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Oxidative polymerization of waste cooking oil with air under hydrodynamic cavitation

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Abstract: Apart from being a component of some animal feed products, the main industrial use of recycled waste frying oils is biodiesel preparation. With the aim of finding a suitable technology for a cost-effective valorization of used cooking oil, we investigated some oxidative treatments under hydrodynamic cavitation with air flow. This process enabled the preparation of a useful precursor of fatliquor used in the leather industry through the efficient oxidation/polymerization of waste oils at 90°C. The same technique enabled a stable dispersion/emulsification in water without surfactants. Thanks to the use of these innovative techniques, a four-fold reduction of the oxidation time of waste oil was achieved. All the results indicate that the use of a highly efficient rotor-stator generator of hydrodynamic cavitation is compatible with a process scaling up for potential industrial applications.

Keywords: hydrodynamic cavitation; oxidative polymerization; process intensification; rotor-stator reactor; waste cooking oil.

1 Introduction

Deep-fat frying is one of the oldest and most popular methods of food preparation. Vegetable oils used in professional fryer machines are heated several times in temperatures ranging from 90°C to 175°C. Such high temperatures enable food surface dehydration and Maillard reactions that, in turn, break down sugars and proteins, thereby creating the golden brown exterior of the food. Prolonged oil heating in the presence of moisture, salts, and air can result in oil degradation and alteration of food quality [1, 2]. The management of waste oils and fats pose a significant challenge because of problems related to their disposal and their possible contamination of water and land resources. The recovery of waste cooking oil for new uses and applications after suitable physico-chemical treatments is a challenging goal in relation to economic and environmental issues [3–5]. The annual worldwide total amount of waste cooking oil is estimated to be more than 5 million tons. Deep-fat frying generally involves different types of chemical reactions, such as hydrolysis, oxidation, and polymerization with the production of volatiles or solid compounds. Furthermore, it decreases the unsaturated fatty acids of oil as well as increases foaming, color, viscosity, density, specific heat, as well as contents of free fatty acids, polar materials, and polymeric compounds [6].

Apart from biodiesel production [7], used cooking oil can be purified and used as an ingredient in animal feed supplements. The purification generally requires a pre-treatment step to reduce the free fatty acids and water contents in the feed stream. Very recently, we reported an efficient conversion of waste frying oils to high quality biodiesel using a rotor-stator type generator of hydrodynamic cavitation (HC) [8], an innovative technology that resulted in a competitive process of recycling used oil in terms of treatment time, energy consumption, and scalability.

In leather industries, mineral and vegetable oils, such as oil/water emulsions, are employed in the production of fatliquors, which are then used to lubricate tanned leather fibers to achieve softness and improve the robustness of the final product [9]. In recent years, waste cooking oils have been introduced as an alternative to rapeseed, linseed, or castor oil. However, waste cooking oil must undergo suitable treatments before it can be used, such as the filtration on paper or cloth filter, which removes food bits, insoluble particles, adsorbent degradation products, and water [10]. After this process, the waste cooking oil can be recycled and used just like other vegetable oils to produce fatliquors. Typically, this

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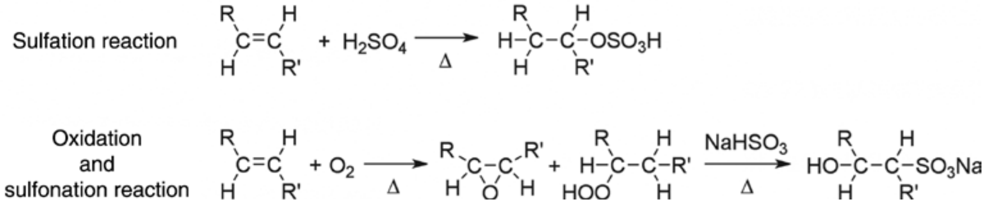
preparation includes sulfation or sulfonation processes that facilitate the fatliquor oils emulsion in water [11, 12] (Scheme 1).

Sulfate moiety, which is obtained by the action of sulfuric acid, is relatively unstable because it is prone to hydrolysis under acidic conditions [13]. This drawback is usually overcome by producing sulfonated fatliquors, which can be obtained by the action of sodium bisulfite on oxidized oils, resulting in a more resilient C-S bond rather than a C-O-S group. A common means of producing sulfonated fatliquors is to react oils with air at high temperatures to promote the formation of high levels of hydroperoxides and epoxides, which are subsequently reacted with sodium bisulfite. However, the oxidation and sulfonation reactions are time-consuming processes.

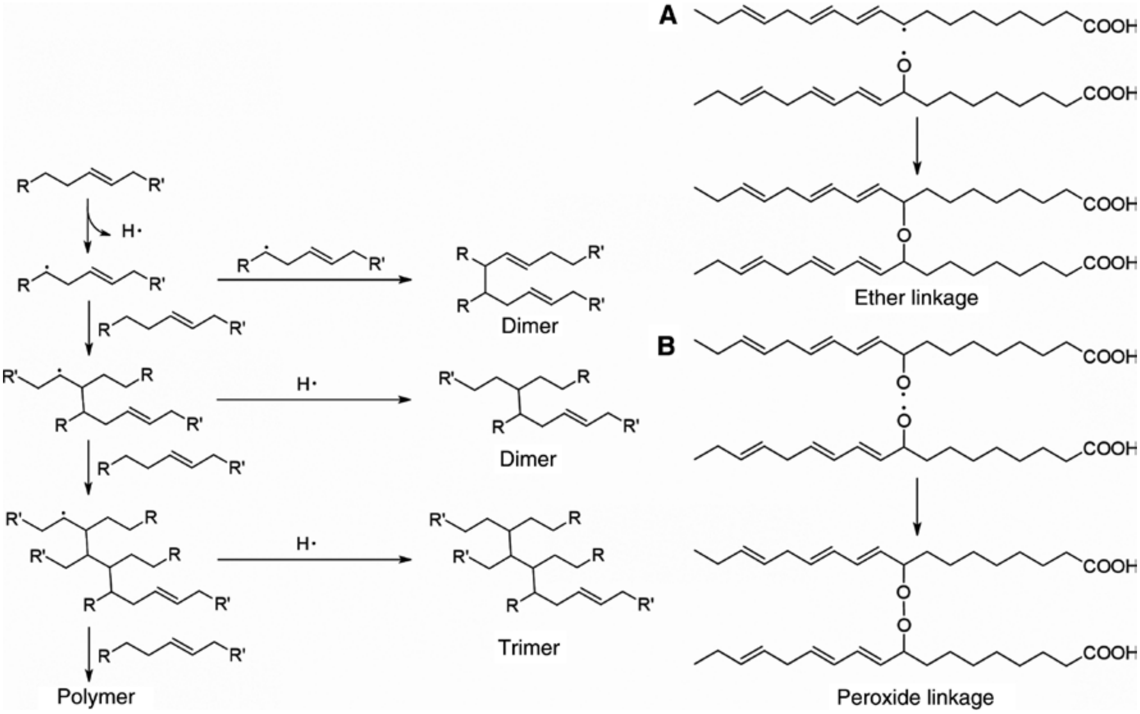
Aside from these oxidized intermediates, polymerization takes place during the oxidation process to form dimers, oligomers, and polymers, which are structures with high molecular weight that are formed by cross-linking bridges with -C-C-, -C-O-C-, and -C-O-O-C- bonds (see Scheme 2).

The formation of polymers determines a progressive increase of viscosity. In the literature [14], the correlation of viscosity with free fatty acids and total polar materials is considered as a reference and is also used as an indicator of the degree of oil oxidation. Oil viscosity is a parameter that can be easily and rapidly measured using a viscometer, a popular technique employed in the online monitoring of the oil oxidation process in industrial plants.

In the process of oxidation, the reaction rate is negatively affected by the poor mass transfer between air and



Scheme 1: Typical reactions for fatliquor production.



Scheme 2: Possible formations of different polymer types during the treatment via cross-linking oxygen bonds: (A) ether; (B) peroxide.

oil. The choice of air instead of oxygen is due to safety reasons: oxygen at high pressure can violently react with oil and grease. Mass transfer in heterogeneous liquid/liquid or liquid/gas systems, can be dramatically improved by HC [15]. Cavitation is a phenomenon characterized by the formation, growth, and collapse of bubbles within a liquid. Four types of cavitation exist: hydrodynamic, acoustic, optical, and particle-induced cavitation [16]. Both HC and ultrasonic cavitation enhance the mass transfer coefficient [17, 18], with classical applications in advanced oxidation processes [19] and bioremediation [20]. HC is produced by large pressure differentials within a flowing liquid, which generates turbulence that can increase the mass transfer rates and provide better contact between the reactants [21]. The HC phenomenon involved in high-pressure homogenizers is based on the pumping of the liquid at very high pressure through a constriction that then converts its pressure energy into kinetic energy. At extremely high kinetic energy levels, the pressure is reduced below the liquid vapor pressure, thus generating cavitation [22, 23]. The cavitation phenomenon also results in the formation of highly reactive free radicals [24]: the higher temperature of the gas phase inside the bubbles at the final stage of the collapsing process leads to a higher generation rate of radicals [25]. In addition, a more violent collapse at a higher number of cavitation events permits the migration of some radicals to the bulk liquid [26].

HC has been reported to be more energy efficient than acoustic cavitation [27, 28], with additional advantages when fine and stable oil/water emulsions are required [29]. Previous applications of combined HC and reacting gas have been described in plants for water treatments with continuous ozone inlet [18, 30, 31]. When gas is used in HC units, the main advantage is a micro dispersion of bubbles with a mass transfer enhancement and a faster dissolution in the liquid. Some examples of sonochemical treatments for fatliquor production have been described in the literature [32–34].

With the aim of promoting the oxidation of waste cooking oil, different HC systems with air-flow were tested in the present study. Aside from a classic HC unit typically used for wastewater treatments [35] and chemical reactions in heterogeneous aqueous systems [36], we employed a new type of rotating generator of HC equipped with a high-speed rotor with suitable indentations. Similar reactors and homogenators generating HC by rotation have been previously described by other authors, who have proven its significant advantages in terms of efficiency and versatility [28, 37–39]. To the best of our knowledge, this is the first study focused on waste oil oxidative treatments under HC conditions with air flow.

2 Materials and methods

2.1 Materials and procedures

The waste cooking oils were kindly provided by the Silvateam and used without further purification. All chemicals were purchased from Sigma-Aldrich (Milan, Italy) and used without further purification. Three different procedures were carried out using 1) conventional heating, 2) a standard HC unit, and 3) a new rotor-stator type generator of HC.

2.2 Conventional set-up

A 2 l four-necked round bottom flask equipped with a condenser, a thermocouple, an air inlet, and an external gas flow-meter, was placed in a electric heating mantle. The oil (1.5 l) was heated under a constant air flow of 20 nl/h. The instantaneous power consumption was measured with a plug power meter.

2.3 Lab-scale HC unit

A lab-scale device with two orifice restrictions, one in suction and one in pressure, which was already described in the literature [14], was equipped with an air inlet and an external gas flow-meter. The HC unit consisted of a centrifugal pump, a double orifice, a heat exchanger, a water tank, a manometer, a liquid flow-meter and the required connecting tubings. All of the contacting surfaces were made of stainless steel (SS316). The centrifugal pump (Speck GY-028-2, 2750 rpm, Roth, Germany) was capable of generating a negative pressure of – 0.04 MPa (suction) and a max flow rate of 1980 l/h. The nominal electrical power was set at 1.1 kW. The total volume of the oil was set at 800 ml. The temperature of bulk liquid was maintained

Figure 1: Rotor-stator generator of HC.

Figure 2: Dispersion of fine air bubbles in oil after treatment with the rotor-stator generator of HC.

constant by using a cooling circulator and a heat exchanger. A venturi tube with a throat diameter of 6 mm was attached at the inlet of pump, so that the cavitation was mainly induced by suction. The inner diameter for the connecting pipes was 21 mm. Air was introduced into the solution under the suction orifice. The instantaneous power consumption of the centrifugal pump was measured using a plug power meter.

2.4 HC unit with a continuous rotor-stator type reactor

The unit is a commercial unit designed by E-PIC S.r.l. (Mongrando, Italy), as described in a previous paper [6], and characterized by a rotating apparatus equipped with a three-phase 7.5 kW electric motor (Figure 1). The absorbed power of the HC unit was constantly monitored by a digital ammeter, with a sampling frequency of 1 s.

2.5 General procedure

In all systems, the oil was heated at 90°C under a controlled air flow for a defined time, in order to obtain a viscosity of 70 cSt. This viscosity is the standard requirement for the subsequent reaction with sodium bisulfite.

2.6 Analysis

Three main parameters were controlled during the process, namely, peroxide value (PV), viscosity, and Fourier transform-infrared (FT-IR) spectra. Conventionally, oxidation reaction was monitored by following the oil PV using the AOCS iodometric method [40], which was expressed as mEq of peroxide oxygen per kilogram of oil (mEq/kg). From the perspective of the operator, this method is time-consuming and difficult to use when disposing hazardous reagents; hence, viscosity is the preferred indicator of constant reaction monitoring. A Cannon-Fenske 350 series viscometer for transparent liquids (State College, PA, USA), with a thermostatic bath (Type M900-TI, MPM Instruments Srl, Bernareggio, Italy), was used to measure the viscosity of all samples at 50°C. The temperatures were checked with a digital thermometer within the thermostat and the viscometer. At the beginning of each measurement, about 7 ml of the sample was filled into the measuring cup. A Perkin Elmer, Spectrum 100 Spectrometer (Shelton, CT, USA) was used for the FT-IR analysis.

3 Results and discussion

The present investigation started from a series of oxidations performed under conductive heating in a conventional electric mantel, in order to obtain a set of reference data. The conventional conditions mimicked the industrial set up, in which the mixing was only provided by the air stream; therefore, mass transfer between air and the oil was limited by the big size of the bubbles. The use of an air inlet with little orifices along with adequate stirring may reduce air bubbles dimensions. As expected, the reaction was very slow and no changes in viscosity occurred in the first hours. Differently, as shown in Figure 2, a fine dispersion was obtained after treatment with the rotor-stator generator of HC.

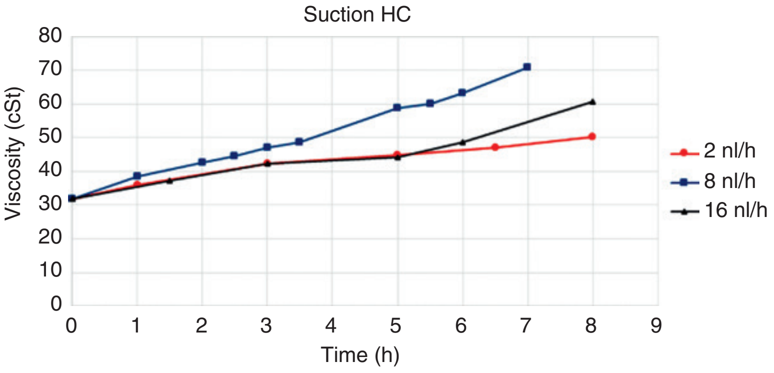


Figure 3: Viscosity changes by HC treatment at different flow rates.

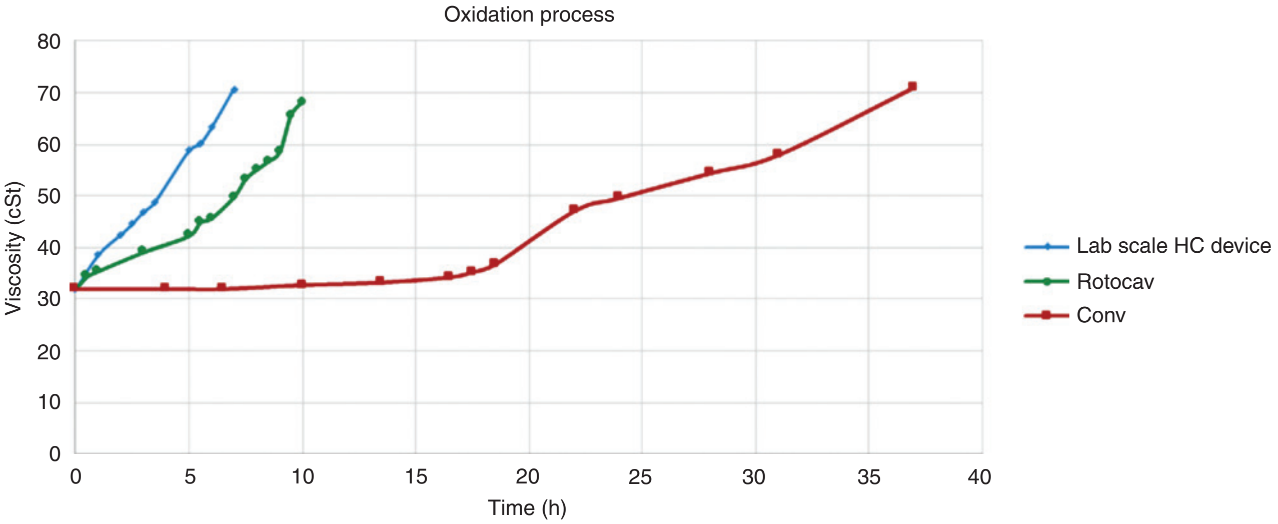


Figure 4: Viscosity monitoring during the oxidation process.

Table 1: Average measurements after oxidative treatments.

	Untreated	Conventional heating (37 h)	HC unit (7 h)	Rotating HC generator (10 h)
Peroxide value (mEq/kg)	≈ 0	600	18	21
Unit energy consumption (kWh/kg)	–	15	7.4	4.6
Air consumption (nl/kg)[a]	–	500	80	10.3

[a] Air consumption = volume of air introduced in the system per weight of treated oil.

HC systems have been introduced to decrease the bubble size into micro bubbles and, therefore, to reduce reaction time. The use of a lab scale HC device gave a product with desired viscosity in a much shorter period of time. Different air flows were studied and used as optimal flows, as shown in the suction HC changing flow rate in Figure 3. This is probably the best compromise between providing enough reagent and strong cavitation. In fact, when the air flow was 16 nl/h the cavitation decreased because of the large amount of air into the oil [41]. The viscosity followed a nearly linear increment.

The second type of HC unit with a continuous rotor-stator reactor aside from intense HC exerted a stronger mechanical stress due to the high-speed rotor action. This device helped decrease the air bubble size until it reached micrometric dimension with a peculiarly low coalescence tendency (Figure 2). As shown in (Figure 4), in 10 h at 90°C, almost 10 l of waste cooking oil gained the target viscosity. The viscosity enhancement had nearly linear trend. The conventional procedure required 40 h at 90°C to obtain a viscosity of about 70 cSt. The main parameters were measured for each set of experiments. The average values are displayed in Table 1.

The energy values reported in Table 1 are the so-called mechanical output energies: this means that the measured electric powers are multiplied by the respective motor efficiency. Hence, the calculated mechanical output energies are independent from the efficiencies of the electric motors. Meanwhile, for the conventional heating process, the efficiency of the heating mantle in estimating the real thermal energy input into the system was calculated by monitoring the instantaneous electric power and the oil temperature change in a predetermined time. Efficiency is defined as

$$\text{Efficiency\%} = \frac{(\text{Mass of oil}) \times (\text{Specific heat capacity}) \times (\text{change in temperature})}{\text{Electric energy}} \times 100.$$

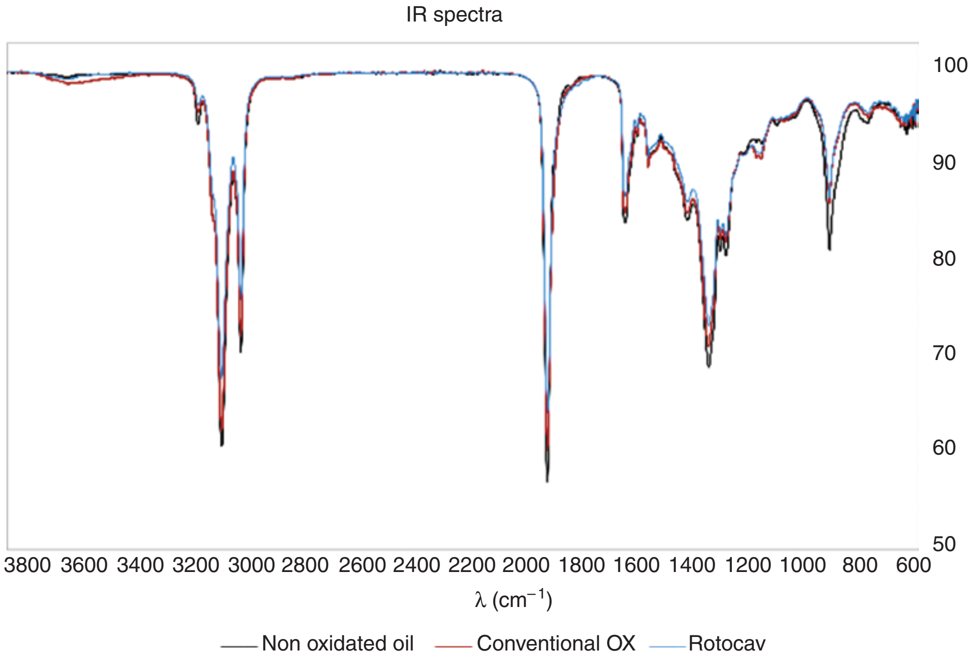


Figure 5: FT-IR spectra.

In a conventional heating process, PV is higher than the values observed from the two HC systems. Cavitational events may promote the peroxide scission and the formation of new -O-O- cross linking bridges [42]. In HC systems, the formation of dimers and trimers is favored at the expense of peroxide species. HC accelerates radical formations and, consequently, promotes the growth of the polymeric chain.

Furthermore, IR measurement (Figure 5) was conducted on the starting material and the treated oils for qualitative analysis [43–45]. The main changes after oxidative treatments reported in the literature included the disappearance of peaks at 3011 and 1654 cm^{-1} and the decrease of the absorption at 723 cm^{-1}, which can be attributed to isolated double bonds. The appearance of a broad band centered at ca. 3430 cm^{-1}, which was due to hydroxyl groups, and of a weak absorption at 1633 cm^{-1} can be attributed to the formation of conjugated double bond. Both conventional and HC processes showed the same changes in the IR spectra in the area of -OH stretching band at 3434 cm^{-1}. In general, all the treatments with HC generated less hydroxyl groups.

The measurement of energy consumption showed higher values for the conventional heating process (15 kWh/kg) and for the lab scale HC apparatus (7.4 kWh/kg) compared with the rotating generator of HC (4.6 kWh/kg). This was because the latter enabled a higher amount of oil to be processed per unit time. Scaling up experiments are in progress with a bigger tank that uses a bigger rotating cavitator with a higher feeding rate. With the aim of producing fatliquors, further tests will be performed to understand whether this type of oxidation is suitable for the subsequent sulfonation reaction.

4 Conclusion

This work demonstrated that HC systems can be successfully employed to promote the oxidative polymerization and emulsification of oils. The use of a rotor-stator generator of HC is compatible with a scaling up of the process thanks to the low-energy consumption of the generator. The production of fatliquors from waste frying oils is a process with a huge industrial impact for leather production and beyond, thus ensuring the full application of the circular economy's recycling concepts.

References

[1] Melton SL, Jafar S, Sykes D, Tigriano MK. *J. Am. Oil Chem. Soc.* 1994, 71, 1301–1308.
[2] Aladedunye FA. *Eur. J. Lipid Sci. Technol.* 2015, 117, 1867–1881.
[3] De Araújo CDM, de Andrade CC, Silva EDE, Dupas FA. *Renew. Sust. Energ. Rev.* 2013, 27, 445–452.
[4] Maddikeri GL, Pandit AB, Gogate PR. *Fuel Proc. Technol.* 2013, 116, 241–249.
[5] Maddikeri GL, Gogate PR, Pandit AB, *Fuel* 2014, 137, 285–292.
[6] Choe E, Min DB. *J. Food Sci.* 2007, 72, 77–86.

[7] Banerjee R. *Res. Conserv. Recycling*. 2009, 53, 490–497.
[8] Crudo D, Bosco V, Cavaglià G, Grillo G, Mantegna S, Cravotto G. *Ultrason. Sonochem.* 2016, 33, 220–225.
[9] Zhang Y, Wang L. *Polym.-Plast. Technol*. 2009, 48, 285–291.
[10] Dawei T, Hong L, Zhen W, Bo Z, Yanfei L. *Food Anal. Methods*. 2014, 7, 1263–1270.
[11] Dutta, SS, *An introduction to the principles of leather manufacture*, 4th ed., Indian Leather Technologists Association, Calcutta, 2000.
[12] El-Shahat HA, Nashy MG, Megahed MA, Abd EG. *J. Am. Oil Chem. Soc.* 2011, 88, 1239–1246.
[13] Burgess D. *J. Soc. Leather Technol. and Chemists*. 1993, 78, 39–47.
[14] Wu Z, Franke M, Ondruschka B, Zhang Y, Ren Y, Braeutigam P, Wang W. *J. Hazardous Mat.* 2011, 190, 375–380.
[15] Gogate PR. *Chem. Eng. Process*. 2008, 47, 515–527.
[16] Shah, YT, Pandit, AB, Moholkar, VS, Eds., *Cavitation Reaction Engineering*, 1st ed., Springer US: New York, 1999.
[17] Chedeville O, Debacc M, Almanza MFA, Porte C. *Sep. Purif. Technol.* 2007, 57, 201–208.
[18] Weavers LK, Hoffmann MR. *Environ. Sci. Technol.* 1998, 32, 3941–3947.
[19] Bremner D, Di Carlo S, Chakinala AG, Cravotto G. *Ultrason. Sonochem.* 2008, 15, 416–419.
[20] Li WX, Tang CD, Wu Z, Wang WM, Zhang YF, Zhao Y, Cravotto G. *Env. Sci. Pollut. Res.* 2015, 22, 6298–6307.
[21] Chakinala AG, Bremner DH, Gogate PR, Namkung KC, Burgess AE. *Appl. Catal. B – Environ*. 2008, 78, 11–18.
[22] Gogate PR, Pandit AB. *Ultrason. Sonochem*. 2005, 12, 21–27.
[23] Nikitenko SI, Le Naour C, Moisy P. *Ultrason. Sonochem*. 2007, 14, 330–336.
[24] Sayyaadi H. *Chem. Eng. J.* 2015, 272, 79–91.
[25] Musmarra D, Prisciandaro M, Capocelli M, Karatza D, Iovino P, Canzano S, Lancia A. *Ultrason. Sonochem*. 2016, 29, 76–83.
[26] Sayyaadi H. *Fluid Dynam. Res.* 2010, 42, 055503–055522.
[27] Gogate PR, Kabadi AM. *Biochem. Eng. J.* 2009, 44, 60–72.
[28] Petkovšek M, Zupanc M, Dular M, Kosjek T, Heath E, Kompare B, Širok B. *Sep. Purif. Technol.* 2013, 118, 415–423.
[29] Crudo D, Bosco V, Cavaglià G, Mantegna S, Battaglia L, Cravotto G. *AgroFOOD Ind. High-Tech* 2014, 25, 55–59.
[30] Wu ZL, Ondruschka B, Zhang YC, Bremner DH, Shen HF, Franke M. *Green Chem.* 2009, 11, 1026–1030.
[31] Gogate PR, Mededovic-Thagard S, McGuire D, Chapas G, Blackmon J, Cathey R. *Ultrason. Sonochem.* 2014, 21, 590–598
[32] Sivakumar V, Prakash RP, Rao PG, Ramabrahmam BV, Swaminathan G. *J. Clean. Prod.* 2008, 16. 549–553.
[33] Sivakumar V, Gayathri VK, Pranavi PS, Chandrasekaran F. *J. Clean. Prod.* 2012, 37, 1–7.
[34] Sivakumar V, Rao PG. *J. Clean. Prod.* 2001, 9, 25–33.
[35] Cvetkovic M, Kompare B, Klemencic AK. *Envir. Sci. Pollut. Res.* 2015, 22, 7422–7438.
[36] Cravotto G, Borretto E, Oliverio M, Procopio A, Penoni A. *Catal. Commun.* 2015, 63, 2–9.
[37] Kumar PS, Pandit AB. *Chem. Eng. Technol.* 1999, 22, 1017–1027.
[38] Badve M, Gogate P, Pandit A, Csoka L. *Sep. Purif. Technol.* 2013, 106, 15–21.
[39] Petkovšek M, Mlakar M, Levstek M, Stražăr B, Širok M, Dular M. *Ultrason. Sonochem.* 2015, 26, 408–414.
[40] American Oil Chemists' Society, *Official and Recommended Practices of the American Oil Chemists' Society*, 4th ed., Champaign, 1989.
[41] Wu Z, Cravotto G, Ondruschka B, Stolle A, Li W. *Sep. Purif. Technol.* 2016, 161, 25–31.
[42] Encina MV, Lissi E, Sarasua M, Gargallo L, Radic D. *J. Polym. Sci. Polym. Lett. Ed*. 1980, 18, 757–760.
[43] Lazzari M, Chiantore O. *Polym. Degrad. Stab*. 1999, 65, 303–313.
[44] van de Voort FR, Ismail AA, Sedman J, Emo G. *Ibid*. 1994, 71, 243–253.
[45] Yildiz G, Wehling RL, Cuppett SL. *JAOCS*. 2001, 78, 495–502.

Bionotes

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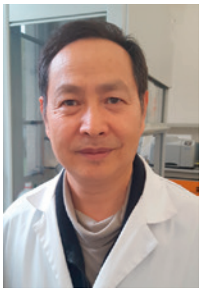
Laura Rinaldi received her PhD in Chemical and Material Sciences in February 2015, working on green technologies for the synthesis of fine chemicals and cyclodextrin derivatives. Her research activity is centered on innovative non-conventional techniques for process intensification, and is documented by publications.



Zhilin Wu

Zhilin Wu obtained his PhD in 2005 from the Friedrich Schiller University (Jena, Germany), where, as a post doc, he continued his research in the applications of ultrasound and microwaves in green chemistry and environmental remediation. In 2013, he obtained a temporary researcher position at the University of Turin (Italy).

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