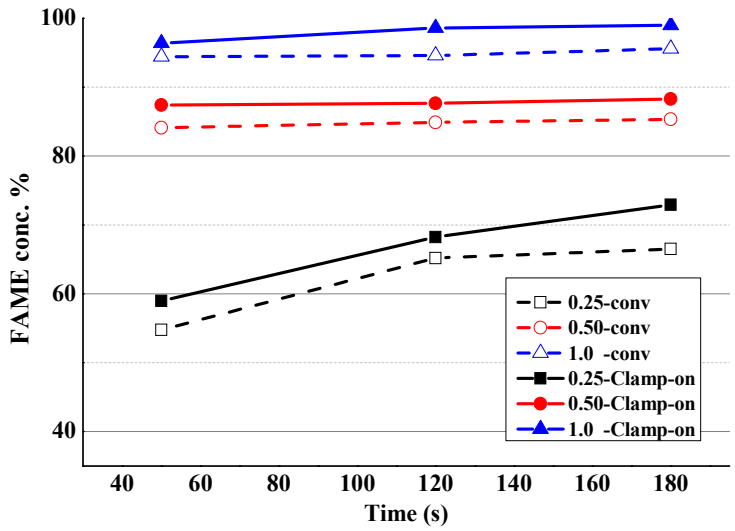


Figure 55. Influence of catalyst concentration, MMM Clamp-on system, amplitude 30%

3.3 Microwave assisted biodiesel production

For the study of the microwave-assisted transesterification reaction, two reactor-assisted constructions have been proposed. The first set of experiments involved the use of a cylindrical glass reactor with a silicone stopper and connections for oil supply, with methanol, respectively the exhaust and a sheath for the temperature sensor on the exhaust connection, shown in Figure 56. The reaction volume (70 mL) is controlled by the height of the glass tube through which the reaction products are discharged. The reactor being a closed vessel, the evacuation is carried out as a result of the pressure created inside the reactor, as the reactor fills up and the liquid level reaches the exhaust tube, the air in the system leads to the evacuation of the reaction products. The process was carried out using a Miniflow device in which microwaves are provided in a dose appropriate to maintaining the reactants at the set temperature of 60°C, the experiments being carried out at a molar methanol: oil ratio of 6 to 1, using potassium hydroxide in a concentration of 1% to the oil as a catalyst.

The process was studied in continuous regime, which is why the first 250 mL collected at the evacuation of the reaction products were not subjected to analyzes, to ensure the entry into continuous regime of the process, and only the next 100 mL were separated, dried and filtered for analysis, for each of the 3 downtimes that were studied. The experimental results corresponding to the samples obtained in the microwave-assisted process for different reaction times are presented in Table 16.

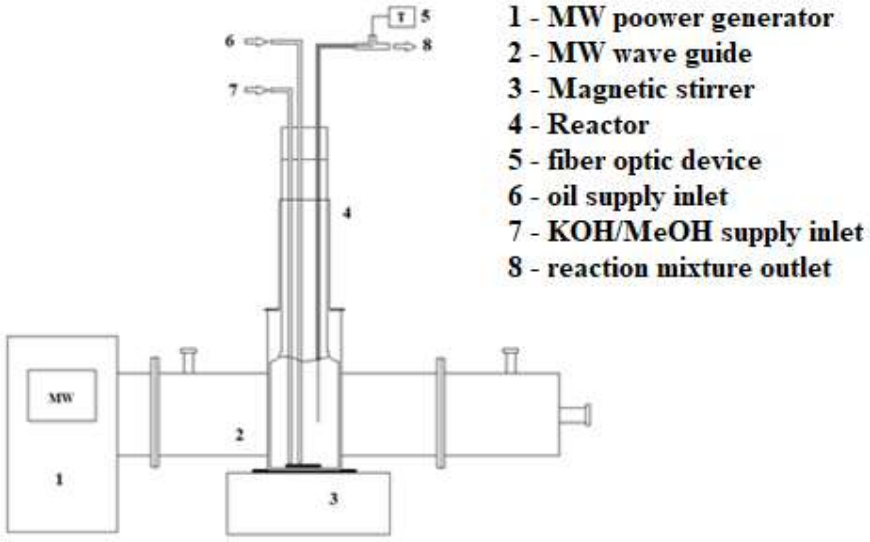


Figure 56. Sketch of the experimental plant for the production of biodiesel in continuous mode in the presence of microwaves, 70 mL reactor

Table 16. Influence of reaction time on the characteristics of reaction products in the microwave-assisted process in the 70 mL reactor

Reaction times	FAME, %	MG, %	DG, %	TG, %	Density 40°C (kg/m^3)	Viscosity (mm^2/s)
4'02"	93.8	0.45	1.35	4.4	875.9	4.30
2'	92.85	0.46	1.58	5.05	894.4	5.72
1'10"	90.21	0.52	2.39	6.35	876.0	4.26

The second set of experiments was conducted using a 60 mL reactor, in which the connections are welded directly to the reactor, according to Figure 57. The reactants are introduced into the reactor at the bottom, they are mixed by the magnetic stirrer, and the reaction products leave the reactor at the top, their temperature being monitored and serving as a control for microwave dosing to maintain a temperature of 40°C. The direct and reflected power is recorded continuously, along with the power consumed from the grid.

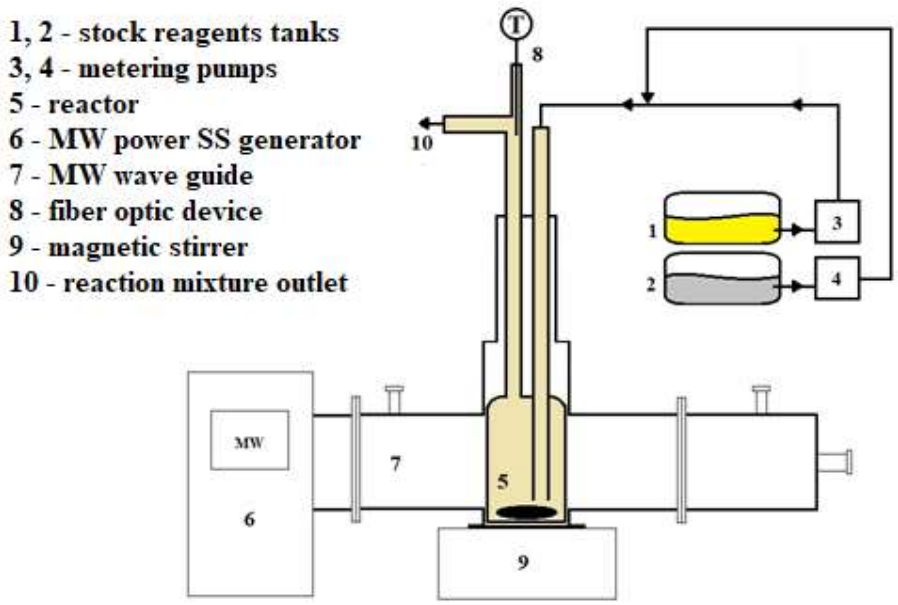


Figure 57. Sketch of the experimental plant for obtaining biodiesel in continuous mode in the presence of microwaves, 60 mL reactor

Experiments were conducted at a molar alcohol-to-oil ratio of 6 to 1, and at different catalyst concentrations, using NaOH in proportions of 0.25, 0.50, 1% against the oil.

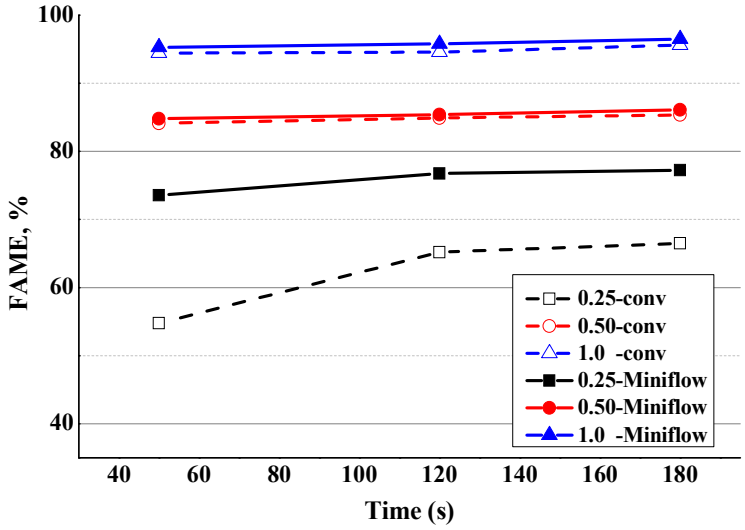


Figure 58. Influence of catalyst concentration and downtime in the microwave assisted process, 60 mL reactor

In this type of equipment, it is not possible to independently modify the microwave power, it is determined by the flow rate of the reactants and is limited by the temperature of

the products, which is why the power absorbed by the reactants is 28, 36 and 60 W for the flow rates corresponding to some downtime of 50, 120 and 180 seconds. From Figure 58, it can be seen that the beneficial effect of microwaves is very pronounced if the catalyst concentration is lower, namely 0.25% NaOH, but in this case the minimum FAME concentration of 96.5% cannot be reached, requiring a reaction time of 180 seconds and a catalyst concentration of 1%.

For all types of assisted processes, ultrasound in the configuration with sonotrode and clamp-on, microwave and hydrocavitation, energy consumption from the grid was recorded, and based on the residence time and volume of the reactor, specific energy consumptions could be estimated according to Table 17. The power consumption for the pre-mixer in the case of the Clamp-on equipment was included in the specific consumptions, namely 6.3, 15 and 22.5 J/mL, corresponding to the residence times 50, 120 and 180s respectively, and the network consumption of the pre-mixer was 5W.

Table 17. Specific energy consumption for the 4 types of assisted processes

Process activation method			**Network power, W**	**Residence time, s**		
				50	**120**	**180**
				Specific consumption, J/mL		
	Amplitude, %	**US Power, W**				
Vibracell (reactor volume=60 mL)	20	18	65	54.2	130	195
	30	33	80	66.7	160	240
	45	60	100	83.3	200	300
	70	160	220	183.3	440	660
MMM Clamp-on (reactor volume=40 mL)	30	-	52+5	71.3	171.0	256.5
	60	-	115+5	150.0	360.0	540.0
Microwave, (reactor volume=60 mL) Timp de rezidență:						
50 s			220	183.3		
120 s			170		440	
180 s			160			660
Hydrocavitation, (reactor volume =175 mL)			2200	629	1509	2263

The cost of biodiesel at the end of 2019 ranged from 0.8 to 0.84 euro/L, which corresponds to a price of 900 €/t. [20, 21]. The data presented in Table 18, obtained by calculating the energy contribution of each type of equipment to the total cost of biodiesel, shows that for the Vibracell type device, this contribution is between 0.08 and 0.5%, while for MMM Clamp-on it is between 0.29 and 0.62%, and for microwaves these is about 1.49%. This data could be useful for a small biodiesel production line, dedicated to farm-level use. Depending on the size of the farm and the annual consumption of diesel-type fuel, the selection

of one of the 3 types of equipment could ensure a biodiesel production of up to 100 t/ year without significant energy consumption.

Table 18. Production in biodiesel and energy consumption for each equipment used for a stationary time long enough to achieve the minimum ester concentration

Equipment	**Vibracell**			**MMM Clamp-on**		**Miniflow**
Amplitude, %	45	30	70	30	60	-
Residence time, s	20	100	60	68	70	180
Network power, W	100	80	220	57	120	220
Production, t/year	101.65	20.33	33.88	17.03	16.5	11.29
Total Energy per year, kWh	800	640	1760	458.3	964.8	1760
Energy consumption, kWh/t	7.87	31.48	51.94	29.91	64.81	155.83
Energy price, €/t	0.68	2.71	4.47	2.58	5.58	13.42
%	0.08	0.30	0.50	0.29	0.62	1.49

3.4 The synergistic MW-US effect in the transesterification reaction

For the study of the synergistic MW-US effect on the continuous transesterification reaction, the presented configuration for the synthesis of microwave-assisted biodiesel in the 70 mL reactor using the Miniflow 200SS equipment was used.

For this configuration, the magnetic stirrer was replaced by the ultrasonic bath in which paraffin oil was introduced, due to the ability to transmit ultrasound without allowing the occurrence of the phenomenon of acoustic cavitation. The ultrasound bath was connected by means of the internal cooling coil to a cryostat, in which the thermal agent is an ethylene glycol-water mixture in a volumetric ratio of 1:1 that allows cooling to the temperature up to - 30 °C. In order to ensure some mixing of the reactants, we opted for bubbling air in the reactor with the help of a compressor, according to figure 59.

The experiments were carried out starting from an alcohol-to-oil ratio of 6 to 1, using a catalyst concentration of 1% KOH, allowing the system to enter continuous regime.

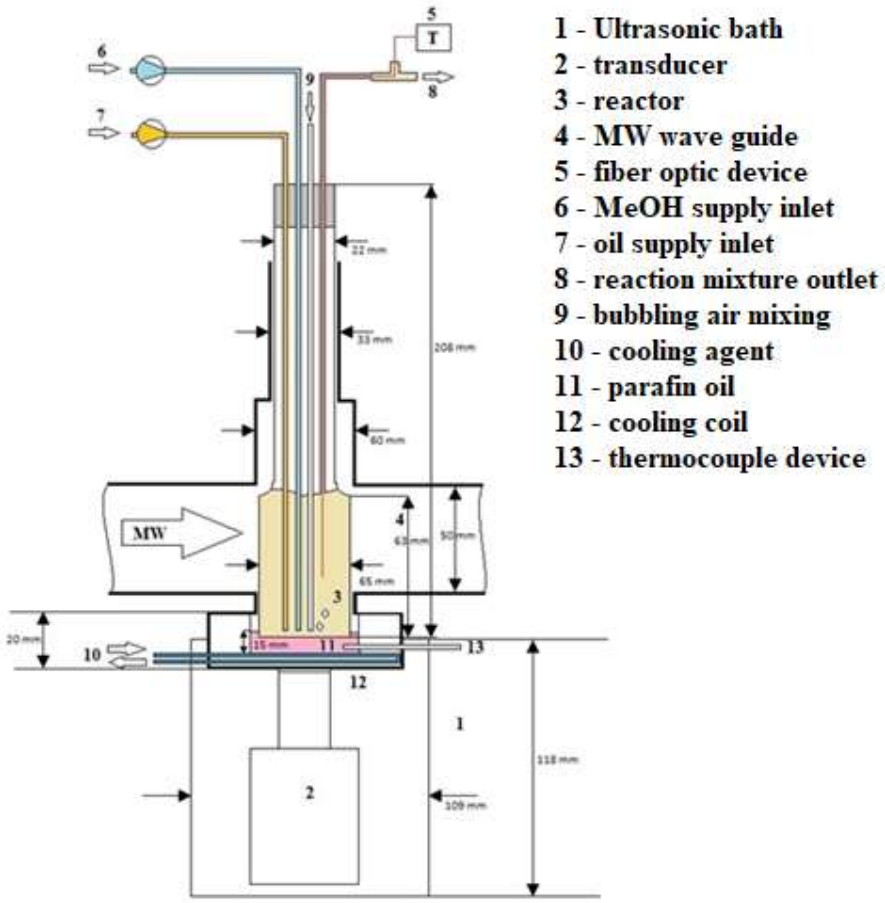


Figure 59. Sketch of the experimental installation for the study of the synergistic effect MW-US in obtaining methyl esters

Table 19. Influence of reaction time on the characteristics of reaction products in the microwave/microwave-ultrasound assisted process in the 70 mL reactor

Type of assisted process	Time	% FAME	Viscosity (mm^2/s)
MW+US without controlled cooling	4'28"	94.58	4.63
MW+US without controlled cooling	2'10"	92.94	5.10
MW+US without controlled cooling	1'14"	91.4	4.26
MW+US with controlled cooling	3'52"	95.38	4.17
MW+US with controlled cooling	2'03"	95.43	4.25
MW+US with controlled cooling	1'07"	91.07	4.71
MW	4'03"	93.8	4.92
MW	2'	92.85	4.27
MW	1'10"	90.21	4.35

The results obtained through GC analysis show that although the transesterification reaction is a fast one, completing and thus achieving conversions large enough to be in line with the existing standards requires a longer reaction time. The microwave and ultrasound assisted process reveals the beneficial synergistic effect, in both cases, with and without controlled cooling, the results, presented in Table 19, are better than those obtained in the process with mechanical agitation and microwave assisted.

3.6 Synthesis of FAEE under non-miscibility conditions

I. Influence of the type of oil used

For the comparative study of the ultrasonically assisted ethyl esters (Vibracell) extraction reaction, starting from different types of oils, the experiments were carried out in a reactor made specifically for the ultrasonic probe, with a conical bottom to allow for a better dispersion of ultrasound in the reaction mass, with a volume of 70mL, the plant being shown in Figure 68. The processes were conducted at a molar ratio of 1:6, NaOH catalyst concentration, 0.17% to the oil, percentage by mass, on the ice bath, the temperature being monitored in the reactor using a thermocouple with digital display, at a reaction time of 30 minutes.

Figure 68. Temperature evolution during discontinuous transesterification using the Vibracell processor in the metal reactor

For the determinations of cloud point, glass vials, fitted with magnetic stirrer, were used, into which the oil and alcohol without catalyst were introduced, and glass tubes provided with mechanical agitation for the reaction products. For both determinations, the temperature was increased, respectively decreased, gradually, checking the degree of turbidity at intervals

of 5 °C. When the mixture seemed clear, allow it to cool/heat and check in incremental degrees whether it is cloudy or not in order to increase the accuracy of the measurement.

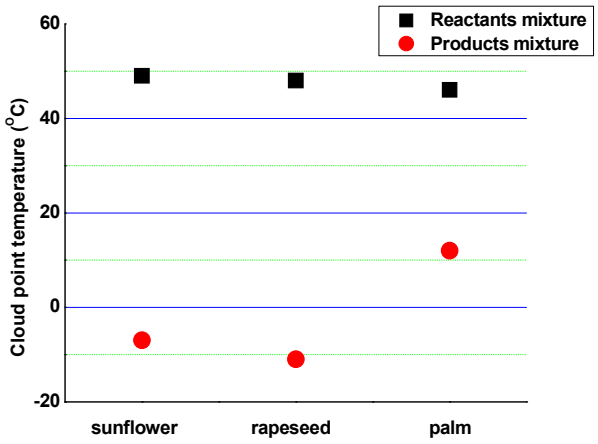


Figure 69. Influence of the type of oil on the cloud temperature

The values obtained for oil-ethanol mixtures are relatively close, a more significant difference occurs in the case of products, as can be seen in Figure 69, where the presence of unreacted palm oil leads to disturbance of the mixture at a temperature higher than that of the samples obtained from sunflower and rapeseed.

Table 23. FAEE synthesis assisted by US starting from different types of oil

	Sunflower		Rapeseed		Palm	
Power US (W)	29	90	29	89	31	91
Amplitude (%)	30	70	30	70	30	70
Energy (J)	52313	162676	52739	160184	55924	163519
Time (min)	30	30	30	30	30	30
Maximum temperature (°C)	30	45	30	48	25	46
FAEE content (%)	78.88	78.40	47.39	39.81	70.08	62.85

In the ultrasound-assisted process, the increase in the ultrasonic power leads to an increase in temperature during the course of the reaction, the temperature being recorded inside the reactor according to Table 23. It can be seen that the beneficial effect of ultrasound is more pronounced in the case of sunflower oil and palm oil, and less in the case of rapeseed oil. As for palm oil, the rather high melting point makes it difficult to process, being necessary to carry the separation at higher temperatures to avoid solidification of the unreacted oil and the

incorporation of the ester. In the case of ethyl esters in sunflower, the potential of vacuum distillation to increase purity was also pursued.

Figure 70. Vacuum distillation set-up used for the purification of ethyl esters

Based on the results obtained through GC, confirmed by the TGA analysis, a purity of over 97 % was achieved in FAEE, without the purification method leading to the formation of degradation by-products. The installation used consisted of a round-bottomed flask into which an air-bubbling capillary was inserted, a distillation head fitted with a thermometer, a descending refrigerant, a collecting flask, a vacuum pump and a heating nest, as shown in Figure 70. For the distillation of ethyl esters, in the first step a light fraction is collected, consisting mostly of alcohol, at a peak temperature of about 80 °C, at atmospheric pressure. When the light fraction no longer appears to distil, remove the heating nest, change the collection flask, and start collecting the ester-rich fraction, simultaneously starting the heating and vacuum pump, the esters collecting to a peak temperature of 220 °C and at a pressure of up to 20 mmHg.

From the TGA analysis, a similar behavior can be observed in the case of the 3 oils, with only a small difference in terms of maximum temperature. It is noticed that sunflower oil has a slightly higher thermal resistance, the order depending on the temperature being palm oil, rapeseed oil, respectively sunflower oil. In all cases, the absence of the formation of a residue as a result of heating the oil is observed, confirming that the loss of mass at a single stage is appropriate to an evaporation process.

The TGA curves of ethyl esters from sunflower oil by transesterification with ethyl alcohol were compared with the TGA analysis of sunflower oil. The non-distilled samples are composed of by-products, which have been removed after distillation under vacuum. In the case of the FAEE, a single step of mass loss is observed confirming its purification by

distillation. For the non-distilled product, 2 loss-of-mass steps corresponding to the ester, in the first step, and to the raw material in the second step, are observed. From the evaluation of the curve for the non-distillated product it is noted that the oil represents approximately 16%, percentage by mass, this corresponds to an esters concentration of 84% compared to 78% from the GC determination. This conclusion is based on the fact that before the TGA analysis the transesterification product was subjected to the washing and separation of the phases for the removal of glycerin.

In the case of FAEE from rapeseed oil, two steps of mass loss can be observed. The first step corresponds to the ester while the second corresponds to the fraction of oil not transformed or partially transformed. From the data obtained, an ester concentration of 55% was determined compared to 47% from GC analysis without separation. In the case of palm oil, three steps of mass loss were observed, the first of 5.4% corresponds to the unreacted alcohol but which was embedded in the organic phase by the unreacted palm oil, the second step corresponds to the evaporation of the FAEE, 73.9% compared to 70% from GC analysis, and the last step corresponds to the unreacted or partially reacted oil. From both the TGA analyses and the GC analyses, it was observed that the sunflower oil allows to achieve a higher concentration of FAEE, and its purity can be increased by vacuum distillation of the reaction product.

II. Use of inorganic salts

In the case of the addition of inorganic salts initially, the impact of the presence of salts on the point of disturbance of the reactants was monitored. Based on the literature data on the solubility in ethyl alcohol of the proposed inorganic salts, almost saturation alcoholic solutions were prepared starting from potassium iodide, potassium bromide and sodium bromide. Data on disturbance temperatures are presented in Table 24. For the synthesis reactions, sodium and potassium bromides were chosen to be compared, which also have higher solubilities in ethyl alcohol. The reactions were carried out with the help of the Vibracell probe.

Table 24. Effect of the use of inorganic salts on the cloud temperature of the reaction mixture

Salt	**KI**	**KBr**	**NaBr**
m_{salt} (g)	0.05	0.1025	0.1
$m_{alcohol}$ (g)	4	4	4
Concentration (mass %)	1.23	2.54	2.44
Oil: Alcoholic solution ratio	1:6	1:6	1:6
Cloud temperature (°C)	47	49	61

Table 25. Comparison between the use of sodium bromide and potassium bromide in terms of FAEE content and the cloud temperature of the reaction products

Salt	KBr	NaBr
Salt content, % by mass (versus mixture)	0.5	0.5
Reaction time, min	30	30
Amplitude, %	20	20
Energy, J	27650	27532
Power, W	15.4	15.3
FAEE content, %	46.1	50.8
Cloud temperature (°C)	-5	-6

As can be seen from Table 25, the use of sodium bromide has led to a higher FAEE content than with the use of potassium bromide, which is why we have opted for the use of sodium bromide in the study of the effect of using an aqueous solution of inorganic salt.

III. Use of aqueous solution of NaBr

By adding an aqueous solution of sodium bromide, it was desired to take advantage of the high solubility of sodium bromide in water and to trace the effect of the presence of water on the reaction in both the conventional and ultrasound-assisted process. The presence of water in the reaction leads to the consumption of the catalyst, with the obtaining of soaps, but if an increase in productivity could be achieved in the presence of water, a reduction in the costs associated with the ethanol dewatering stage in order to obtain absolute alcohol would be achieved. Before the reaction was carried out, the aqueous solution of 50% concentration was prepared by dissolving the potassium bromide in distilled water, from which the equivalent of water corresponding to the use of 96% purity ethanol was used in the reaction.

Figure 76. Ultrasound-assisted synthesis of ethyl esters in the presence of an aqueous solution of sodium bromide

As can be seen from Figure 76, the presence of water led to an increase in the degree of non-homogeneity of the reaction mixture, unlike in previous cases in which a few minutes after the start of the reaction a clarification of the mixture took place, in this case the presence of water allowed a separation of the phases and a maintenance of the heterogeneity of the mixture. Immediately after stopping the magnetic shaking, phase separation also took place.

Table 26. Effect of the use of aqueous NaBr solution on the cloud temperature of the reaction mixture

	Conventional	**US continuous**	**US pulses**
Reaction time, min	30	30	60
Reaction temperature (°C)	35 (±1)	35 (±1)	34 (max)
Amplitude, %	-	20	70
Energy, J	-	25231	157534
Power, W	-	14	43.8
FAEE content, %	10.1	15.2	17.6
Cloud temperature of reactants (°C)	93		
Cloud temperature of reaction products (°C)	99	92.6	86

The presence of water in the reaction led to a drastic decrease in conversion as a result of consuming the catalyst in the secondary reactions as expected, as soon as the mixing stopped, the phase separation took place. The use of ultrasound in this case highlighted the beneficial effect of the asymmetrical collapse of bubbles specific to heterogeneous systems, leading to an increase in the content of FAEE compared to that obtained in the conventional process, as can be seen in Table26. In order to diminish the effect of saponification, it was proposed to increase the amount of catalyst.

Table 27. FAEE concentration comparison in the presence of aqueous NaBr solution

	Conv.	**US**	**Conv.**	**US**	**Conv.**	**US**
NaOH catalyst concentration (% vs. oil)	0.17	0.17	0.5	0.5	0.5	0.5
Reaction temperature (°C)	35 (±1)	35 (±1)	35 (±1)	35 (±1)	50(±1)	50(±1)
Amplitude, (%)	-	20	-	20	-	20
Energy, (J)	-	25231	-	28650	-	25088
Power, (W)	-	14	-	15.9	-	13.9
FAEE content, (%)	10.1	15.2	29.5	33.3	22.25	28.15
Cloud temperature of reactants (°C)	93					
Cloud temperature of reaction products (°C)	98-99	92-93	92-93	90-91	92-93	93-94

By increasing the concentration of the catalyst from 0.17% to 0.5% there is an increase in the concentration of FAEE, as a result of the increase in the reaction speed, but the increase in temperature from 35 to 50°C has been shown to be detrimental to the reaction of obtaining ethyl esters. The temperature of the product disturbance was not much different from the reaction temperature of the mixture of reactants in the absence of catalyst, i.e., 93°C. Although the concentrations obtained in US-assisted processes are higher than those obtained in the conventional process at the same temperature, by increasing the catalyst concentration the beneficial effect of ultrasound diminishes, thus from an increase in the concentration of FAEE of 50% compared to conventional in the case of the US-assisted process using a catalyst concentration of 0.17%, at a concentration of 0.5% the increase in the concentration of FAEE as a result of the use of US is 13% at 35°C and 25% at 50°C respectively. The data obtained are given in Table 27. By increasing the amount of catalyst to 1% the gelling of the samples took place almost immediately after the end of the reaction, as a result of the side-reactions favored by the use of a larger amount of catalyst.

4. PARTIAL CONCLUSIONS

- Transesterification processes with ultrasound and microwaves in continuous flow have been developed and compared in terms of the concentration of methyl esters and specific energy consumption.
- The use of these process intensification methods has proven to be useful in obtaining higher conversion values for short reaction times.
- Two of the processes involving the use of an ultrasound and a Clamp-on MMM equipment were the most promising for the small-scale production of biodiesel, the improvements being due to the better mass transfer between the two immiscible reactants through the formation and collapse of the asymmetric cavitation bubbles.
- The main disadvantage of the large-scale transition of ultrasonically based processes is related to the potential volume limitation of the reactor due to the low depth of ultrasonic penetration, a problem that can be eliminated by opting for a device based on hydrodynamic cavitation.
- Large-scale production of esters would be most easily achieved by increasing the number of transesterification reactors, and not by increasing the size of a single reactor.

GENERAL CONCLUSIONS

The purpose of this doctoral thesis was to capitalize on unconventional process intensification techniques for the synthesis of biofuels, with a special emphasis on bioethanol, by using the biological effects of microwaves to favor the metabolic activity of *Saccharomyces cerevisiae* yeast, and biodiesel, by developing continuous-flow biodiesel production facilities.

Based on the research strategies adopted and the experimental results obtained, the following conclusions can be formulated:

- An optimal range of exposure of yeast to microwaves has been identified, between 15 and 25 $W \cdot kg^{-1}$, for which an increase in fermentation rate of 20% was achieved, the beneficial effect being due to the non-thermal effects of microwaves.
- The possibility of temperature gradients being present in the fermentation vessel was excluded by modelling, and theoretical calculations excluded the manifestation of the phenomenon of selective heating as the main driving force for the intensification of the process.
- In the irradiation interval studied, no pronounced negative effects of microwaves on the viability and structure of yeast cells have been identified.
- Experimental installations in continuous flow assisted by ultrasound, microwaves and hydrocavitation were made to obtain methyl esters, which allowed the comparison of process intensification techniques in terms of energy efficiency and efficiency.
- In the configurations studied, ultrasound-assisted processes have been identified as more efficient than those assisted by microwaves and hydrocavitation.
- High purity ethyl esters were synthesized for testing as alternative solvents.

PERSPECTIVES

Taking into account the results of this work, among the potential directions of expanding and adding value to the work, it can be identified the obtaining of an integrated system in which the bioethanol obtained by microwave-assisted alcoholic fermentation can be recovered by distillation and used for the synthesis of ethyl esters, which can serve as green solvents for the extraction of fat-soluble biocompounds from biomass, and the depleted biomass to be used as a substrate for fermentation, aiming to obtain streams of high-value products. Another direction of capitalization of the research results is the implementation of pilot installations at farm-type economic agents, in order to obtain biofuels for their own use

using raw materials available at the location of the economic agent, ensuring the energy autonomy of the partner.

PERSONAL CONTRIBUTIONS

The elements of originality that are distinguished as a result of this research are:

- Realization of an experimental installation that allows the monitoring of temperature and microwave power during the fermentation process, made from a "solid state" microwave generator with a coaxial antenna
- Highlighting the importance of the specific microwave absorption dose by identifying an optimal range for the fermentation process
- Realization of the installations for the synthesis of methyl esters in continuous flow with an accurate monitoring of the specific energy consumption, which allowed the establishment of the most efficient process of intensification of transesterification
- Realization of a continuous flow installation that allowed the highlighting of the microwave-ultrasound synergistic effect in the synthesis of methyl esters
- Development of a method of synthesis and purification of ethyl esters so that they can be used as green solvents for fat-soluble compounds.

DISSEMINATION OF RESULTS

Published articles

1. **Vlaicu A.**, Calinescu I., Posea C., Chipurici P., 2021, A study on methyl and ethyl esters production - from seed preparation to product purification, *U.P.B. Sci. Bull.*, Series B, Vol. 83, Iss. 2, 2021; FI=0.53
2. Diacon A., Călinescu I., Vinatoru M., Chipurici P., **Vlaicu A.**, Boscornea A.C., Mason T.J., Fatty Acid Ethyl Esters (FAEE): A New, Green and Renewable Solvent for the Extraction of Carotenoids from Tomato Waste Products, *Molecules*, Vol. 26, Iss. 14, 2021, 4388; FI 2020 = 4.411
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Conference attendance

1. **5th Green and Sustainable Chemistry Conference 2020**, Dresda, Germania - Chipurici P., **Vlaicu A.**, Calinescu I., Vinatoru M., Ignat N., Voicu G., Diacon A., Heterogeneous catalyst activation and process intensification of biodiesel synthesis using ultrasound
2. **5th Green and Sustainable Chemistry Conference 2020**, Dresda, Germania - **Vlaicu A.**, Diacon A., Rusen E., Busuioc C., Chipurici P., Ignat N., Calinescu I., Vinatoru M., Biodiesel synthesis through heterogeneous catalysis using organic bases supported on magnetic silica nanoparticles
3. **4th International Caparica Conference on Ultrasonic-based Applications: from analysis to synthesis 2020**, Costa de Caparica, Portugalia - Calinescu I., Vinatoru M., Chipurici P., **Vlaicu A.**, Ignat N., Mason T., Ultrasonic, hydrodynamic and microwave biodiesel synthesis – A comparative study for continuous process
4. **Chemisty Conference for Young Scientists - ChemCYS 2020**, Blankenberge, Belgia - **Vlaicu A.**, Chipurici P., Calinescu I., Diacon A., Vintila A., Vinatoru M., Study on the effects of microwave and/or ultrasound during the pretreatment with DMP of wet *Nannochloris sp.* biomass
5. **International Chemical Engineering & Catalysis Conference 2019**, Londra, Marea Britanie - Chipurici P., Diacon A., **Vlaicu A.**, Calinescu I., Vinatoru M., Intensification of

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6. **21st Romanian International Conference on Chemistry and Chemical Engineering (RICCCE) 2019**, Constanta-Mamaia, Romania - Chipurici P., Diacon A., Calinescu I., Vinatoru M., Trifan A., **Vlaicu A.**, Optimization of Ultrasound - Assisted Extraction (UAE) of Lycopene from Tomato Skins
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9. **4th Asia-Oceania Sonochemical Society Conference 2019**, Nanjing, China - Calinescu I., Vinatoru M., **Vlaicu A.**, Chipurici P., Trifan A., Ultrasonic and hydrodynamic biodiesel synthesis-energetic considerations for continuous reactor
10. **4th Green and Sustainable Chemistry Conference 2019**, Dresda, Germania - **Vlaicu A.**, Chipurici P., Vintila A., Calinescu I., Vinatoru M., Trifan A., Diacon A., Effects of processing parameters on ultrasound-assisted carotenoids and chlorophyll extraction from *Nannochloris sp.* and *Arthrospira platensis* dry biomass determined by factorial experiment design
11. **2nd Young Researchers International Conference on Chemistry and Chemical Engineering (YRICCCE II) 2018**, Budapest, Hungary - **Vlaicu A.**, Calinescu I., Chipurici P., Vinatoru M., A comparative study of hydrocavitation and ultrasound assisted biodiesel production
12. **The international symposium "Priorities of Chemistry for a Sustainable Development - PRIOCHEM" 2018**, Bucharest, Romania – **Vlaicu A.**, Chipurici P., Calinescu I., Effects of microwave exposure on cell viability of *Saccharomyces cerevisiae* during glucose fermentation
13. **16th Meeting of the European Society of Sonochemistry 2018**, Besancon, France - Calinescu I., Vinatoru M., Chipurici P., **Vlaicu A.**, Biodiesel Synthesis Assisted by Ultrasound, Microwave and Hydrodynamic Cavitation – A Comparative Study

14. **20th Romanian International Conference on Chemistry and Chemical Engineering (RICCCE) 2017**, Poiana Brasov, Romania - **Vlaicu A.**, Chipurici P., Lavric V., Ighigeanu D., Calinescu I., Unconventional methods for enhancing the fermentation process
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16. **20th Romanian International Conference on Chemistry and Chemical Engineering (RICCCE) 2017**, Poiana Brasov, Romania - Lavric V., Calinescu I., **Vlaicu A.**, Chipurici P., Modeling microwave heating in a multimod applicator – Comsol approach
17. **16th International Conference on Microwave and High Frequency Heating AMPERE 2017**, Delft, The Netherlands - Calinescu I., **Vlaicu A.**, Chipurici P., Lavric V., Ighigeanu D., Alcoholic fermentation in the presence of microwaves

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