UNIVERSITATEA NAȚIONALĂ DE ȘTIINȚĂ ȘI TEHNOLOGIE ”POLITEHNICA” BUCUREȘTI

ȘCOALA DOCTORALĂ DE INGINERIE CHIMICĂ ȘI BIOTEHNOLOGII

FACULTATEA DE INGINERIE CHIMICĂ ȘI BIOTEHNOLOGII

DEPARTAMENTUL DE BIORESURSE ŞI ŞTIINŢA POLIMERILOR

THESIS

Intensificarea proceselor cu ajutorul microundelor și ultrasunetelor

Intensification of processes with the help of microwaves and ultrasound

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Doctoral thesis summary

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CONTENT

B. OBJECTIVES OF THE EXPERIMENTAL STUDY

Three research directions were pursued:

- The efficiency of resonant, multimode, and monomode microwave applicators;
- The effect of the position and shape of the reactor on the transfer of ultrasonic energy in a single transducer bath;
- Design and testing of an installation for the combined use of ultrasound and microwaves to enhance physico-chemical processes.

Each research direction had its specific objectives:

- **Eficiența aplicatoarelor de microunde, rezonant, multimod și monomod**

- Designing and constructing a resonant microwave applicator.
- Experimentally assessing the resonant applicator's performance, focusing on energy transfer efficiency and heating uniformity. Conducting comparative tests between the resonant applicator and conventional applicators (monomode or multimode) using various liquids with different microwave absorption capacities.
- Utilizing Comsol for modeling the three types of applicators and comparing the simulation results with the experimental findings.

- **Effect of the position and shape of the reactor on the transfer of ultrasonic energy in a single transducer bath**

- Developing an experimental methodology that allows any user of a single transducer ultrasonic bath (a widely used laboratory ultrasound equipment) to identify optimal conditions (reactor type and position) to effectively highlight the ultrasonic effect and ensure experiment reproducibility.
- Investigating various types of reaction vessels and coupling liquids.
- Monitoring the transfer of ultrasonic energy from the transducer to the liquid in the reactor using both calorimetric and chemical methods (with KI), particularly in the case of water.

- **Design and testing of an installation for the combined use of ultrasound and microwaves to enhance physico-chemical processes**

- Designing an installation that enables concurrent ultrasound and microwave-assisted experiments. The reactor is equipped with a cooling system allowing continuous treatment of the reaction medium with both microwaves and ultrasound while maintaining the reaction temperature at predetermined values.

- Testing the installation to establish working conditions that enable the maintenance of a constant temperature even with continuous supply of ultrasound and microwave energy.

- Conducting experiments on the setup to highlight the separate or combined effects of ultrasound and microwaves.

The purpose of the conducted research was to create an installation that enables the enhancement of physico-chemical processes through the simultaneous application of microwaves and ultrasound. These can be applied continuously, with significant power, while maintaining precise temperature control. Ultrasound and microwaves can be generated with different powers and frequencies (for ultrasound: 20-5000 kHz, for microwaves: 2.43-2.47 GHz), allowing the intensification of a wide range of processes that require either mild or energetic conditions.

Thus, several critical parameters for the correct application of these two energy sources in this type of reactor were experimentally determined. These parameters include the optimal position of the reactor, as defined by calorimetric determination of the powers absorbed by ultrasound (US) and microwaves (MW). Real examples of transformations, such as the transesterification of vegetable oil with ethanol, were also examined to illustrate the potential of this system for enhancing chemical processes.

The installation for the combined use of ultrasound and microwaves to enhance physico-chemical processes is characterized by providing structural and functional flexibility through the following possible adjustments:

- Adapting the installation for the intensification of different types of processes by modifying the frequency of the supplied ultrasound.
- Adjusting the reaction temperature by setting the powers of ultrasound and microwaves in the system and the cooling agent's temperature.

- Continuous supply of ultrasound and microwave powers throughout the process, maintaining the reaction temperature through an efficient heat transfer system.
- Modifying the distribution of ultrasound powers in the reactor and coupling liquid by adjusting the reactor's position in the ultrasound bath.

PART I - EFFICIENCY OF MICROWAVE APPLICATORS, RESONANT, MULTIMODE, AND MONOMODE

The performances of a new microwave applicator based upon two concepts: resonance and focus of the electromagnetic field on the target are described. At resonance frequency, the cavity stores the MWs energy – therefore, no MWs are reflected back into the wave guide. The focusing capacity of the applicator is measured via e energy transfer efficiency and heating uniformity. This new applicator was tested for several liquids with very different dielectric parameters behavior, namely: water, ethylene glycol, acetic acid and 2-propanol and its performance has been compared to that of the single-mode and multimode applicators.

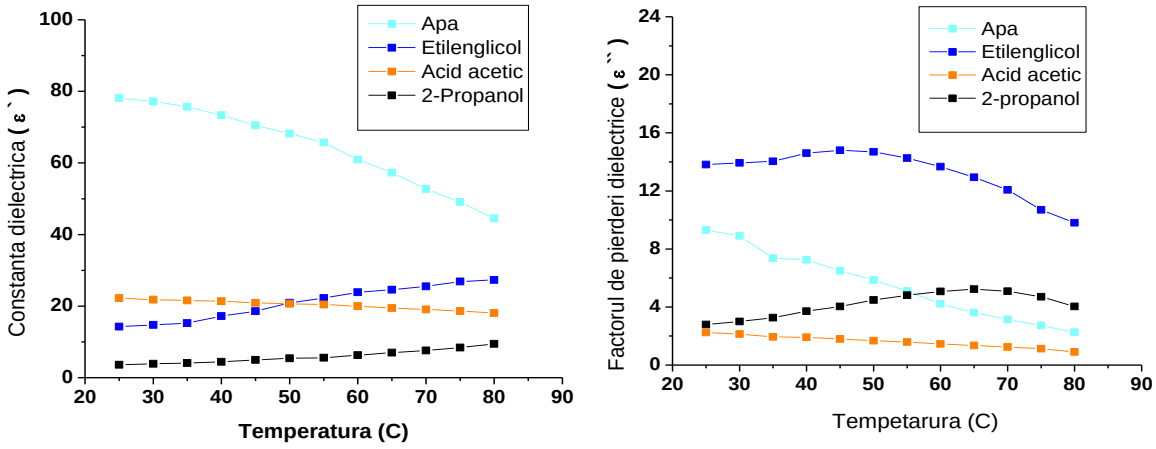
The use of single-mode applicators involves some penalties that must be weighed carefully. They are product specific rather than general purpose and in operation can be very sensitive (i.e., tuned off-resonance) to changes in product properties, geometry, and position, the treated samples are very small to preserve the advantages of the single mode applicator.

Multimode applicators are often used for processing bulk materials or arrays of discrete material, whose overall dimensions are too large (larger than the wavelength of the operating frequency) to permit consideration for use in a single-mode oven. These applicators, in their simplest configuration, take the form of a metal box that is excited (driven) at a frequency well above its fundamental cutoff frequency. For example, the common home microwave oven typically has internal dimensions on the order of 30 to 40 cm., while the wavelength is 12.2 cm. The larger dimension corresponds to a cutoff frequency of about 400 MHz as compared with the operating frequency of 2.450 GHz [7]. When the electromagnetic energy, externally generated, is fed by some means into a cavity with specific dimensions, it induces an internal resonant electromagnetic field that extends throughout the entire cavity [47]. Some workloads have such a low value of loss factor" that the heat dissipation density using monomode or multimode applicators is too low at the electric-field intensities they create. In such cases, by using resonance, the field intensity can be raised considerably, giving satisfactory heat dissipation [48]. Except for plasma generation,

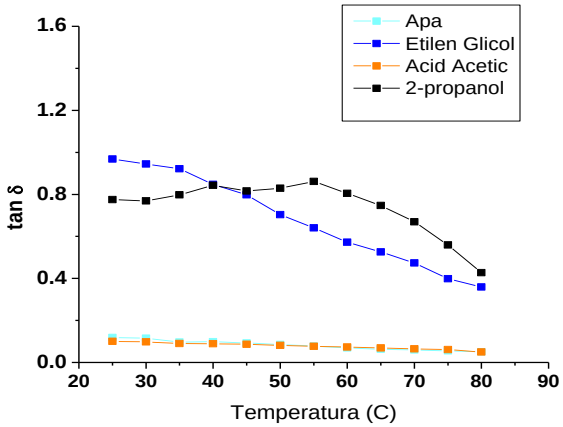
resonant systems have not been widely used in industrial production because of control difficulties. As the workload properties and other parameters of the system change with temperature and wear, both the cavity resonant frequency and the generator frequency drift, and power transfer falls. Retuning is necessary to restore the correct operating conditions. In most cases, this is necessary so frequently that an automatic frequency control (AFC) is required, in order to get back the applicator closer to the resonant state [49]. However, such a system involves very expensive components for controlling and adapting the microwave frequency depending on the reflected power. Our idea was to design and make an applicator that does not deviate too much from the resonant state during operation even if the frequency is maintained the same. In order to compare the efficiency of this new type of applicator power tests were performed using this new resonant applicator and two monomode and multimode type applicators.

1.1.Materials

The experiments were performed using liquids that have very different dielectric properties: distilled water, ethylene glycol (Chimopar), 2-propanol (Chemical) and glacial acetic acid (Chimreactiv). From these, two liquids have high values of tangent loss (ethylene glycol and 2-propanol), while the other two have lower values (water and acetic acid). Fig. B-1 (a, b, c) shows the dielectric properties of these selected substances in the temperature range 20-80°C, as documented in literature [50].



a) Dielectric constant (Ɛ') b) Dielectric loss factor (Ɛ'')



c) Dissipation factor (tan δ = Ɛ”/ Ɛ‘)

Fig. B-1 Dielectric properties [50]

For the experiments with the selected liquids, three different applicators were used:

1. The monomode applicator, the one provided by SAIREM as part of the MINIFLOW 200 SS system [51], being an applicator that works in TE mode (Fig. B-2 si B-3 a).

2. The resonant applicator is a new applicator built by us (Fig. B-3 b), being an aluminum cube with a side of 145.3 mm. In this applicator the microwaves are provided by a transition coaxial adapter to waveguide WR340.

3. The multimode applicator is adapted from a classic microwave oven, with a volume of 18 L, in which a slot was cut to mount the transition coaxial adapter to waveguide WR340 (Fig.B-3 c).

In all these applicators the microwave energy is supplied by the same solid-state microwave generator (Fig.B-2, 6) via a coaxial cable, which allows the recording of the absorbed and the reflected power. In single-mode and resonant applicators, a sliding short-circuit device (Fig. B-2 și 3, 4), can also be mounted, which is a waveguide-based component used in tuning applicators for the adjustment of the resonance frequency.

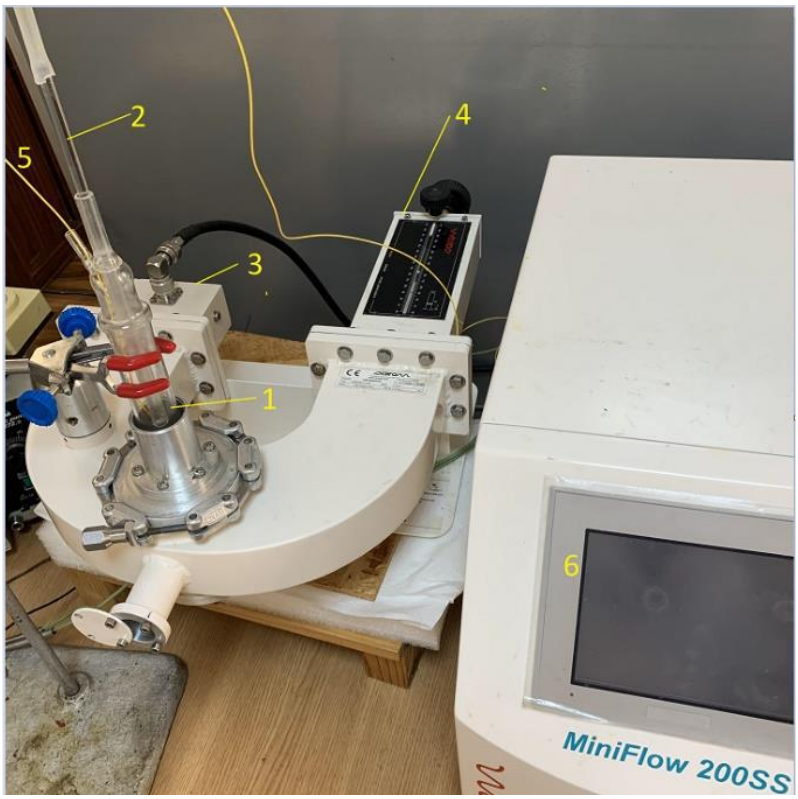


Fig. B-2 Fig. 2. Mini-Flow 200SS used with TE type cavity
1 – reactor; 2 – stirrer; 3 - transition coaxial adapter to waveguide; 4 – sliding short circuit; 5 – optical fiber; 6 – SS MW generator

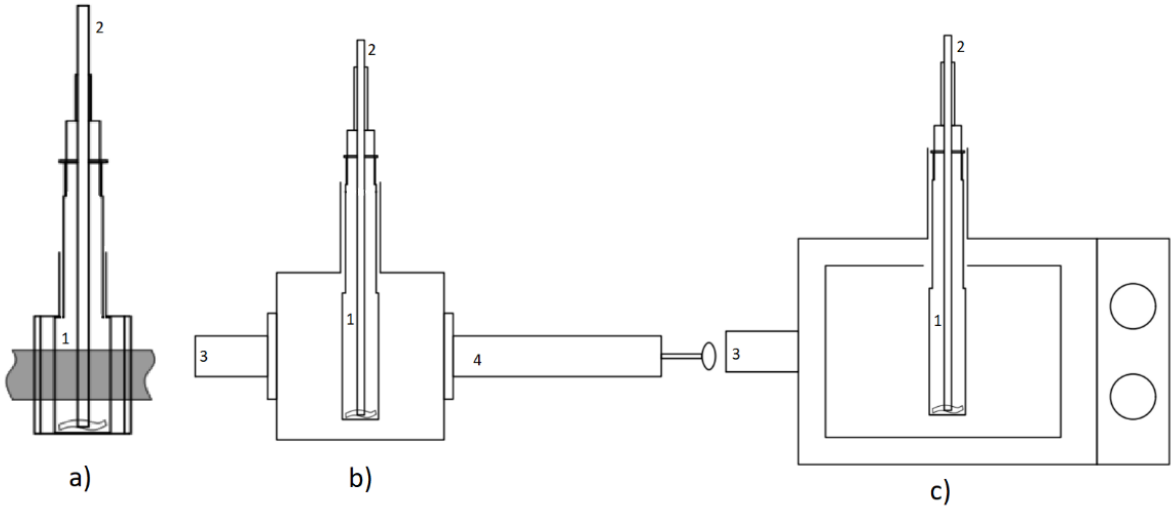


Fig. B-3 Microwave applicators used: a) monomode, TE type, b) resonant cavity, c) multimode
1 – reactor; 2 – stirrer; 3 - transition coaxial adapter to waveguide; 4 – sliding short circuit Setare experimentala

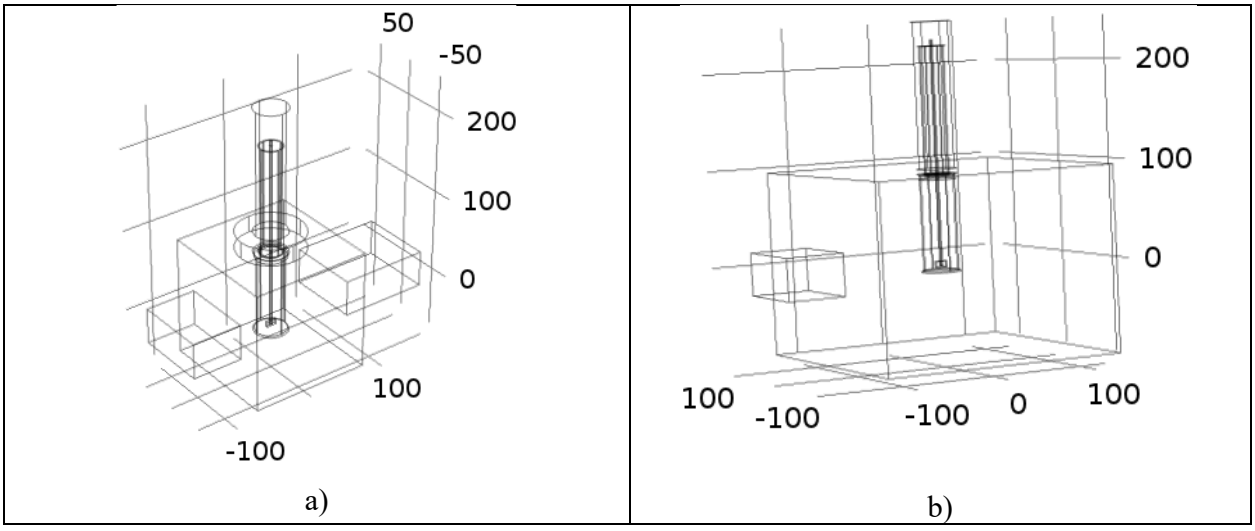
The experiments were performed using the same load in all applicators (a cylindrical vessel5 with a useful volume of 100 mL, provided with a mechanical stirrer). After positioning

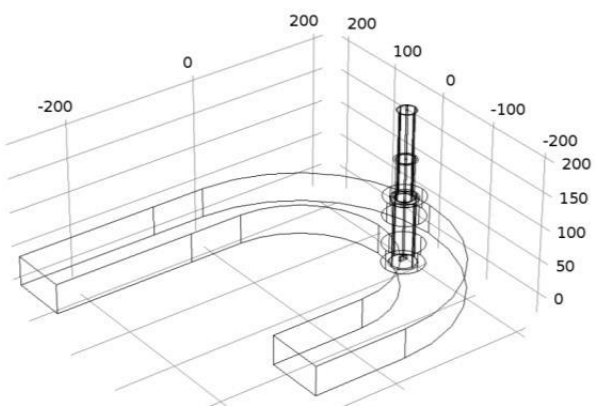
the reactor symmetrically to the waveguide, the stirring is started. The initial temperature was measured with optical fiber then the SS MW generator was turned on and set to a certain power for 60 seconds. When the microwave generator is turned off the final temperature was measured.

Determinations of power losses in the load were made starting from the same temperature (25°C).

1.2.*COMSOL® modeling*

Using the basic building blocks from COMSOL® (Block, Cone, Cylinder and Sphere), together with the Boolean operation (Union, Intersection, Difference, Compose), the three applicators were built according to their geometrical characteristics (Fig. B-4). After this first step, the geometry of each applicator was meshed, so that the solving algorithm to be able to accurately compute the electromagnetic wave field. To this end, the mesh maximum dimension should equal the tenth of the wavelength. The dielectric properties of each of the four liquids were introduced, according to literature data and the "Electromagnetic Waves, Frequency Domain" physics was used, to compute field distribution inside the applicator. The computation was done according to the "Frequency Domain" study, which uses the "multifrontal massively parallel sparse direct solver" implementation in COMSOL®, with the default options.





c)

Fig. B-4 The COMSOL® built models of the laboratory applicators a) resonant; b) multimode; c) monomode

1.3.Results and discussion

The energy transfer efficiency (ηL) in the liquid expected to be heated can be expressed as the ratio of power losses in the load PL to the total power loss, P. The total power loss is expressed as a sum of ohmic losses determined by eddy currents obtained by reflection loss of the electromagnetic waves within the resonator walls (PR), power loss of the load (PL) and power loss of the coupling port (PC) [5]:

$$P = P_R + P_L + P_C \qquad \textbf{Ec 1}$$

$$\boldsymbol{\eta_L = \frac{P_L}{P} = \frac{Q}{Q_L}} \qquad \textbf{Ec 2}$$

The Q factor is a measure of the efficiency of electromagnetic storage in the applicator. It is correlated with the existing loss mechanisms and is given by the ratio between stored and lost energy [5].

$$\boldsymbol{Q = \frac{\text{Stored energy}}{\text{Lost energy} \cdot \text{Oscillation period}}} \qquad \textbf{Ec 3}$$

For the experiments performed in this work, power losses in the load (P_L) were calculated by the equation (12). Because short irradiation times were used, the temperature increases in the reactor (ΔT) were small and for this reason lost power was neglected ($P_{lost} = P_R + P_C$)[5].

$$\mathbf{P_L = \frac{m \cdot C_p \cdot \Delta T}{Timp} + P_{lost}} \qquad \textbf{Ec 4}$$

where:

m - mass of liquid in the reactor, g;

Δt - temperature difference, (°C) recorded after the working time: 60 s

Cp - specific heat, (J / g · °C);

Time - is the time of microwave heating (s).

Table B-1 shows the values obtained for the power losses in the load, for the three types of applicators, when the power provided by the solid-state microwave generator was 25W. The results in the table are consistent with the literature information: the higher the loss tangent (tan □), the better the conversion of microwave energy into heat [51]. Regarding the type of applicator, it can be seen that our resonant applicator adapts well to all liquids used (reflected power is zero) and allows attaining the best values for energy transfer efficiency.

Tabel B-1. Power absorbed for the 4 liquids tested in the 3 microwave applicators

Liquids	Applicator type	P_L	Reflected power	Energy transfer efficiency
		W	W	
Ethylene glycol	Multimode	20.11	0.29	0.81
	Resonant	**24.17**	0.00	**0.97**
	Monomode	21.03	2.10	0.92
2-propanol	Multimode	21.29	1.72	0.91
	Resonant	**22.86**	0.00	**0.91**
	Monomode	21.15	0.00	0.85
Water	Multimode	18.14	1.02	0.76
	Resonant	**21.33**	0.00	**0.85**
	Monomode	19.72	2.80	0.89
Acetic acid	Multimode	16.61	5.00	0.83
	Resonant	**21.78**	0.00	**0.87**
	Monomode	20.9	0.00	0.84

Another very important aspect of our resonant applicator is the uniformity of the heating in the reactor. The ideal conditions are those in which the liquid in the reactor is heated evenly within its whole volume. In order to determine the heating uniformity, the data obtained in COMSOL® were processed for modeling these three types of applicators. Heating uniformity can be expressed as an Irregularity index defined as the ratio between the standard deviation and the mean value. The smaller the Irregularity index, the more uniform heating will be in the considered liquid. Fig. 5 shows the Irregularity index for the three applicators. It can be noticed that on our new resonant applicator the lowest values of Irregularity index are obtained for all the studied liquids. In monomode and resonant applicator it is possible to better adapt the load by changing the position of the Sliding short circuit. The optimal position will depend on the dielectric properties of the liquid in the reactor. Because these properties vary with temperature, we have different curves for the two temperatures studied (25 și 50°C).

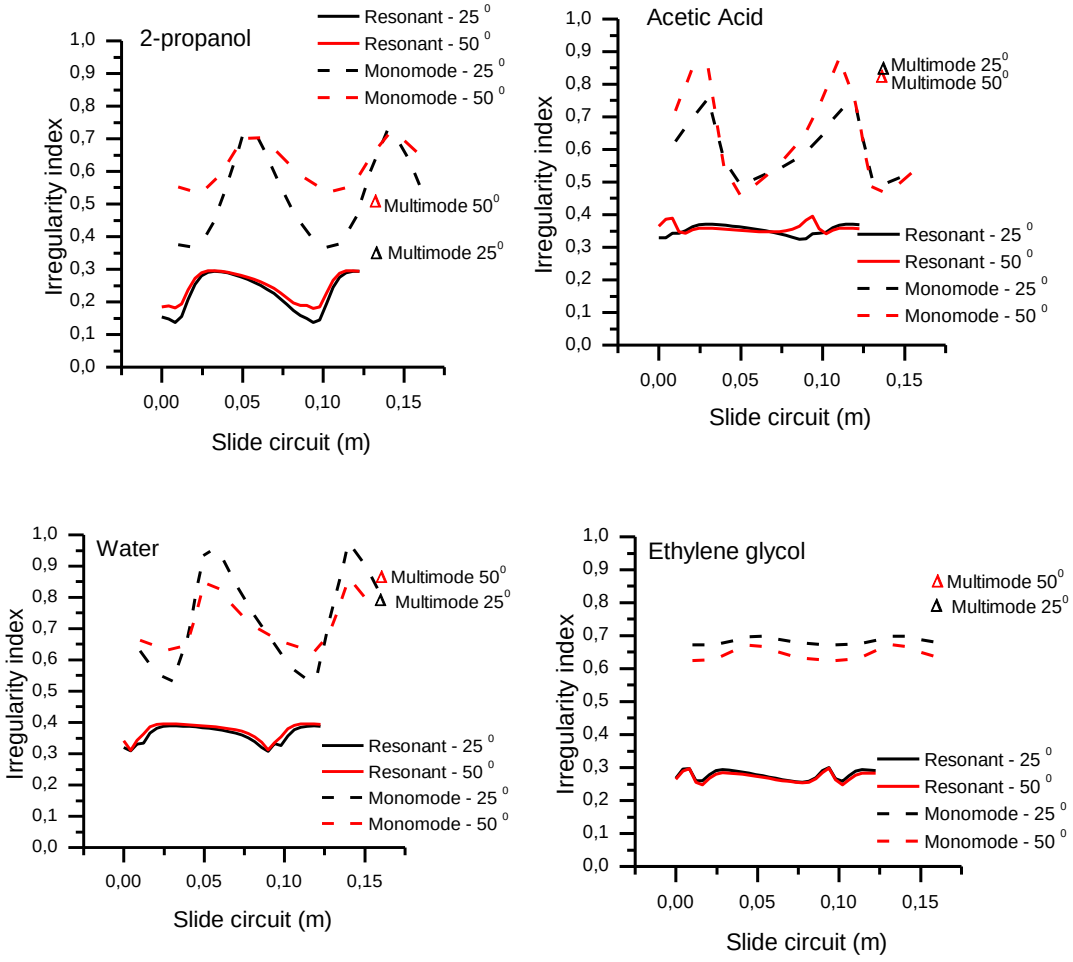


Fig. B-5 Irregularity index for the studied liquids, at 25 și 50 °C - for single-mode and resonant applicators depending on the Short circuit position and for the multimode applicator the point value

1.4.Conclusions

A new type of applicator (resonant applicator, fig. 3b) was designed, built and tested in our laboratory and compared with two types of applicators, monomode and multimode (commercially available). The evaluation was made based on the energy transfer efficiency (determined calorimetrically) and the uniformity of the heating (determined by modeling in COMSOL®).

The experiments performed using these three different microwave applicators: resonant build be us, monomode and multimode applied to the same reactor loaded with identical volume for four different liquids: water, ethylene glycol, isopropyl alcohol and acetic acid, shown that the our new resonant applicator offer features that are better than those of commercially applicators,

in terms of the heating uniformity as well as for energy transfer efficiency. These features are due to the low losses in the cavity walls and to the possibility to reach critical coupling conditions in a large variety of samples and operating conditions.

PART II - THE EFFECT OF THE POSITION AND SHAPE OF THE REACTOR ON THE ULTRASONIC ENERGY TRANSFER IN A SINGLE-TRANSDUCER BATH

The use of ultrasound as one of the methods to intensify processes can be seen as a "green" alternative for energetically efficient processes. [52]. The use of ultrasound at the laboratory level always entails the reproducibility of experiments, and in the case of industrial applications, it involves the design and development of specific systems. [29, 53]. In a paper published in 1996 Kimura and colleagues emphasized that: "It is often challenging to compare sonochimical results reported from different laboratories. This difficulty is well-known as the reproducibility issue in sonochemistry." This problem arises from the nature of ultrasound as a source of energy for chemical reactions. It is incomparable; being mechanical energy in its nature, its effects on chemical reactions largely rely on cavitation effects, where bubbles collapse, releasing a significant amount of energy, a phenomenon known as the "hot spot"[55]. Recently, a new idea has been proposed, namely that sonochemistry can occur in the absence of cavitation. [56].

The ultrasound power transmitted to reaction systems (reactors) varies depending on different equipment, and the energy absorbed by the reaction medium depends on several parameters: ultrasound frequency, temperature, vapor pressure, dissolved gases, solid fraction in suspension, the vessel's placement in relation to ultrasound sources, etc.[40, 57]. The results of sonochemical reactions are not easier to interpret, even in the presence of cavitation, let alone in the case of non-cavitating systems [56].

Sonochemistry covers a wide range of applications, as recently demonstrated [58]. When used as a tool to intensify physico-chemical processes at the laboratory level, an important indicator is the efficiency of energy transfer from the transducer, throughout the coupling liquid, to the reaction vessels.

In this chapter, we aim to provide essential information for those utilizing an ultrasonic bath with an immersed reaction vessel, offering guidance for the proper operation of these instruments. Our objective is to determine the most suitable shape of the reaction vessel (glass) and its

appropriate position in the ultrasonic bath to achieve the optimal sonication effect. This has been achieved by determining the best value of energy density in the reaction vessel and the ratio between the specific power absorbed by the liquid in the reaction vessel and the specific power absorbed by the coupling liquid in the ultrasonic bath.

1.5.Materials and method

Materials

For all experiments, a Bandelin Sonorex RK ultrasonic bath with a single transducer (maximum power 80 W, operating frequency 37 kHz) filled with 1.2 L of water was utilized. A customized vessel support (Fig. B-6) was employed, equipped with a mechanical system capable of moving the vessel vertically, ensuring precise immersion in the ultrasonic bath.

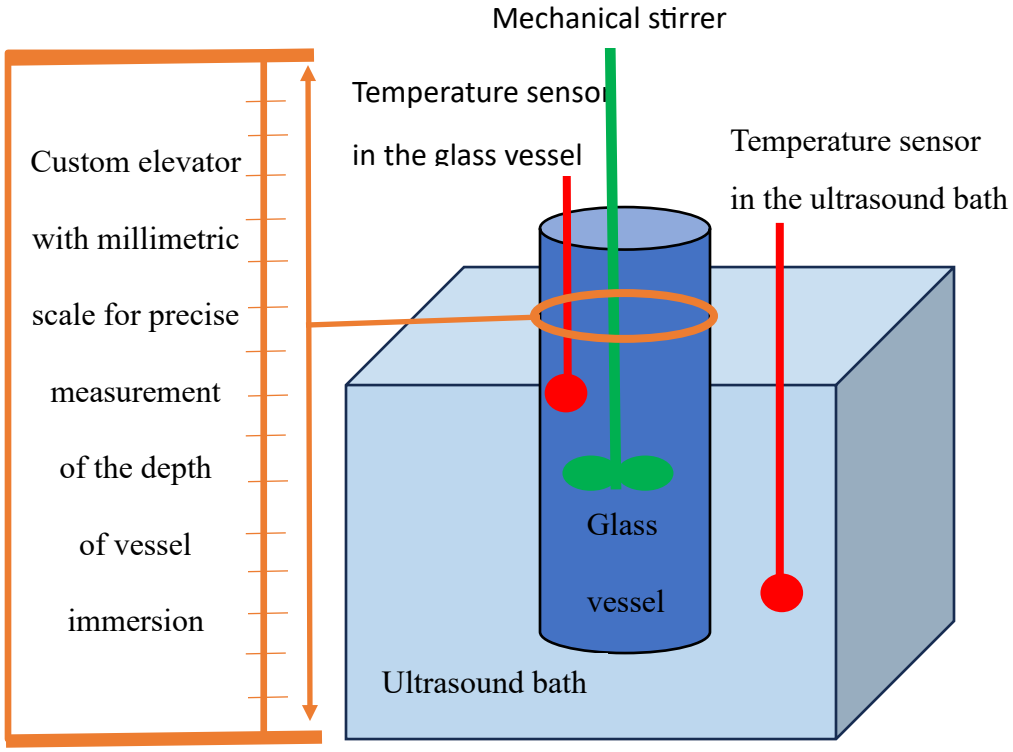


Fig. B-6. The scheme of the experimental set-up (for calorimetric determination of energy transfer from the water in an ultrasound bath to a liquid in a glass vessel immersed in the bath

Apparently, the ultrasonic bath reservoir has a regular cubic shape. The actual shape is slightly different; the upper part is wider than the lower part, and the real dimensions are presented in Fig. B-7.

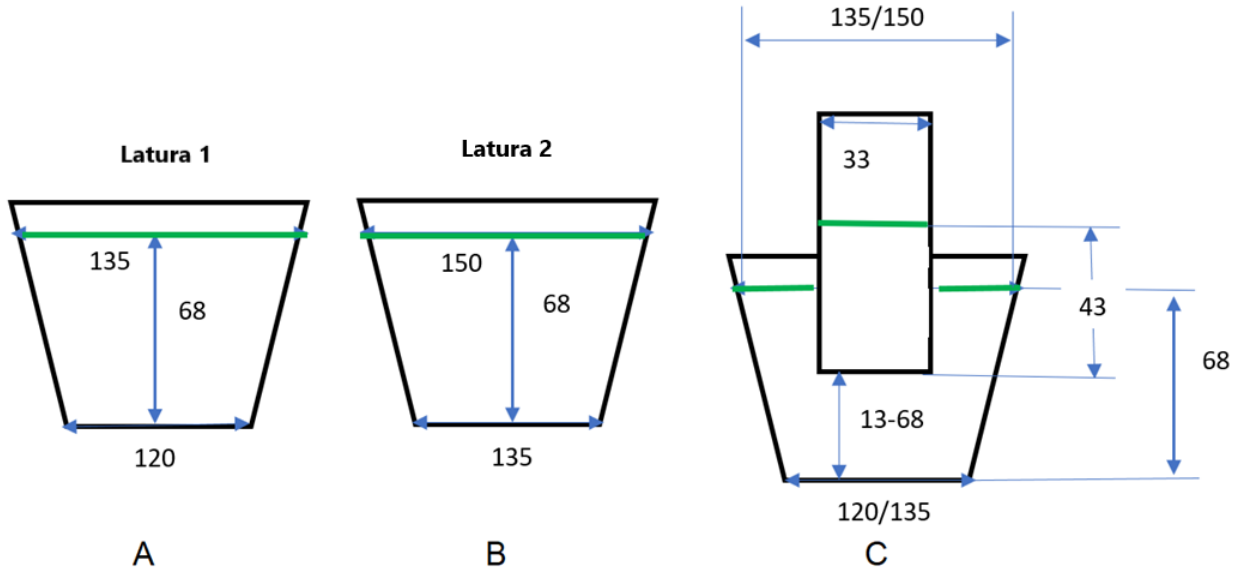


Fig. B-7. The geometry and the dimensions of the ultrasound bath and of the various glass vessels that were used in the calorimetric/ iodometric experiments.

The liquids used in the above-mentioned glass reactors were: distilled water, 96% ethanol (Merck), and commercially available refined sunflower oil (food-grade). Temperature sensors with an accuracy of 0.01 degrees were used to monitor temperature changes during the experimental work. Iodine I_3^- dosimetry was employed as a measure of ultrasonic efficiency concerning the release of iodine from a 0.1 M potassium iodide solution in distilled water (only when water was used as the working liquid). UV-VIS spectrophotometer (Shimadzu UVmini-1240) was used for measurements.

Using COMSOL Multiphysics®, the geometries of the ultrasonic bath and reactors were implemented to study the dependence of heat dissipation in the reactor on its distance from the bottom of the ultrasonic bath reservoir.

Method

The three reaction vessels were submerged at different distances from the bottom of the ultrasonic bath. To determine the ultrasonic energy entering the reaction vessels, a calorimetric method was used. For measuring temperature increases, a thermocouple submerged in the reactor liquid was employed (measurements were taken only at the end of ultrasound exposure to avoid disturbing the acoustic field during sonication). The duration of this experiment was limited to 30 seconds to raise the reactor temperature by only one or a maximum of two degrees Celsius. All experiments were conducted after ensuring that the temperatures in the bath and the reaction vessel were identical (temperature homogenization in the reactor was achieved through stirring but only at the end of sonication). The use of mechanical stirring during sonication was avoided as liquid movement in the bath can disrupt the acoustic field by scattering ultrasonic waves [64]. To prevent any possible interference, no stirrers or temperature probes were introduced into the reactor and the ultrasonic bath reservoir during sonication.

The calorimetric method used allows for the determination of the ultrasonic power density in W/mL, which is a sensible measure of the total energy delivered to the ultrasonic system, rather than the intensity of ultrasonic power, which represents the power supplied from the surface of the vibration source in W/cm2 [59].

Various glass vessels filled with different liquids (distilled water, 96% ethanol, and sunflower oil) were gradually submerged (in 5 mm increments) into the ultrasonic bath using a custom elevator with a millimeter scale (Fig. B-6). The liquid volumes in the bath and the submerged vessels were kept constant throughout all determinations: 1200 mL in the bath and 35 mL in the submerged vessels. The geometries of different experimental conditions (varying immersion levels, different types of glass vessels) were used as input data for simulating ultrasound energy transfer in the Comsol Multiphysics® software.

All experiments were conducted in triplicate, and the experimental data were presented as mean values with ranges. One experiment (water in the Berzelius-type glass vessel) was performed twice, once for calorimetric power determination and once for chemical dosimetry (I_3^-). The correlation between calorimetric determinations and I_3^- dosimetry was evaluated.

For the calorimetric determinations of ultrasound energy dissipation into the liquids from the glass vessels immersed into the bath, the transfered energy and the specific powers were determined with the following relations:

$$E = m \cdot Cp \cdot \Delta T \quad \textbf{Ec 5}$$

where:

E = energy in the ultrasound bath or glass vessel (KJ/Kg)

m = mass (Kg);

Cp = specific heat capacity of the used liquid (KJ/Kg· K);

ΔT = temperature difference (˚K).

$$SP = E /(\tau \cdot m) \cdot 1000 \quad \textbf{Ec 6}$$

where:

SP = Specific Power in the bath or glass vessel (W/Kg)

E = energy (KJ/Kg);

m = mass (Kg),

τ = the time with ultrasound bath on at full power (s);

In the conducted experiments, the ultrasonic treatment time was chosen so that the temperature increase in the glass vessel would be a maximum of 2 degrees Celsius (to limit heat transfer to the liquid in the ultrasonic bath). At these ultrasonic treatment times, the temperature increase in the ultrasonic bath is small (on the order of tenths of a degree), and for this reason, using equation (12) to determine the energy absorbed by the liquid in the bath leads to significant errors (±50%).

For this reason, the energy absorbed by the coupling liquid in the bath was determined to be the difference between the energy supplied by the transducer and the thermal energy captured by the liquid in the glass vessel:

$$\mathbf{E_{bath} = E_{transducer} - E_{reactor}} \quad \textbf{Ec 7}$$

To determine the energy supplied by the transducer, several preliminary experiments were conducted with the ultrasonic bath, without the glass vessel, monitoring the temperature increase in the ultrasonic bath (at least one degree Celsius) and the electrical energy absorbed from the power grid. In this way, an efficiency of converting electrical energy from the power grid into thermal energy of approximately 53.2% was obtained. In each experiment, the electrical energy received from the power grid was monitored using a wattmeter, thus determining the energy supplied by the transducer:

$$\mathbf{E_{transducer} = 0.532 * E_{electrical\_network}} \quad \textbf{Ec 8}$$

The ratio of the specific power in the glass vessels (SP vessel) to the specific power in the ultrasound bath (SP bath) is an useful indicator of the distribution of ultrasound energy dissipation pattern in different immersion scenarios.

PR = SP vessel / SP bath **Ec 9**

Where:

PR = Ratio of specific power in the glass vessels to the specific power in the ultrsound bath (non-dimentional)

SP vessel = specific power in the glass vessel (W/mL)

SP bath = specific power in the ultrasound bath (W/mL)

The concentration of $\mathbf{I_3^-}$ was determined spectrophotometrically:

Conc $\mathbf{I_3^-}$ = Abs/e ·1000 [mmol/L] **Ec 10**

Where:

Abs = the UV-VIS absorbance at 352 nm;

e = 26.2

1.6. Effect of geometry of glass vessel immersed into the ultrasound bath

Using water as the coupling liquid in the ultrasonic bath and the glass vessel, the specific powers absorbed by the liquid in the glass vessel were determined (results presented in Fig. B-8). Regarding the type of vessel used, the results are consistent with literature data. [35, 64]: the best type of glass vessel is the one with a flat bottom (Berzelius beaker).

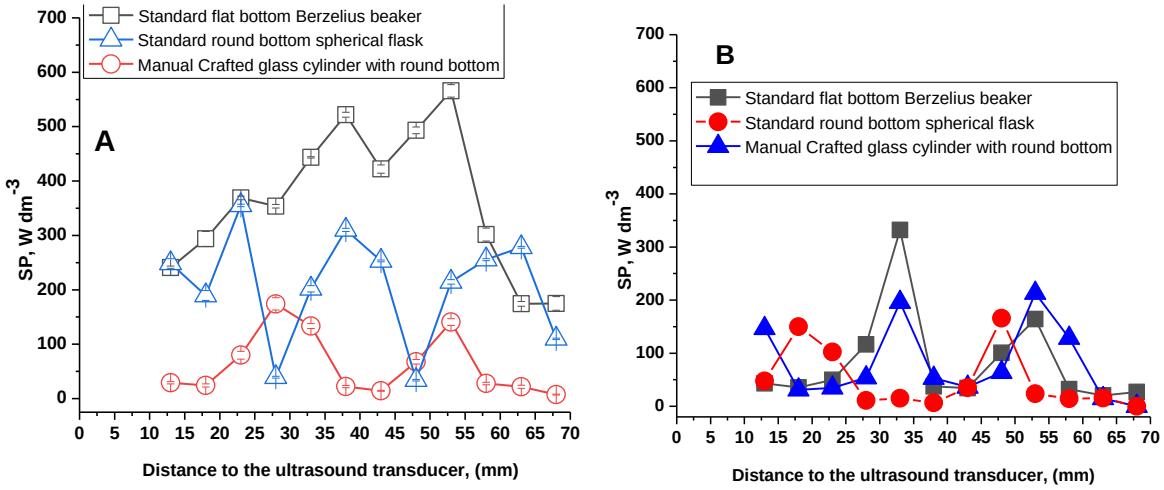


Fig. B-8 Specific power in different (geometry) shapes of glass vessels in function of the distance of immersion of the vessel in the ultrasound bath filled with distilled water A – experimental values; B – COMSOL Multiphysics® model

The specific power absorbed by the liquid in the tested vessels strongly depends on the vessel's position. When the vessel is right at the surface of the liquid in the bath, the specific power transferred to the liquid in the vessel is very low. As the glass vessel is submerged in the liquid in the ultrasonic bath, the specific power increases, but non-uniformly, with certain distances where it is maximized.

Although the literature data [64, 73, 74] suggest the existence of a maximum at half the ultrasonic wavelength, λ/2, this is only partially true. This is because, in an ultrasonic bath, the pressure wave field results from numerous interferences, generating a complex structure of nodes and antinodes, not precisely distributed at a distance of λ/2. The flat-bottomed cylinder and the rounded-bottom cylinder exhibited three maxima, slightly shifted from the values of λ/2. In the case of the rounded-bottom flask, two maxima are identified, which, however, do not precisely follow multiples of λ/2 concerning the distance from the transducer. This effect is due to the fact that the reflection/interference of acoustic waves with the rounded-bottom glass is more complex

than with the flat bottom. It should also be noted that the ultrasonic wavelength of the investigated liquids depends on the frequency and sound velocities (Eq. 18 and Table B-2):

$$\text{wavelength} = \text{velocity}/\text{frequency} \qquad \text{Ec 11}$$

Tabel B-2 The speed of sound and the wavelengths in the analyzed

Liquid	Speed of sound (m/s)	Wavelenght (cm)
Water	1482	4.01
Ethanol	1144	3.09
Vegetable oil	1490	4.02

1.7. Effect of the type of liquid from the glass vessel immersed into the ultrasound bath

When using only the Berzelius beaker containing the same volume of water, ethanol, or vegetable oil, the results obtained are presented in Fig. B-9. According to these results, the best values of specific power in the glass vessel are obtained when it contains water; for ethanol, the values are lower by 30-40%, and for sunflower oil, the values are much lower. In the case of ethanol and water, the distances at which the specific power is maximum are easily identified.

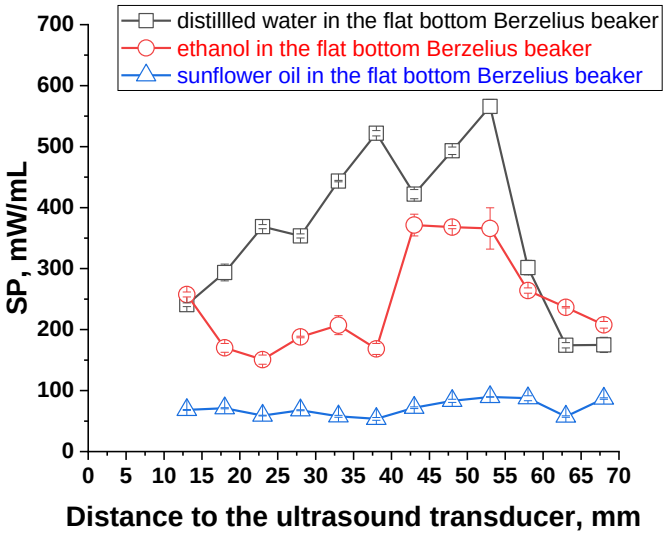


Fig. B-9 Specific power in the standard flat bottom Berzelius beaker in function of the distance of immersion for different types of liquids

1.8. Distribution of the ultrasounds power (specific power ratios) dissipated in the the glass vessels immersed in the ultrasound bath and in ultrasound bath

The glass vessels used function as concentrators of ultrasonic power provided by the transducer. In Fig. B-10, specific power ratios (specific power in the glass vessel to the specific power in the ultrasonic bath) are presented for different shapes (geometries) of glass vessels and different liquids depending on the immersion distance of the vessel in the ultrasonic bath.

It can be observed that the most suitable type of vessel is the one with a flat bottom, and this conclusion aligns with literature data [65]. Regarding the liquid in the glass vessel, the best results are obtained when using water. The differences between the obtained maximum and minimum values are significant, emphasizing once again the importance of the reactor's position in the ultrasonic bath.

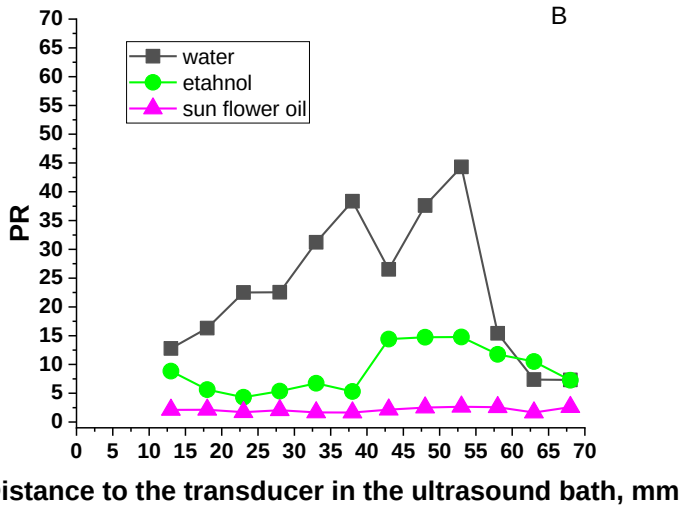


Fig. B-10 Specific power ratios (specific power in the glass vessel (Berzelius beaker) to the specific power in the ultrasonic bath) for different liquids

1.9. Correlation between calorimetric and iodometric assessment of energy dissipated into glass vessel/ultrasound bath

For the case of the flat-bottomed Berzelius beaker containing water, two sets of experiments were conducted: one calorimetric and one chemical dosimetry. As shown by the graph in Fig. B-11, a very good agreement can be observed between the two sets of experiments. At the distance

where the best value of dissipated thermal energy is obtained, the best value of the formed I_3^- concentration is also achieved. This conclusion aligns with literature data [64].

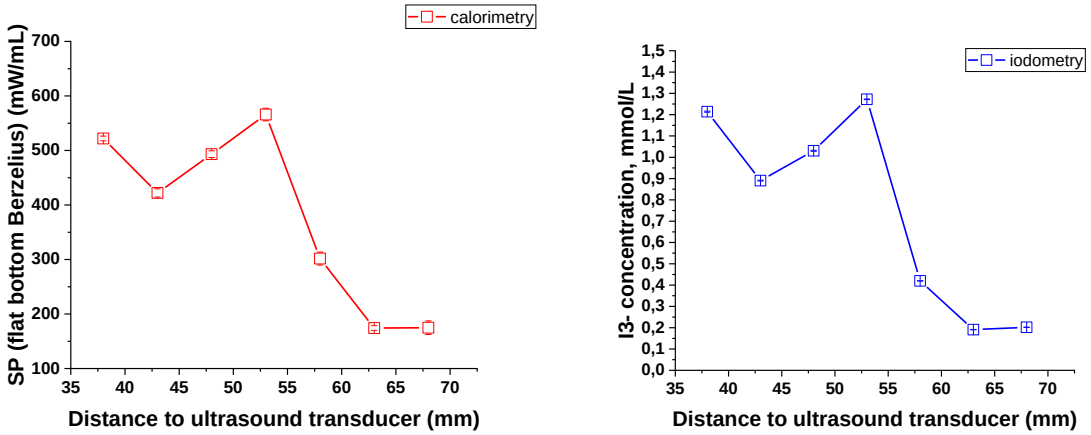


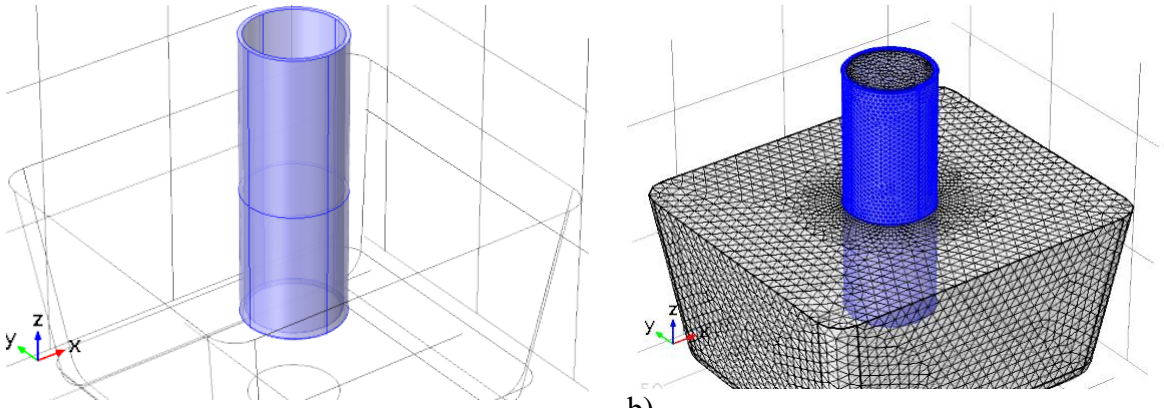
Fig. B-11 Correlation between calorimetry (Specific Power) and iodometry (I_3^- concentration) in in the standard flat bottom Berzelius beaker in function of the distance of immersion of the vessel in the ultrasound bath filled with distilled water

These results confirm I_3^- dosimetry as an alternative method to calorimetry when establishment of the optimum placement of the glass vessels into the ultrasound bath is performed/desired.

1.10. Results obtained from modeling in Comsol

Using Comsol primitives, the fundamental elements of the experiment were implemented to illustrate the dependence of the dissipated heat energy in the reactor on its immersion height.

Simulations were conducted for the ultrasonic bath without the reactor and with the reactor centrally placed above the transducer at various heights, starting from 13 mm and ending at 68 mm (the height of the transmission liquid in the bath), with a step of 5 mm. For each simulation, the transducer amplitude was adjusted so that the introduced power into the bath was 60 W.



a) b)

Fig. B-12 Cylindrical reactor (outer diameter 35 mm) with a flat base - liquid volume 35 mL (a) and the mesh approximation (b)

Results of the modeling are presented in Fig. B-12b. Analyzing the results obtained for the power density in different reaction vessels containing water (Fig. B-8), similarities and differences between experimental and modeling results can be observed. In both cases, there are maxima and minima, but their positions and amplitudes differ. Possible explanations include irregularities in the geometry of the glass vessels (varying thickness of the glass wall and imperfect shapes) as well as the fact that the COMSOL model does not account for the cavitation effect.

Analyzing the power density ratios (Reactor/Ultrasonic bath), as shown in Fig. B-10, it can be observed that both for experimental data and COMSOL results, this ratio is above unity. This is due to the different distribution of the ultrasonic field (sound pressure intensity, dB) in the reactor and in the ultrasonic bath. In the reactor, the proportion of areas with increased intensity is significantly higher than in the ultrasonic bath (see Fig. B-13).

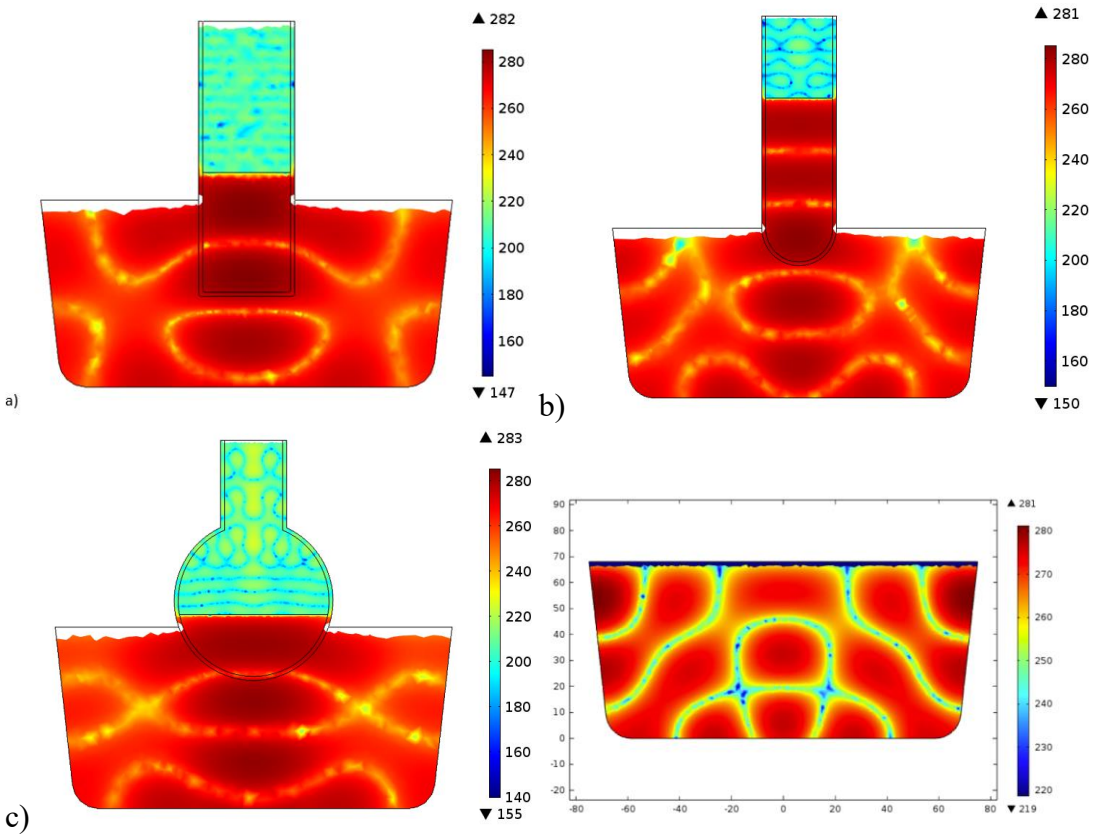


Fig. B-13 Sound pressure intensity in glass vessels positioned at a distance from the ultrasonic transducer where power density is maximum

1.11. Partial Conclusions

In this chapter, the successful recording of ultrasonic power entering a reaction vessel from a single transducer was achieved. Three types of glass vessels (a flat-bottomed cylindrical vessel, a spherical vessel, and a cylindrical vessel with a round bottom) were placed at different distances from the transducer, directly above it. Three different liquids were used in the glass vessel: water, 96% ethanol, and vegetable oil. The ultrasonic energy transmitted to the reaction liquid in the glass vessels was determined both calorimetrically and chemically.

COMSOL modeling of interactions between the transducer, the liquid in the ultrasonic bath, the glass vessel, and the liquid in the glass vessel was also conducted. The current research aimed to establish a working method to determine the best shape and position of glass vessels used as

reactors in various sonochemical applications. The recommended evaluation method is calorimetric, confirmed by chemical dosimetry in the case of water. Calorimetric measurements can be applied regardless of the type of liquid in the reactor. This method is easy to apply in any laboratory and allows for the establishment of both conditions and reproducibility of experiments where the sonication effect is most effective. The COMSOL modeling method has its limitations due to its inability to model the cavitation phenomenon.

In the absence of calorimetric determinations for a studied application, there is a risk that the results may not be reproducible (if the same type of reaction vessel and the same positions in the ultrasonic bath are not used). Additionally, the ultrasonic effect will not be carefully quantified, as at different positions of the reactor, the specific ultrasonic power absorbed by the liquid in it can vary within very wide limits. The obtained results are in line with other literature data but complement them by conducting studies over a wider range of distances between the ultrasonic transducer and the glass vessel.

PART III - THE INSTALLATION FOR THE COMBINED USE OF ULTRASOUND AND MICROWAVES TO ENHANCE PHYSICO-CHEMICAL PROCESSES

Ultrasound (US) and Microwaves (MW) are effective methods for processes intensification. Their combined use in the same reactor can lead to remarkable results. Recently there has been a resurgence of interest in this field for new synthetic applications using reactors based upon existing technologies. We describe here a new type of apparatus in which the thermal energy is continuously removed from the system making possible the use of high power and adjustable ultrasonic and microwave densities throughout the process. The installation consists of a glass reactor located in a monomode applicator which is immersed at the same time in an ultrasonic device which can be operated at different frequencies and powers. A liquid, transparent to microwaves, was used to couple ultrasonic energy to the reactor and to remove the heat generated. Comsol software was used to get information about the distribution of ultrasonic and microwave energy between the reactor liquid and the coupling fluid. The performance was assessed using the conversion of p-nitrophenol into 4- nitrocatechol as a chemical dosimeter and a transesterification.

The aim of this paper is to determine experimentally several parameters critical for the correct application of these two energy sources in this recently designed reactor. These include the optimal position of the reactor as defined by the calorimetric determination of US and MW absorbed powers and real examples of transformations (such as the transesterification of vegetal oil with ethanol) to illustrate the potential for this system to be used for the intensification of chemical processes.

The single reactor approach as described by Leonelli and Mason [44] was chosen by our group to build a new type of MW and multifrequency US, combined reactor. However, our equipment design differs significantly from those described in recent publications because:

- The equipment is fully controllable from the point of view of both sources of energy US and MW.
- It can be operated at different frequencies (24, 580, 864 and 1146 kHz).

- The MW generator is solid-state (not magnetron) allowing a well-controlled adjustment of power (from 0 to 200 W) not possible with magnetron type MW. In addition, the frequency can be adjusted within the range of 2.43 up to 2.47 GHz.
- The MW cavity is monomode not a multimode, allowing a more uniform treatment of reaction mixtures.
- It can be used continuously at a constant reactor temperature regardless the MW or US powers used because the reactor is partially immersed in the liquid of the US bath which is continuously cooled by means of a jacket through which a coolant can circulate.

1.12.Materiale și metode

The experiments were performed using dodecane as the coupling and cooling fluid (>95%), 4- nitrophenol (analytical standard), ethanol (absolute) all from Sigma-Aldrich and edible sunflower oil. The equipment is shown in Figure 3 and is the subject of a patent application [20]. It consists of a single glass reactor with a volume of 100 mL (1) equipped with a mechanical stirrer and three K type thermocouples T1 in the reactor with T2 and T3 monitoring the inlet and outlet temperatures of the coupling fluid. The coupling fluid is cooled by a jacket of circulating liquid and the reactor is partially immersed in the coupling fluid in order to control the reaction temperature. The reactor can receive at the same time microwaves and ultrasounds via the coupling liquid (4). Ultrasonic power is provided through a multifrequency transducer (5), from a frequency generator (7) and a power amplifier (6). Microwave energy is supplied from a solid-state MW generator (12) via a single mode applicator (2) with a volume of 282 mL (components of Sairem - Miniflow 200 SS system).

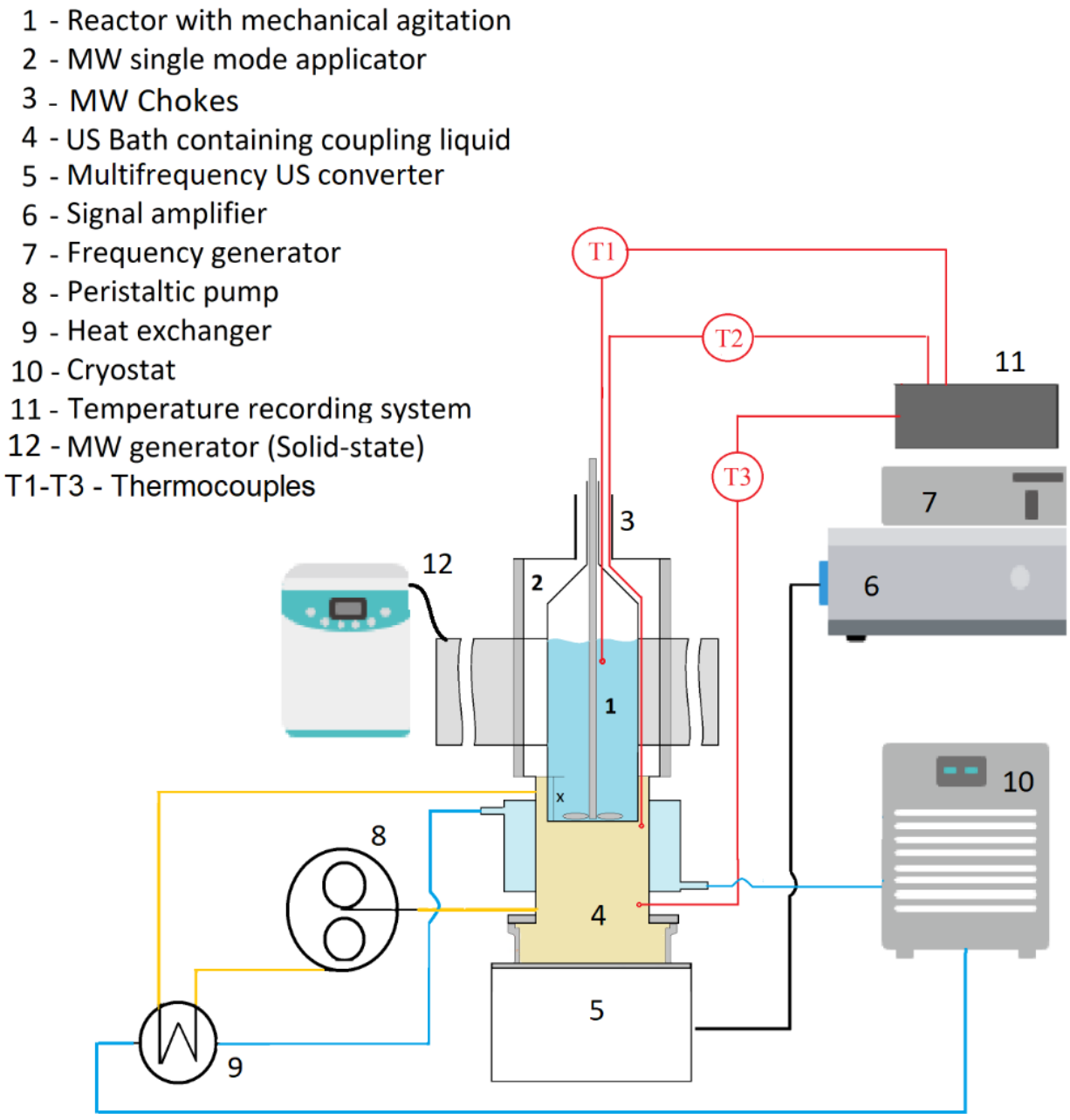


Fig. B-14 . Ultrasound and Microwave hybrid installation

1.13. Procedure and experimental setup

The reactor is loaded with the reaction mixture without catalyst or any other key component. All ultrasonic and microwave generation systems are started at the desired power levels with coupling fluid and coolant recirculation systems in place. By adjusting the system thermal

equilibrium can be established at the desired reaction temperature (50°C in our case for both reactions studied), the catalyst or key component is added, and the process is monitored through sampling and analysis at predetermined time intervals. The control (conventional) reaction was performed under conventional heating at 50°C. In case of p-nitrophenol (PNP) degradation, a solution with a concentration of 100 micromoles/L was used, with corrected pH to 5 with 1N HCl. The degradation of PNP was followed by monitoring its concentration via spectrophotometric method.

1.14. Results and discussions

1.14.1. The optimal position of the reactor within the installation

In order to determine the optimal position of the glass reactor within this installation with respect to the input of ultrasound and microwave energy together with effective heat withdrawal by the coupling fluid Comsol software was employed. This modelling suggested that the reactor should be immersed in the coupling fluid (dodecane) at 20 mm and this was used throughout the experiments. The MW loss in the chokes was also found to be low and less than the limits of EU Directive 2013/35, which states a much higher limit of 50W/m^2 [88].

Tabel B-3 Absorption efficiency of MW energy and the level of MW losses as a function of the penetration depth of the reactor into the coupling liquid

Immersion depth, mm	Efficiency of MW energy absorption, %	MW losses at the top of the reactive shock, W/m^2
0	85	0.01
5	83	0.06
10	90	0.02
15	94	0.01
20	96	0.005
25	97.9	0.004
30	98	0.002
35	97.8	0.001
40	94	0.0015

The analysis of these data shows that there is an optimal position of the reactor with perfect mixing in the US bath (between 10 and 40 mm), so that both the absorption efficiency of MW energy is within very good limits (over 90%).

Furthermore, the same system consisting of a US bath (containing alkanes C13-C18) and a reactor containing water was simulated in Comsol to highlight the effect of the reactor position on the distribution of absorbed powers by the coupling liquid and the liquid in the reactor when treated with 24 kHz US. From the analysis of the data presented in Table B-4, it is observed that the absorbed US power by the liquid in the reactor changes depending on the immersion depth of the reactor. This is a significant advantage, demonstrating the flexibility of the installation. The data in Table B-4 also show that the reactor can act as a power concentrator, depending on its position. In the best position, the intensity of the US field in the reactor is 11 dB higher than the calculated value in the US bath.

Tabel B-4 The intensity of the US field and the fraction of heat dissipated in the US bath and in the reactor during treatment with 24 kHz US

Immersion depth, mm	**Fraction of total dissipated heat**		**Intensitatea câmpului de US, dB**			
	Coupling liquid - US bath	Liquid in Reactor	Coupling liquid - US bath		Liquid in Reactor	
			maximum	medium	maximum	medium
0	0.802	0.198	276.28	269.67	278.8	272.54
10	0.399	0.601	274.15	266.06	283.34	277.3
20	0.767	0.233	279.21	268.95	280.09	272.79
30	0.856	0.144	275.75	267.88	274.99	266.95
40	0.602	0.398	275.83	266.51	279.73	270.9

1.14.2. Calorimetric determination of US and MW absorbed powers

The calorimetric determination of the US power absorbed by liquid in the glass reactor and separately by the coupling fluid were carried out using procedures described in the literature[89, 90]. Distilled water (100 mL) was added to the reactor, and dodecane (150 mL) to the US bath. The US and MW were switched on for a short time (10-30s). By measuring the temperature rise in the coupling fluid (T2) and in the reactor liquid (T3) respectively, the calorimetric values of the

dissipated powers in the reactor liquid and in the coupling, fluid were determined. The measurements were performed for the US multifrequency transducer from Meinhardt Ultrasonics (580; 864 and 1146 kHz) and the 24 kHz device from REUS. The position of the reactor in the coupling fluid was at a depth of 20 mm. in the reactor itself (1) and in the coupling fluid in the US bath (4) at different frequencies are presented in Tables B-5 and B-6.

Tabel B-5 Calorimetric measurement of ultrasonic power for multifrequency US convertor

Amplitude	**Power, W**					
	580 kHz		**864 kHz**		**1146 kHz**	
	In the US bath	In the reactor	In the US bath	In the reactor	In the US bath	In the reactor
5	3.7	5.3	4.2	4.9	3.9	5.3
6	7.5	8.8	7.0	8.4	10.2	10.0
7	11.7	13.2	12.3	12.6	16.1	13.0

Tabel B-6 Calorimetric measurement of ultrasonic power for 24 kHz transducer

% of full power (supply voltage)	**Power, W**	
	In the US bath	In the reactor
15 (100V)	5.0	1.9
20 (120V)	10.0	5.0
30 (140V)	19.3	11.6

An important advantage of this installation is that the microwave and/or ultrasound energy can be continuously supplied and controlled to the same reaction mixture in such a way as to not exceed a prescribed temperature. This is possible because the heat absorbed in the reactor is transferred to the coupling liquid and this, in turn, to the coolant flowing through the jacket (as can be seen in Fig B-17).

Dodecane is an excellent coupling liquid because it combines two remarkable properties: it is a non-polar solvent that has a very small dielectric constant (ε=2,01) [91] and is almost transparent in the microwave range. It is also unaffected by sonication over a wide temperature

range [89]. This makes it entirely suitable for use as a coolant for the removal of excess heat from a microwave cavity, besides coupling ultrasound with the reactor [92].

Microwave energy was applied using the same configuration as for ultrasonic energy. The power absorbed by the liquid in the reactor was nearly the same as the power provided by the MW generator (confirming microwave energy absorption efficiencies of over 96%). In addition, the temperature in the US bath did not rise. This shows that the MW applicator is well tuned, there is no reflected MW power and that the coupling fluid was well chosen in that it did not absorb MW energy. When used in the hybrid configuration (simultaneously applied US and MW) a simple additive effect of the absorbed powers was observed.

1.14.3. Determination of the effectiveness of the Hybrid Reactor

Measurement of p-nitrophenol degradation

The degradation of p-nitrophenol (PNP) is one of the methods used to measure the efficiency of generating active radical species (especially OH radicals) by cavitation during sonochemistry [92-94].

The working procedure in this series of experiments was as follows: the configuration from Figure B-16 B was used, the mixture of alkanes C13-C18 was used as the coupling liquid in the ultrasonic bath; 96 mL of distilled water was added to the reactor, and the system (microwaves and/or ultrasonics) was started with the appropriate adjustment of the cooling agent temperature, so that the temperature in the reactor stabilized at 50 °C; after the temperature stabilized, 4 mL of PNP solution was added to the reactor, and the experiment began; at 10-minute intervals, 2 mL samples were collected, which were analyzed spectrofotometrically to determine the concentration of PNP (Ct). Thus, the degradation efficiency of PNP was determined at various reaction times.

$$\mathbf{Ef}(\%) = \frac{\mathbf{C0}-\mathbf{Ct}}{\mathbf{C0}} * \mathbf{100}, \% \qquad \textbf{Ec 12}$$

A set of experiments was conducted at the same temperature of 50 °C, using different heating methods: conventional heating, microwave (MW) only, ultrasonic (US) only, or combined MW and US. The results are presented in Table B-9.

A process intensification factor was also determined by comparing the degradation efficiency obtained under specific conditions (MW and/or US) to the degradation efficiency obtained under conventional heating. Analysis of these data shows that PNP is very stable under conventional heating (very low degradation), moderately stable under MW heating alone (degradation below 8.3%), and can be efficiently degraded by ultrasound. As the ultrasound frequency increases, the degradation efficiency also increases. In experiments where both US and MW were used, the degradation efficiency is significantly higher than when using only US, and the intensification factors reach significantly higher values. The optimal conditions are those where MW and US with a frequency of 580 kHz were used.

Tabel B-7. Degradation efficiency of PNP depending on the treatment conditions (reaction time 50 220 min, (C0) 2.8*10-5 mmoli/mL; temperatura 50 °C)

The intensification method			**Time, min**	**The degradation efficiency of PNP, %**	**Intensification factor**
MW	**US**				
Power, W	**Frequency**	**Power, W**			
-	-	-	30	0.25	-
			50	0.3	-
10	-	-	30	6.5	26.0
			50	8.3	27.7
-	580	13.2	30	18.5	74.0
			50	28.2	94.0
-	864	12.6	30	20.2	80.8
			50	31.5	105.0
-	1146	13.0	30	24.3	97.2
			50	38.8	129.3
10	580	13.2	30	30.9	123.6
			50	41.3	137.7
10	864	12.6	30	30.0	120.0
			50	41.3	137.7
10	1146	13.0	30	23	92.0
			50	35.2	117.3

Figure B-18 shows the degradation efficiency of PNP under different conditions in the Hybrid Reactor: conventional, microwave-only (10W), ultrasound-only (12-13W), and combined MW and US at different frequencies. No effect of normal stirring or MW alone plus stirring on PNP breakdown would be anticipated. However, MW and stirring produce a slight degradation (less than 0.9%). If this is due to the formation of hydroxyl radicals under microwave heating, it is unclear and even somewhat unlikely, as at the same temperature, with stirring alone, PNP essentially shows zero degradation within the experimental error. In 2015, there was a report on "Fenton-like Process" assisted by microwaves, but this was a catalyzed reaction, unlike the one studied here [95]. The results obtained only with ultrasound are as expected regarding the frequency and ultrasound power, with increasing frequency leading to more efficient degradation, consistent with literature data [96].

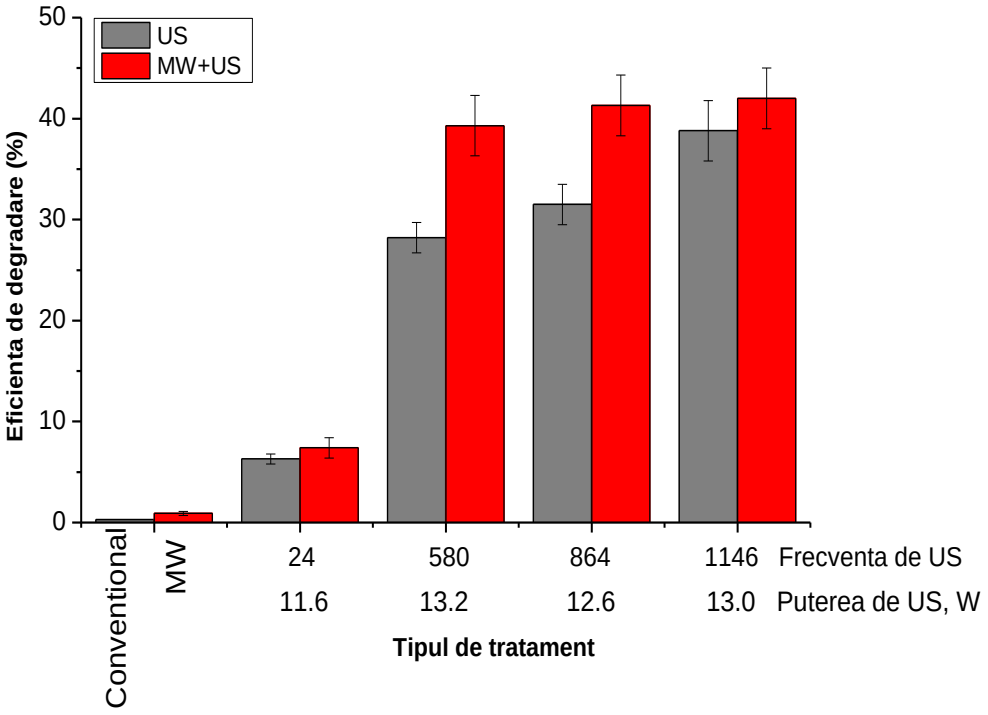


Fig. B-15 Degradation efficiency of PNP depending on the treatment conditions (reaction time 50

220 min)

It is the experiments in which US and MW are combined that produce the most interestin results in that MW can be seen to significantly increased the degradation of PNP compared with US alone. We believe that this might be the first clear chemical evidence for a synergism of US+MW.

The combined effects of US and MW on transesterification

The transesterification of vegetal oil with ethanol, under heterogenous acidic catalysis, is of great interest in the production of biofuels and has been well documented and provides a challenge in terms of process optimization [97, 98]. Ultrasonic energy can emulsify the reactants to reduce the 230 catalyst requirement, alcohol-oil ratio, reaction time and reaction temperature [99].

Sunflower oil (52.5 mL) and ethanol (17.5 mL) were placed in the Hybrid Reactor and subjected to a series of experiments involving separately US and MW irradiation and in each case 3g of Amberlite IR 120 (H form, corresponding to 0.1 mol H+/L) was added but only when the temperature stabilized. The oil/ethanol mixture was analysed by GC-FID according to the EN 14103 standard method for biodiesel The results, for 24 kHz ultrasound frequency, are shown in the Figure B-19 below:

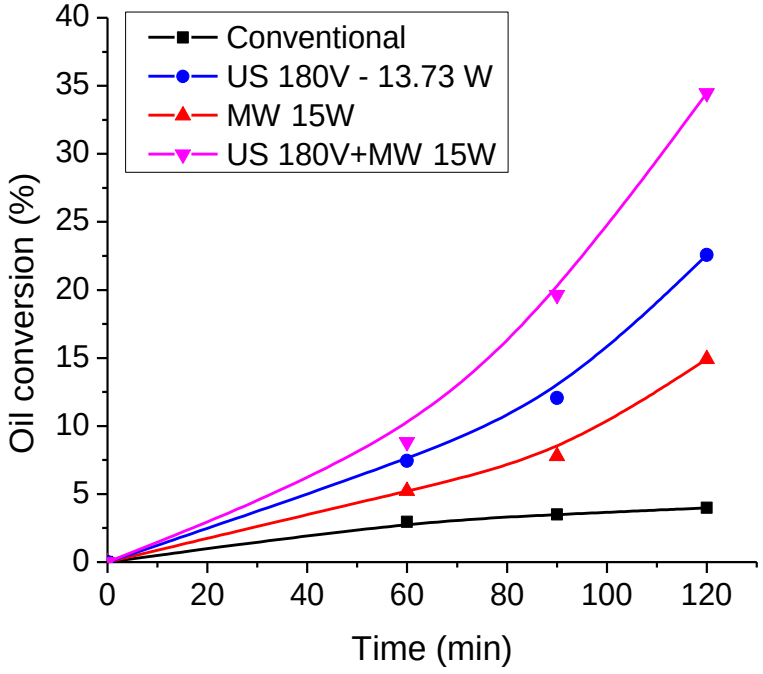


Fig. B-16 Transesterification of sunflower oil with ethanol over Amberlite IR 120

Once again there are the results obtained when US and MW are combined which provide the most interesting data. It can be seen that there is a high synergetic effect for this transesterification reaction which itself is known to be slow under normal acidic catalysis [101].

1.15. Partial Conclusions

A new combined (hybrid) ultrasonic and microwave installation was designed, built and characterized. This new system maintains a low temperature in the reaction medium even when using high-power densities (of the order of 1-2 W/mL) which is extremely important for the:

- extraction of valuable active principles from plants;
- reduction in degradation of thermolabile compounds;
- intensification of the ultrasonic and microwave processes in solution

In addition, synergetic effects on the degradation of *p*-nitrophenol and the transesterification of sunflower oil under heterogenous acidic catalysis shows the synergism in this ultrasound and microwave hybrid device.

B. GENERAL CONCLUSIONS

This doctoral thesis focused on three research directions:

- The efficiency of microwave applicators, including resonant, multimode, and monomode types;
- The effect of the position and shape of the reactor on the transfer of ultrasonic energy in a bath with a single transducer;
- Design and testing of an installation for the combined use of ultrasound and microwaves to enhance physico-chemical processes.

General conclusions for these three research directions are as follows:

- A new type of applicator, the resonant applicator, was designed, constructed, and tested. Comparative experiments with two commercially available applicators (monomode and multimode) showed that the resonant applicator outperforms commercial applicators in terms of heating uniformity and energy transfer efficiency.
- The effect of the position and shape of the reactor on the transfer of ultrasonic energy in a bath with a single transducer was investigated through calorimetric measurements, confirmed by chemical dosimetry experiments with water. Excellent agreement was obtained between the two types of experiments, highlighting that the most suitable reactor is the Berzelius beaker with a flat bottom. Regarding the liquid in the glass vessel, the best results are obtained when using water. The significant differences between the obtained maximum and minimum values emphasize the importance of the reactor's position in the ultrasonic bath.
- A new hybrid installation combining ultrasound and microwaves was designed, constructed, and characterized. The synergistic effects on the degradation of p-nitrophenol and the transesterification of sunflower oil under heterogeneous acid catalysis demonstrate the quality of this ultrasound and microwave hybrid device.

C. PERSPECTIVES OF RESEARCH DEVELOPMENT

The development prospects for each research direction are outlined as follows:

- Further development of the monomode applicator will involve the integration of an automatic resonance maintenance system. This system could utilize either frequency modulation of the microwave generator or an automatic impedance adapter;
- The research on the efficiency of energy transfer in an ultrasonic bath will be disseminated through the publication of an open-access article to promote this method;
- Future efforts will focus on expanding the applications of the hybrid ultrasound and microwave reactor. New applications utilizing such a reactor will be explored, and the system will be enhanced by incorporating a cup-horn type ultrasound generator. This upgrade aims to provide better control over the delivered ultrasonic energy in the system.

D. ORIGINAL CONTRIBUTIONS

- Designing and testing a resonant microwave applicator to optimize energy transfer and ensure heating uniformity.
- Developing an experimental methodology that allows any user of a single transducer ultrasonic bath (the most common ultrasonic equipment in laboratories) to find suitable conditions (reactor type and position) to maximize the ultrasonic effect and ensure experiment reproducibility.
- Creating an experimental setup for conducting experiments simultaneously assisted by ultrasound and microwaves. The reactor includes a cooling system to maintain constant ultrasound and microwave irradiation.
- Patenting the installation for the combined use of ultrasound and microwaves for the intensification of physico-chemical processes at OSIM (State Office for Inventions and Trademarks), 2020, RO134747A0.

E. DISSEMINATION OF RESULTS

Published articles

1. Calinescu, I., Vinatoru, M., **Ghimpeteanu, D**., Lavric, V., Mason, T.J., A new reactor for process intensification involving the simultaneous application of adjustable ultrasound and microwave radiation, Ultrasonics Sonochemistry, 2021, 77, p. 105701, https://doi.org/10.1016/j.ultsonch.2021.105701, IF = 9.336

2. **Ghimpețeanu, D**., Lavric, V., Calinescu, I., Vinatoru, M., Patrascu, M., Efficiency of microwave applicators: rezonant, multimod and monomod, U.P.B. Sci. Bull., Series B, Vol. 83, Iss. 2, 2021

3. Vasile, S., Calinescu, I., Vinatoru, M., Popa, I.,**Ghimpeteanu, D**., Mason, T.J., The efficient extraction of β-carotene from sea buckthorn berries with FAEE using a combination ultrasounds and microwaves, Agronomy, 2024, **14**, (3), 416; https://doi.org/10.3390/agronomy14030416; IF 3,95

Patent granted

1. Calinescu, I., **Ghimpeteanu, D.**, Vinatoru, M., Lavric, V., Ignat, N., Installation for the combined use of ultrasound and microwaves in order to intensify physical-chemical processes RO134747A0 (51) B01J 19/10, B01J 19/12, publicat in BOPI nr. 2/2021

Participation in conferences

1. **Ghimpețeanu, D.**, Lavric, V., Calinescu I., Patrascu, M., Calorimetric determination of microwave energy absorption in - rezonant or multimod applicators in a continuous-flow reactor, 21st Romanian International Conference on Chemistry and Chemical Engineering, 4-7 September 2019, Constanța, Romania.

2. **Ghimpețeanu, D.**, Lavric, V., Calinescu I., Patrascu, M., Intensification of physico-chemical processes using microwaves by calorimetric determination of microwave energy absorption in rezonant or multimodal applicators in a continuous flow reactor, Chemistry Conference for Young Scientists (Chemcys 2020), 19-21.02.2020, Blankenberge, Belgia.

3. **Ghimpețeanu, D.**, Calinescu, I., Vinatoru, M., Temperature measurement in the ultrasonic bath, 4th International Caparica Conference on Ultrasonic based Applications: from analysis to synthesis, 20-23 July 2020, Caparica, Portugal.
4. **Ghimpețeanu, D.**, Lavric, V., Calinescu, I., Vinatoru, M., The effect of the position and shape of the reaction vessel on the transfer of ultrasonic energy from the coupling fluid to the reaction mixture, Materials, Methods &, Technologies, 14-26 August 2020 in Burgas, Bulgaria.

F. BIBLIOGRAPHY:

1. Gupta, M. and E.W.W. Leong, *Microwaves and metals*. 2008: John Wiley & Sons.
2. Stankiewicz, A.I. and J.A. Moulijn, *Process intensification: transforming chemical engineering.* Chemical engineering progress,, 2000. **96**(1): p. 22-34.
3. Sturm, G., et al., *Design principles of microwave applicators for small-scale process equipment.* Chemical Engineering Processing: Process Intensification, 2010. **49**(9): p. 912-922.
4. Wang, W.Z., C.; Sun, J.; Wang, X.; Zhao, X.; Mao, Y.; Li, X.; Song, Z., *Quantitative measurement of energy utilization efficiency and study of influence factors in typical microwave heating process.* Energy, 2015. **87**: p. 678-685.
5. Link, G. and V. Ramopoulos, *Simple analytical approach for industrial microwave applicator design.* Chemical Engineering Processing-Process Intensification, 2018. **125**: p. 334-342.
6. Houšová, J. and K. Hoke, *Microwave heating–the influence of oven and load parameters on the power absorbed in the heated load.* Czech journal of food sciences, 2002. **20**(3): p. 117-124.
7. *Microwave Processing of Materials*, ed. N.R. Council. 1994, Washington, DC: The National Academies Press. 164.
8. Michael P Mingos, D., *Tilden Lecture. Applications of microwave dielectric heating effects to synthetic problems in chemistry.* Chemical society reviews, 1991. **20**(1): p. 1-47.
9. Wang, W., et al., *Quantitative measurement of energy utilization efficiency and study of influence factors in typical microwave heating process.* 2015. **87**: p. 678-685.
10. Kappe, O.S., A.; Dallinger, D.; Mannhold, R.; Kubinyi, H.; Folkers, G., *Microwaves in Organic and Medicinal Chemistry*. Second ed. 2012: Wiley-VCH Verlag GmbH&Co.
11. Kaatze, U.J., *Fundamentals of microwaves.* Radiation physics chemistry - A European Journal, 1995. **45**(4): p. 539-548.
12. H. Iovu, I.C., D. Martin, *Materiale polimerice. Noi procedee de sinteza si aplicatii.* Editura Printech, 1998. **Cod ISBN 973-9402-58-5.- MANUAL**.
13. Beseaga, M.F.O., *Ghiduri de unda.* Universitatea Tehnică a Moldovei, 2011: p. 282-285.
14. Erle, U., P. Pesheck, and M. Lorence, *Development of Packaging and Products for Use in Microwave Ovens*. 2020: Elsevier Science.
15. Stefanidis, G.D., et al., *A helicopter view of microwave application to chemical processes: reactions, separations, and equipment concepts.* Reviews in chemical engineering, 2014. **30**(3): p. 233-259.
16. Elisabetta Zerazion, R.R., Erika Ferrari, Paolo Veronesi, Cristina Leonelli, Monica Saladinic and Anna Maria Ferraria, *Phytochemical compounds or their synthetic counterparts? A detailed comparison of the quantitative environmental assessment for the synthesis and extraction of curcumin.* The Royal Societyof Chemistry 2016. **18**: p. 1807–1818
17. www.scientia.ro, *https://www.scientia.ro/tehnologie/39-cum-functioneaza-lucrurile/8374-cum-functioneaza-cuptorul-cu-microunde-de-ce-nu-e-eficient-in-cazul-alimentelor-inghetate.html*. 2024.
18. Kappe, C.O., D. Dallinger, and S.S. Murphree, *Practical Microwave Synthesis for Organic Chemists: Strategies, Instruments, and Protocols*. 2008: Wiley.
19. Monzó-Cabrera, J., J.L. Pedreño-Molina, and A. Toledo, *Feedback control procedure for energy efficiency optimization of microwave-heating ovens.* Measurement, 2009. **42**(8): p. 1257-1262.
20. Buffler, C.R., *Microwave cooking and processing: engineering fundamentals for the food scientist.* 1993.
21. Mudgett, R., *Microwave Properties and Heating Characteristics of Foods.* Food Technol., 1992. **27**: p. 153-157.
22. Sellman, J.D., *Microwave technology In: COLLISON R. (ed.): Catering for tomorrow.* Horton Publ. Ltd., Bradford, 1991.

23. Gruneberg, M., *Untersuchungen und Modellbildung zur Mikrowellenerwarmung von Lebensmitteln im Mikrowellenherd. [Dissertation.].* Technische Hochschule Karlsruhe, 1994.
24. Sun, J., W. Wang, and Q. Yue, *Review on microwave-matter interaction fundamentals and efficient microwave-associated heating strategies.* Materials, 2016. **9**(4): p. 231.
25. Ripley, E.B. and J.A. Oberhaus, *Melting and Heat Treating Metals Using Microwave Heating-The potential of microwave metal processing techniques for a wide variety of metals and alloys is.* Industrial heating, 2005. **72**(5): p. 65-70.
26. Rybakov, K.I., E.A. Olevsky, and E.V. Krikun, *Microwave sintering: fundamentals and modeling.* Journal of the American Ceramic Society, 2013. **96**(4): p. 1003-1020.
27. Mason, T.J. and J.P. Lorimer, *Sonochemistry: theory, applications and uses of ultrasound in chemistry.* Ellis Horwood, 1988.
28. Suslick, K.S., *Sonochemistry.* Science, 1990. **247**(4949): p. 1439-1445.
29. Yao, Y., Y. Pan, and S. Liu, *Power ultrasound and its applications: A state-of-the-art review.* Ultrasonics sonochemistry, 2020. **62**: p. 104722.
30. Dong, Z., et al., *Continuous Ultrasonic Reactors: Design, Mechanism and Application.* 2020. **13**(2): p. 344.
31. Asakura, Y., et al., *Development of a large sonochemical reactor at a high frequency.* Chemical Engineering Journal, 2008. **139**(2): p. 339-343.
32. Francony, A. and C. Petrier, *Sonochemical degradation of carbon tetrachloride in aqueous solution at two frequencies: 20 kHz and 500 kHz.* Ultrasonics Sonochemistry, 1996. **3**(2): p. S77-S82.
33. Gamboa-Santos, J., et al., *Air-borne ultrasound application in the convective drying of strawberry.* Journal of Food Engineering, 2014. **128**: p. 132-139.
34. Cruz, L., et al., *Air-borne ultrasonic application in the drying of grape skin: Kinetic and quality considerations.* Journal of Food Engineering, 2016. **168**: p. 251-258.
35. Kulkarni, V.M. and V.K. Rathod, *Mapping of an ultrasonic bath for ultrasound assisted extraction of mangiferin from Mangifera indica leaves.* Ultrasonics sonochemistry, 2014. **21**(2): p. 606-611.
36. Kiani, H., D.-W. Sun, and Z. Zhang, *The effect of ultrasound irradiation on the convective heat transfer rate during immersion cooling of a stationary sphere.* Ultrasonics sonochemistry, 2012. **19**(6): p. 1238-1245.
37. www.nuclear-power.com, *https://www.nuclear-power.com/nuclear-engineering/heat-transfer/introduction-to-heat-transfer/characteristic-numbers/what-is-nusselt-number/*. 2024.
38. Chen, Y., et al., *Influence of ultrasound to convectional heat transfer with fouling of cooling water.* Applied Thermal Engineering, 2016. **100**: p. 340-347.
39. Nguyen, D.D., et al., *A new approach involving a multi transducer ultrasonic system for cleaning turbine engines' oil filters under practical conditions.* Ultrasonics, 2016. **71**: p. 256-263.
40. Kimura, T., et al., *Standardization of ultrasonic power for sonochemical reaction.* 1996. **3**(3): p. S157-S161.
41. Ebrahiminia, A., M. Mokhtari-Dizaji, and T. Toliyat, *Correlation between iodide dosimetry and terephthalic acid dosimetry to evaluate the reactive radical production due to the acoustic cavitation activity.* Ultrasonics Sonochemistry, 2013. **20**(1): p. 366-372.
42. Gude, V.G., *Synergism of microwaves and ultrasound for advanced biorefineries.* Resource-Efficient Technologies, 2015. **1**(2): p. 116-125.
43. Cravotto, G. and P. Cintas, *The combined use of microwaves and ultrasound: improved tools in process chemistry and organic synthesis.* Chemistry–A European Journal, 2007. **13**(7): p. 1902-1909.
44. Leonelli, C. and T.J. Mason, *Microwave and ultrasonic processing: Now a realistic option for industry.* Chemical Engineering and Processing - Process Intensification, 2010. **49**(9): p. 885-900.

45. Chemat, F., et al., *An original microwave-ultrasound combined reactor suitable for organic synthesis: application to pyrolysis and esterification.* Journal of microwave power electromagnetic energy, 1996. **31**(1): p. 19-22.
46. Munoz-Almagro, N., et al., *Hybrid high-intensity ultrasound and microwave treatment: A review on its effect on quality and bioactivity of foods.* Ultrasonics Sonochemistry, 2021. **80**: p. 105835.
47. Hauck, H.S., *Design considerations for microwave oven cavities.* IEEE Transactions on Industry General Applications, 1970(1): p. 74-80.
48. Meredith, R.J., *Engineers' handbook of industrial microwave heating*. 1998, London: The Institution of Electrical Engineers.
49. Kimura, H., et al., *Development of a resonant-type microwave reactor and its application to the synthesis of positron emission tomography radiopharmaceuticals.* Journal of Labelled Compounds Radiopharmaceuticals, 2014. **57**(12): p. 680-686.
50. Horikoshi, S., et al., *Microwave frequency effects on dielectric properties of some common solvents and on microwave-assisted syntheses: 2-Allylphenol and the C12–C2–C12 Gemini surfactant.* Radiation Physics Chemistry, 2012. **81**(12): p. 1885-1895.
51. Becht, S., et al., *An industrial view of process intensification.* Chemical Engineering Processing: Process Intensification, 2009. **48**(1): p. 329-332.
52. Stankiewicz, A.I. and J.A. Moulijn, *Process intensification: transforming chemical engineering.* Chemical engineering progress, 2000. **96**(1): p. 22-34.
53. Chemat, F., et al., *Ultrasound assisted extraction of food and natural products. Mechanisms, techniques, combinations, protocols and applications. A review.* Ultrasonics sonochemistry, 2017. **34**: p. 540-560.
54. Kimura, T., et al., *Standardization of ultrasonic power for sonochemical reaction.* Ultrasonics Sonochemistry, 1996. **3**(3): p. S157-S161.
55. Fitzgerald, M.E., V. Griffing, and J. Sullivan, *Chemical effects of ultrasonics—``hot spot''chemistry.* The Journal of Chemical Physics, 1956. **25**(5): p. 926-933.
56. Vinatoru, M. and T.J. Mason, *Can sonochemistry take place in the absence of cavitation?–A complementary view of how ultrasound can interact with materials.* Ultrasonics Sonochemistry, 2019. **52**: p. 2-5.
57. Sharma, C., et al., *Energy dissipation study of ultrasound bath to identify suitable zone for better performance of the bath.* Materials Today: Proceedings, 2022. **57**: p. 2412-2416.
58. Mason, T.J. and M. Vinatoru, *Sonochemistry: Fundamentals and Evolution*. 2023: Walter de Gruyter GmbH & Co KG.
59. Mason, T.J. and J.P. Lorimer, *Applied sonochemistry: the uses of power ultrasound in chemistry and processing*. Vol. 10. 2002: Wiley-Vch Weinheim.
60. Weissler, A., H.W. Cooper, and S. Snyder, *Chemical effect of ultrasonic waves: oxidation of potassium iodide solution by carbon tetrachloride.* Journal of the American Chemical society, 1950. **72**(4): p. 1769-1775.
61. Gogate, P.R., et al., *Cavitation reactors: efficiency assessment using a model reaction.* AIChE journal, 2001. **47**(11): p. 2526-2538.
62. Nascentes, C.C., et al., *Use of ultrasonic baths for analytical applications: a new approach for optimisation conditions.* Journal of the Brazilian Chemical Society, 2001. **12**: p. 57-63.
63. Parag R. Gogate, P.A.T., Parag M. Kanthale, and Aniruddha B. Pandit, *Mapping of Sonochemical Reactors: Review, Analysis, and Experimental Verification.* AIChE Journal, 2002. **48**: p. 1542-1560.
64. Gogate, P.R., et al., *Mapping of sonochemical reactors: review, analysis, and experimental verification.* AIChE Journal, 2002. **48**(7): p. 1542-1560.

65. Rao, P.R. and V.K. Rathod, *Mapping study of an ultrasonic bath for the extraction of andrographolide from Andrographis paniculata using ultrasound.* Industrial Crops Products, 2015. **66**: p. 312-318.
66. Martin, C. and A. Law, *Design of thermistor probes for measurement of ultrasound intensity distributions.* Ultrasonics, 1983. **21**(2): p. 85-90.
67. Fry, W.J. and R.B. Fry, *Determination of absolute sound levels and acoustic absorption coefficients by thermocouple probes—experiment.* The Journal of the Acoustical Society of America, 1954. **26**(3): p. 311-317.
68. Zhou, Y., et al., *Measurement of high intensity focused ultrasound fields by a fiber optic probe hydrophone.* The Journal of the Acoustical Society of America, 2006. **120**(2): p. 676-685.
69. Canney, M.S., et al., *Acoustic characterization of high intensity focused ultrasound fields: A combined measurement and modeling approach.* The Journal of the Acoustical Society of America, 2008. **124**(4): p. 2406-2420.
70. Crawford, A., *The measurement of cavitation.* Ultrasonics, 1964. **2**(3): p. 120-123.
71. Krefting, D., R. Mettin, and W. Lauterborn, *High-speed observation of acoustic cavitation erosion in multibubble systems.* Ultrasonics Sonochemistry, 2004. **11**(3-4): p. 119-123.
72. Kikuchi, T. and T. Uchida. *Calorimetric method for measuring high ultrasonic power using water as a heating material*. in *Journal of Physics: Conference Series*. 2011. IOP Publishing.
73. Pugin, B., *Qualitative characterization of ultrasound reactors for heterogeneous sonochemistry.* Ultrasonics, 1987. **25**(1): p. 49-55.
74. Romdhane, M., et al., *Experimental study of the ultrasound attenuation in chemical reactors.* Ultrasonics sonochemistry, 1997. **4**(3): p. 235-243.
75. Mason, T. and J.L. Luche, *Ultrasound as a New Tool for Synthetic Chemists*. 1996. p. 317-381.
76. Deshayes, S., et al., *Microwave activation in phase transfer catalysis.* Tetrahedron, 1999. **55**(36): p. 10851-10870.
77. Loupy, A., *Microwaves in Organic Synthesis*. 2002, Weinheim: Wiley-VCH Verlag GmbH&Co.
78. Maeda, M. and H. Amemiya, *Chemical effects under simultaneous irradiation by microwaves and ultrasound.* New journal of chemistry, 1995. **19**(10): p. 1023-1028.
79. Leonelli, C. and T.J. Mason, *Microwave and ultrasonic processing: Now a realistic option for industry.* Chemical Engineering Processing: Process Intensification, 2010. **49**(9): p. 885-900.
80. Vinatoru, M.C., I., *Microwave and ultrasounds together – A challenge.* AMPERE 2019 - 17th International Conference on Microwave and High Frequency Heating, 2019: p. 105-112.
81. Yan, J., et al., *Efficient production of biodiesel from ionic liquid catalyzed esterification using ultrasonic-microwave combined intensification.* Chemical Engineering Processing-Process Intensification, 2020. **149**: p. 107870.
82. Habinshuti, I., T.-H. Mu, and M. Zhang, *Ultrasound microwave-assisted enzymatic production and characterisation of antioxidant peptides from sweet potato protein.* Ultrasonics Sonochemistry, 2020. **69**: p. 105262.
83. Zuliani, A., et al., *Improving the electrocatalytic performance of sustainable Co/carbon materials for the oxygen evolution reaction by ultrasound and microwave assisted synthesis.* Sustainable Energy & Fuels, 2021. **5**(3): p. 720-731.
84. Moran, M.J., et al., *Tuneable copper catalysed transfer hydrogenation of nitrobenzenes to aniline or azo derivatives.* Advanced Synthesis Catalysis, 2020. **362**(13): p. 2689-2700.
85. Wilber, W.D. and D.B. Shuping, *Tubular choked waveguide applicator.* US9642194B2, 2015.
86. Van de Voort, F., et al., *A practical thermocouple for temperature measurement in microwave ovens.* Canadian Institute of Food Science Technology Journal, 1987. **20**(4): p. 279-284.
87. Calinescu, I., et al., *Installation for the combined use of ultrasound and microwaves in order to intensify the physico-chemical processes*, in *OSIM*. 2020, UPB: Romania.

88. *Directive 2013/35/EU of the European Parliament and of the Council.* 2013.
89. Löning, J.-M., C. Horst, and U. Hoffmann, *Investigations on the energy conversion in sonochemical processes.* Ultrasonics Sonochemistry, 2002. **9**(3): p. 169-179.
90. Plattes, M., C. Köhler, and T. Gallé, *Disequilibrium calorimetry for determination of ultrasonic power in sonochemistry.* MethodsX, 2017. **4**: p. 274-278.
91. https://www.engineeringtoolbox.com/liquid-dielectric-constants-d_1263.html, *Liquids - Dielectric Constants.* 07.11.2023.
92. Grant, E. and B.J. Halstead, *Dielectric parameters relevant to microwave dielectric heating.* Chemical society reviews, 1998. **27**(3): p. 213-224.
93. Kotronarou, A., G. Mills, and M.R. Hoffmann, *Ultrasonic irradiation of p-nitrophenol in aqueous solution.* The journal of physical chemistry, 1991. **95**(9): p. 3630-3638.
94. Pradhan, A.A. and P.R. Gogate, *Degradation of p-nitrophenol using acoustic cavitation and Fenton chemistry.* Journal of hazardous materials, 2010. **173**(1-3): p. 517-522.
95. Pan, W., et al., *Degradation of p-nitrophenol using CuO/Al 2 O 3 as a Fenton-like catalyst under microwave irradiation.* RSC advances, 2015. **5**(34): p. 27043-27051.
96. Barbier, P.F. and C. Petrier, *Study at 20 kHz and 500 kHz of the ultrasound-ozone advanced oxidation system: 4-nitrophenol degradation.* Journal of Advanced Oxidation Technologies, 1996. **1**(2): p. 154-159.
97. Melero, J.A., J. Iglesias, and G. Morales, *Heterogeneous acid catalysts for biodiesel production: current status and future challenges.* Green Chemistry, 2009. **11**(9): p. 1285-1308.
98. Brunschwig, C., W. Moussavou, and J. Blin, *Use of bioethanol for biodiesel production.* Progress in Energy Combustion Science, 2012. **38**(2): p. 283-301.
99. Ramachandran, K., et al., *Recent developments for biodiesel production by ultrasonic assist transesterification using different heterogeneous catalyst: A review.* Renewable Sustainable Energy Reviews, 2013. **22**: p. 410-418.
100. En, V., *Liquid Petroleum Products—Fatty Acid Methyl Esters (FAME) for Use in Diesel Engines and Heating Applications—Requirements and Test Methods.* European Committee for Standardization: Brussels, Belgium, 2018: p. 14538.
101. Cabral, N.M., et al., *Solid acid resin Amberlyst 45 as a catalyst for the transesterification of vegetable oil.* Frontiers in chemistry, 2020. **8**: p. 305.