



An ultrasonic-accelerated oxidation method for determining the oxidative stability of biodiesel

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ABSTRACT

Biodiesel is considered an alternative energy because it is produced from fats and vegetable oils by means of transesterification. Furthermore, it consists of fatty acid alkyl esters (FAAS) which have a great influence on biodiesel fuel properties and in the storage lifetime of biodiesel itself. The biodiesel storage stability is directly related to the oxidative stability parameter (Induction Time – IT) which is determined by means of the Rancimat[®] method. This method uses conductimetric monitoring and induces the degradation of FAAS by heating the sample at a constant temperature. The European Committee for Standardization established a standard (EN 14214) to determine the oxidative stability of biodiesel, which requires it to reach a minimum induction period of 6 h as tested by Rancimat[®] method at 110 °C. In this research, we aimed at developing a fast and simple alternative method to determine the induction time (IT) based on the FAAS ultrasonic-accelerated oxidation. The sonodegradation of biodiesel samples was induced by means of an ultrasonic homogenizer fitted with an immersible horn at 480 Watts of power and 20 duty cycles. The UV–Vis spectrometry was used to monitor the FAAS sonodegradation by measuring the absorbance at 270 nm every 2. Biodiesel samples from different feedstock were studied in this work. In all cases, IT was established as the inflection point of the absorbance versus time curve. The induction time values of all biodiesel samples determined using the proposed method was in accordance with those measured through the Rancimat[®] reference method by showing a $R^2 = 0.998$.

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1. Introduction

Biodiesel is an important alternative fuel that appears as a renewable natural fuel. It is non-toxic; it has a superior lubricity, a high flash point and cetane number, and high oxygen content. It has been proven that biodiesel emits lower emissions of particulate matter, and it does not increase CO₂ levels in the atmosphere at all. It is produced from renewable biological sources such as vegetable oils of various types of oilseed crops [1,2]. Biodiesel is highly biodegradable. Makarevic and Janulis [3] showed that in comparison with diesel fuel, rapeseed oil ethyl ester in an aqua environment is more readily degraded by microorganisms. Usually, biodiesel is obtained by a transesterification of triglyceride with

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alcohol, using an alkaline catalyst to produce fatty acid esters and glycerol. It is widely known that the transesterification process is more efficient when an alkaline catalyst is used [4].

The biodiesel properties are strongly influenced by the structure and concentration of the fatty acids esters that compose it [5]. However, when compared with petroleum diesel, biodiesel has lower oxidation stability due to its high content of unsaturated methyl esters, especially poly-unsaturated methyl esters which can be easily oxidized, such as methyl linoleate (C18:2) and methyl linolenate (C18:3) [6]. Oxidation of biodiesel is initiated by a free-radical mechanism, which produces hydroperoxides, and it continues with the formation of short-chain carboxylic aldehydes, ketones and acids. In certain conditions, a radical polymerization can be initiated forming insoluble polymers, which may cause engine damages. The oxidation reactions also affect the fuel quality of biodiesel during extended storage. However, early degradation can be overcome by the addition of synthetic antioxidants [7,8].

In the last decade, the oxidation stability of biodiesel has been a special subject of study. Knothe [9] has analyzed the composition of oxidized biodiesel by 1H NMR evaluating the effect of its contact

with air. Dunn [10–12] has examined the oil stability index as a parameter for monitoring the oxidative stability of soybean oil from five separate sources, varying storage and handling records. This author has also studied the effect of antioxidants on the oxidative stability of methyl soyate and the suitability of the dynamic mode of positive air purge pressurized-differential scanning calorimetry as a means of evaluating the oxidation reaction of biodiesel during non-isothermal heating scans. Polavka et al. [13] assessed the oxidation stability of methyl esters analyzed by differential thermal analysis and Rancimat[®]. Schober and Mittelbach [14] have evaluated the influence of diesel particulate filter additives on biodiesel fuel quality. Liang et al. [15] investigated the effectiveness of various natural and synthetic antioxidants at different levels of concentration to improve the oxidative stability of soybean oil, cottonseed oil, poultry fat and yellow grease based biodiesel Leung et al. [16] have investigated the characteristics of biodiesel degradation under different storage conditions, temperatures and environments, monitoring them during periods of 52 weeks.

The biofuels industry requires the development of faster methods to be used in the quality control of its products. As a result, in 2003, the European Committee for Standardization established a standard (EN 14214) to determine the oxidative stability of biodiesel, which requires it to reach a minimum induction period of 6 h as tested by Rancimat[®] method at 110 °C. The aforementioned method induces the degradation of FAAS by heating the sample at a constant temperature, which requires a considerable time of 60 min up to the temperature of analysis. This time-consuming sample degradation leads to the use of fast response energy sources, like ultrasonic energy, in order to achieve the same goal in a shorter period of time.

Applications of ultrasound in degradation of organic and inorganic analytes in a wide variety of samples, such as pharmaceuticals and edible oils, have experienced a significant increase in the last decade [17–20]. Chemat et al. [19] affirms that cavitation can cause lipid oxidation by a purely thermal effect, through free radicals created by sonolysis, and shear forces created via shock waves and microcurrents.

The variables that influence the cavitation phenomenon could be taken into account for proper optimization of US action. In general, since the traditional methods of optimization evaluate the effect of one variable at a time, it is not possible to determine either the interaction between variables or their statistical significance. However, chemometrics offers a theoretical basis for the optimization of chemical processes used on analytical methods allowing the saving of time, reagents and experimental work. This technique is based on the use of an optimum set of experiments which allow the simultaneous variation of all the experimental factors studied. Some applications make use of both, experimental design and ultrasound energy simultaneously [21,22]. To our knowledge, no studies have been reported on the degradation of biodiesel using ultrasound energy and the application of chemometric analysis as a method of optimization and data processing for determining the induction point.

The aim of this study was to develop an efficient alternative method to evaluate the oxidative stability of biodiesel. The action of low-frequency ultrasound energy to accelerate the oxidation of FAAS and UV–Vis spectrophotometric detection to monitor the process were used in this method.

2. Materials and methods

All materials used in this work, including those used in handling, preparation and storage of solutions and samples, were properly decontaminated by washing them with a solution of nitric acid at 10% (v/v) and subsequent stages of ultrapure water rinsing.

2.1. Reagents

Pro-analysis grade chemicals and ultra pure water of Milli-Q quality ($18.3 \Omega \text{ cm}^{-1}$) were used. Homogeneous base catalyst solutions at 0.4% and 1% w/w were prepared by dissolving appropriate amounts of both sodium and potassium hydroxides (Merck) in methanol (99%, Merck). Hydrochloric acid solutions 0.25 and 0.5 mol L⁻¹ were prepared by diluting appropriate amounts of hydrochloric acid (Baker) in ultrapure water. Anhydrous sodium sulfate (Merck). Ethanol (99.5%, Cicarelli).

Commercial biodiesel samples were purchased from two regional companies. Sunflower, corn, soybean and grape seed oils were purchased from the local market. The experimental procedure used to obtain free-additive biodiesel samples at laboratory scale are described in the Appendix A. Physical-chemical parameters of all biodiesel samples are contained in that appendix too.

2.2. Apparatus

Sonication was achieved at low frequencies 20 kHz (600 W) using a Cole-Parmer Ultrasonics Homogenizer 4710 Series (Cole-Parmer, Chicago, IL, USA) fitted with an immersible horn that emits the sound vibration into the sample via a titanium alloy rod (25 mm diameter). The ultrasound power was controlled by changing the ultrasonic output level and the duty cycle was varied between 10% and 90%. The duty cycle refers to the ultrasound time per time unit applied, which is the percentage of time in which ultrasound is being generated – pulse duration – over one pulse period.

A cylindrical Pyrex[®] glass vessel (volume 25 mL) was used as a sonoreactor. The temperature was measured by directly inserting a thermometer into the sonoreactor. The experiments were carried out in triplicate. A Velp Scientifica ZX³Vortex (Velp Scientifica, Italy) was used to homogenize all biodiesel ethanol dilutions. An Agilent 8453 diode-array UV–Visible spectrophotometer (Agilent Technologies, Avondale, PA, USA) equipped with a 1 cm optical path quartz cell was used to collect spectra in standard mode. A Metrohm 743 Rancimat[®] instrument (Metrohm AG, Switzerland) was used to determine the induction time of all biodiesel samples according to standard EN 14214.

Degradation products were measured using a gas chromatograph (Hewlett-Packard HP6890GC) coupled with a quadrupole mass spectrometer (Hewlett-Packard HP5972A). The GC was equipped with an HP-5MS fused silica column (30 m; 0.25 mm i.d.; 0.25 μm film thickness) and Helium 5.0 was used as a carrier gas. The mass spectrometer was operated in the electron impact mode (70 eV). The samples were injected in the splitless mode at 280 °C and the temperature program used was as follows: initial temperature 150 °C for 5 min; heated to 250 °C at 4 °C min⁻¹ and held for 2 min. Degradation products were monitored in mode (SCAN).

2.3. Experimental procedure

In optimal experimental conditions, 10 g of biodiesel sample are sonicated. The monitoring was conducted until a large change of the absorbance occurred, depending on the sample at 480 Watts of power and 20% duty cycles. At the end of the degradation process, the temperatures reached 170 ± 5 °C. During sonodegradation, aliquots of 25 μL of the sample are taken every 2 min. Dilutions 1:1000 (v/v) of these aliquots are prepared. The absorbance measurements of solutions are taken at 270 nm.

From absorbance versus degradation time curve, the induction time is obtained at the point of inflection of the curve. This time indicates the maximum point of change in the biodiesel oxidation rate and it is related to the maximum storage time.

2.4. Oxidative stability determination by Rancimat[®] method

Oxidative stability of methyl esters in all biodiesel samples was measured following the European Standard EN 14214 using a Metrohm 743 Rancimat[®] instrument. The tests were carried out with 3.00 ± 0.01 g of biodiesel at 110°C and with an air flow of 10 L h^{-1} and conductimetric monitoring.

3. Results and discussion

3.1. Optimization of experimental variables for oxidative stability study

The optimization of the variables sonication time (t), duty cycles (c) and power (p) was made in order to obtain the best response, which in our case would be the degradation of sunflower biodiesel, which was monitored by means of the absorbance measurements at 270 nm.

The sonication time was introduced in the experimental design in order to determine optimal values of power and duty cycles. Such optimal values were maintained constant while the sonication time was varied in order to determine the induction time for each biodiesel sample by the proposed method.

Before performing the design of the experiments, preliminary tests were conducted which found that the sonication time to optimize the sample was less than 8 min. Therefore, we have included it in the design, even if we knew that this would be different than all the samples.

A circumscribed central composite design (CCCD) was employed in the optimization. The low (-1), central (0), and high ($+1$) levels of the variables are shown in Table 1, as well as the star points, which were located at $\pm\alpha$ from the center of the experimental domain situated in 0 . The precise value of α depends on certain properties desired for the design and on the number of factors involved. In order to establish the rotatability and orthogonality of the experimental design, n was set at 9 and $\alpha = \pm 1.682$ [23]. Therefore, the overall matrix of CCCD design involved 23 experiments. The advantage of CCCD was to study at the same time the main effects and the interaction effects of three independent variables on the response variable studied.

A 3-level design is suitable for exploring quadratic response surfaces and constructing second-order polynomial models. Experiments were randomized in order to minimize the effects of unexplained variability in the actual responses due to extraneous factors. The center point was repeated six times to calculate the repeatability of the method. The data obtained were evaluated by an ANOVA test, and the effects were visualized using a Pareto chart (Fig. 1). The vertical line that correlates with the 95% limitation stating statistical importance is shown in the chart. Consequently, if the corresponding bar traverses this vertical line there will be a significant effect. As can be seen, the three variables considered were significant with 95% probability. Ultrasound power and ultrasound duty cycles showed a negative effect, whilst sonication time showed a positive effect upon degradation. Furthermore, examination of the quadratic effects, also shown in Fig. 2, reveal that the

Table 1

Experimental design used in the optimization of experimental variables for biodiesel sonodegradation.

Factor	Experimental domain						
	$-\alpha$	-1	0	1	α	Optimal	
Sonication time [min]	(t)	1,6	3	5	7	8,4	8,4
Power [w]	(p)	96	180	300	420	504	480
Duty cycles [%]	(c)	20	35	55	75	90	20

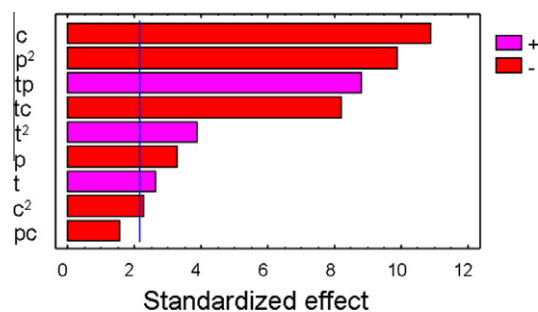


Fig. 1. Pareto chart of the main effects obtained from the circumscribed central composite design (c : duty cycles, p : power, t : sonication time; p^2 , t^2 , c^2 : quadratic effect of the main variables; tp , tc , pc : interactions between main variables). The vertical line represents the 95% confidence interval for a significant effect. – and + signs indicate negative and positive effects, respectively.

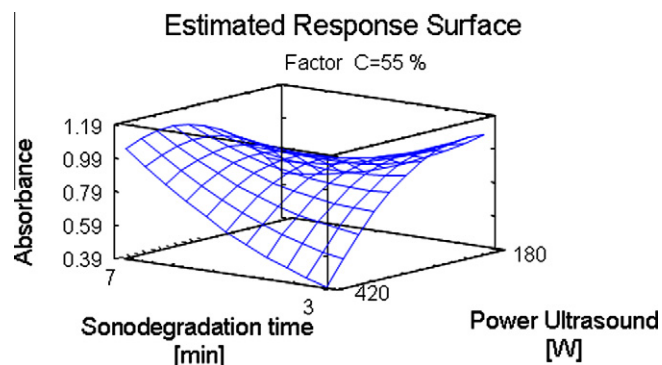


Fig. 2. Response surface plot ($p < 0.05$) of the circumscribed central composite design obtained by plotting sonication time vs. ultrasound power (c : duty cycles).

quadratic effects of ultrasound power (p^2), ultrasound duty cycles (c^2) and sonication time (t^2) were statistically significant, p^2 and c^2 exhibiting a negative effect, and sonication time (t^2) exhibiting a positive effect upon degradation. The interaction between sonication time and ultrasound power (tp) showed a significant positive effect, while the interaction between sonication time and duty cycles (tc) showed a significant negative one. The presence of curvature in 3D response surface plots could be interpreted by the quadratic effects of independent variables. For that reason, plot in Fig. 2 was useful to interpret the variation of the Absorbance at 270 nm as a function of sonication time and ultrasound power with the ultrasound duty cycles fixed at 55. As can be seen, sonication time shows a positive effect upon biodiesel degradation. The optimal conditions for the ultrasound assisted sunflower biodiesel oxidation were 8 min of sonication time, 480 W of power and 20 duty cycles.

3.2. Induction time determination

The induction time determination of biodiesel samples from different feedstock was made in optimal experimental conditions of 20 duty cycles and 480 W of power. As can be seen in Fig. 3, two bands at 232 and 270 nm exhibit similar behavior and the degradation may be followed by any of them. However it is more apparent at 270 nm and thus it was chosen to monitor the measurements by the proposed method. After 16 min the absorbance measurements did not vary significantly.

A gradual and considerable increasing of absorbance can be observed in the band at 270 nm which can be related to the concentration of the secondary products of biodiesel oxidation (methyl esters as short-chain aldehydes and carboxylic acids) and which

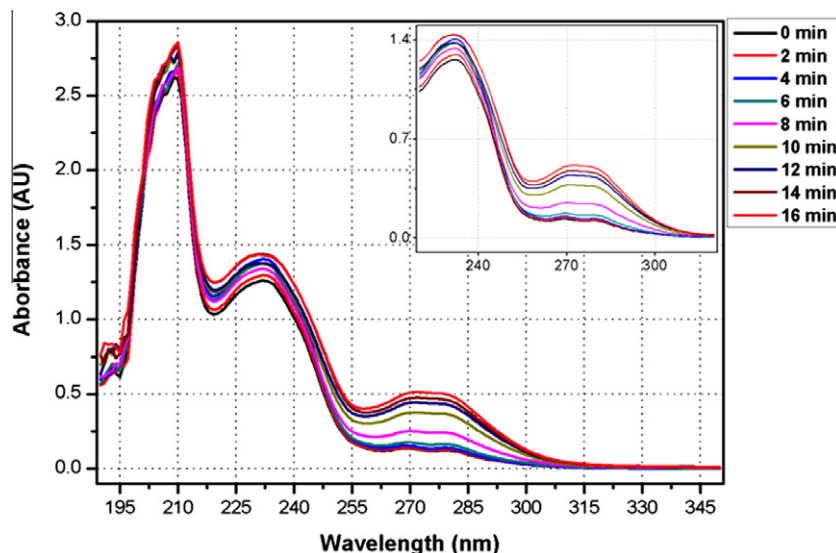


Fig. 3. UV spectra recorded during the sonodegradation of the sunflower biodiesel.

could be used in the determination of induction time. The working spectral region used in the analysis of the oxidative stability of all biodiesel samples covers the range from 220 to 320 nm. The region between 190 and 220 nm has high saturation and the region above 320 nm does not provide relevant spectral information. Dantas et al. [24] have observed the same behavior in the biodiesel corn oxidation that is thermally induced at 150 °C, in which an increase of the absorbances at 232 and 272 nm was found.

A simple and faster way to determine the induction time is to study the biodiesel oxidative stability at a single wavelength which was selected for this work. Fig. 4 shows second derivative and absorbance (at 270 nm) versus degradation time curves of sunflower biodiesel. On the other hand, a complementary study of the induction time assessment based on the work of Zawadzki et al. [25] was made where the absorbance index ($AI = 10E[A_{270} - (A_{260} + A_{280})/2]$) is described as a measurement of the shape of the absorbance curve. To calculate the absorbance index, the absorbance measurements at 260, 270, and 280 nm were

used. It was observed that the AI curve in time function has a common sigmoid shape with the absorbance curve at 270 nm in time function which was described earlier. Therefore, the induction time values found via the AI index of the second derivative versus time curve were comparable with the one which was chosen for this work.

3.3. Biodiesel degradation induced by ultrasound

During the experimental procedures, a rancid odor and a change in color were detected for biodiesel treated by ultrasound. The various unsaturated compounds that comprise the complicated process of biodiesel degradation can produce several degradation products. Several mechanisms are connected with the oxidation of unsaturated double bonds free fatty acid. It is possible to classify them as primary oxidation and secondary oxidation products. The former participates in initiation, propagation and termination. The biodiesels analyzed by CG-MS have several compounds such as

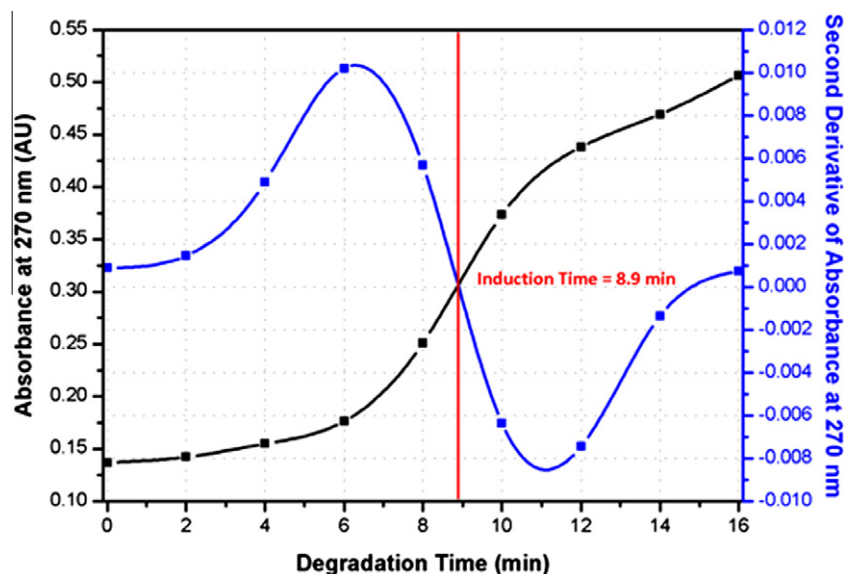


Fig. 4. Second derivative and absorbance (at 270 nm) versus degradation time curves of sunflower biodiesel.

the methyl esters of C18:0, C18:1, C18:2 cis 9, 12, among others. If we look at the degradation compounds, we noted that the original double bonds may have shifted or undergone cis/trans isomerization (9, 12 to 9, 11; 9, 12 to 10, 13; 9, 12 to 8, 11 and 9, 12 to 9, 15), in accordance with what is indicated in the literature [26]. Later, the formation the compound 6E, 8E dodecadien-1-ol was observed, which demonstrates the degradation process.

3.4. Comparison between the proposed and Rancimat® method

The induction time values obtained by means of the proposed and by the Rancimat® reference method (Table 2) were compared through a Student's paired *t*-test at 95% confidence level. The experimental value of calculated *t* was lower than the critical value for a two-tailed test ($t = 1.83$; $t_c = 2.36$) showing that there are no significant differences between the induction time values obtained by both methods with a significant level of $\alpha = 0.05$.

The results of these studies show that the biodiesel IT of companies 3 and 4 are 60 and 96 min respectively, probably due to the various percentages of saturated fatty acid. On the other hand, since the samples of companies 1 and 2 were exposed to greater storage time their biodiesel IT levels were lower.

Fig. 5 shows the regression line corresponding to the biodiesel samples induction time values obtained through the proposed method and those obtained from the Rancimat® reference method. The correlation coefficient obtained for the straight line was 0.998.

The standard EN 14214 establishes a minimum limit of 6 h for induction time (equal to 360 min) as tested by Rancimat® method at 110 °C. With the proposed method, a limit equivalent to 65.49 min was obtained from the equation $Y = 0.1725X + 3.2823$ (Fig. 5) by extrapolation of the Rancimat® minimum limit of 360 min.

Table 2
The induction time values obtained by means of the proposed and the Rancimat® reference method.

Sample	Induction time (min)	
	Proposed method	Rancimat® method
Sunflower biodiesel	7 ± 0.4	21 ± 4.2
Corn biodiesel	10 ± 2.6	36 ± 7.2
Grape seeds biodiesel	5 ± 1.3	10 ± 2
Soybean biodiesel	8 ± 1.2	25 ± 5
Biodiesel company 1	9 ± 2.2	33 ± 6.6
Biodiesel company 2	11 ± 0.2	43 ± 8.6
Biodiesel company 3	60 ± 2.5	349.2 ± 10
Biodiesel company 4	96 ± 3.1	523.2 ± 9.4

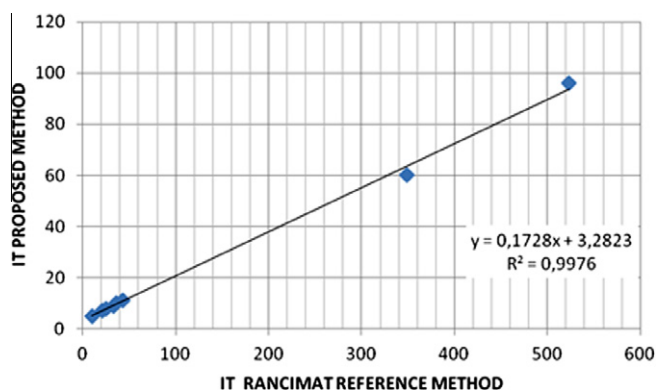


Fig. 5. Correlation plot between the proposed method and the Rancimat® reference method (IT: Induction time).

4. Conclusions

The oxidative stability of biodiesel is a very important quality parameter that is established through the determination of induction time directly related to the biodiesel storage lifetime. In this work, an efficient system to accelerate the oxidation of FAAS through the action of ultrasounds has been developed in order to study the oxidative stability. This required the development of a spectrometric method to determine the induction time by means of the absorbance measurements at 270 nm in time function. The proposed method is a simple, fast and effective way to assess the biodiesel oxidative stability since the required equipment and instrumentation could be available in every laboratory. The induction time values of all biodiesel samples determined using the proposed method was in accordance with the values measured through the Rancimat® reference method. The proposed method was useful for the induction time evaluation of biodiesel commercial samples and for those obtained at laboratory-scale production.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.ultsonch.2012.10.012>.

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