A new pilot flow reactor for high-intensity ultrasound irradiation: Application to the synthesis of biodiesel

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A new pilot flow-reactor for high-intensity ultrasound irradiation. Application to the synthesis of biodiesel

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Abstract

In recent years, chemistry in flowing systems has become more prominent as a method of carrying out chemical transformations, ranging in scale from microchemistry up to kilogram-scale processes. Compared to classic batch ultrasound reactors, flow reactors stand out for their greater efficiency and flexibility as well as lower energy consumption. This paper presents a new ultrasonic flow reactor developed in our laboratory, a pilot system well suited for reaction scale up. This was applied to the transesterification of soybean oil with methanol for biodiesel production. This reaction is mass-transfer-limited initially because the two reactants are immiscible with each other, then because the glycerol phase separates together with most of the catalyst (Na or K methoxide). In our reactor a mixture of oil (1.6 L), methanol and sodium methoxide 30% in methanol (wt/wt ratio 80:19.5:0.5, respectively) was fully transesterified at about 45 _C in 1 h (21.5 kHz, 600 W, flow rate 55 mL/min). The same result could be achieved together with a considerable reduction in energy consumption, by a two-step procedure: first a conventional heating under mechanical stirring (30 min at 45 °C), followed by ultrasound irradiation at the same temperature (35 min, 600 W, flow rate 55 mL/min).
Our studies confirmed that high-throughput ultrasound applications definitively require flow reactors..

Keywords: Power ultrasound; Pilot ultrasound reactor; Flow reactor; Biodiesel; Transesterification.

1. Introduction and background

The positive chemical and mechanical effects generated by irradiating a liquid medium with power ultrasound (US) is largely exploited in lab-scale for extraction, synthetic application and persistent organic pollutants (POPs) degradation. The design and optimisation of sonochemical apparatus are still open to advancement. Quite different features and performances were gathered for the three typical 20 kHz ultrasonic devices for laboratory (namely horn, cup horn and cavitating tube), all sharing a scarce homogeneity [1]. In order to achieve uniformity of the acoustic field and optimal acoustic streaming in every part of the reaction vessel, we designed a reactor that could be made to rotate eccentrically around the horn axis and the probe to move alternatively up and down by a predetermined excursion at a chosen speed [2]. In our system a patented electronic device [3] acting on the oscillating circuit continuously adjusts the US frequency to the actual resonance value of the reaction system (which is a function of the irradiated volume, of the viscosity, nature of dissolved gases, surface tension and phase distribution of the mass, etc.). This value is operationally defined as the frequency that maximizes the US output for a given power setting.

As cavitation is mainly concentrated very close to the probe, large scale applications require different design with several transducers. In spite of extensive research on laboratory scale and huge potential for large-scale application, there are only relatively few examples of industrial sonochemical processes. Presumably the cause lies in the complicated design of efficient cavitational reactors, given the lack of data linking bubble dynamics with experimental predictions for large-scale processes. Moreover the reactor characteristics have to be tailored in terms of the rheological properties of the reaction mixture (solution or suspension, viscosity, surface tension, etc.).

Many authors have studied medium and large-scale configurations to optimize the distribution of cavitation in the ultrasonic reactor [4-6]. Horn type transducers were widely studied by mapping the whole sonochemical reactor, but this was limited to low volume and axial vibration [7-10]. About ten years ago Mason published a comprehensive overview on the state of the art and perspectives of large-scale sonochemical processing [11]. Nowadays except for important working applications in the food industry, galvanic processes, sonocrystallization and water treatment processes, the scenario is still relatively poor in new examples. Leading authors in this field, like Pandit and Gogate [12], were able to design new pilot reactors well suited for further scaling up after accurate measurements of local pressure and cavitational intensity [13]. They suggested the development of large-scale multiple frequency/multiple transducer reactors operating in a continuous mode exactly aligned with Bonrath's idea to apply US in large-scale processes by means of continuous procedures in tube reactors [14].

It is relevant to note that industrial sonochemical reactors were pioneered more than 40 years ago by Saracco and Arzano, who described an optimised reactor for the hydrogenation of unsaturated oils. They demonstrated the enormous influence of the reactor geometry on the kinetics of the reaction [15]. In the nineties, a major breakthrough in the industrialisation of sonochemistry was found with the introduction of new loop reactors (Harwell reactor), new cylindrical pipe reactors and reactors with modular units combined in series (Branson Reactor) [16]. An increase in the reactor volume leads to a simultaneous increase in the ultrasonic power to maintain the same power density. Owing to the power limitation of each single transducer, a large-scale reactor, requires several ultrasonic transducers [17] or as suggested by Gondrexon et al. a multi-stage reactor composed of a series of several smaller ultrasonic units [18].

Leaving aside the fundamental technical parameters studied by physicists and engineers, one of the main limitations in the scale up of this equipment is the energy consumption. The efficiency for converting electrical energy into US for systems using piezoelectric transducers is approximately 85%, higher than magnetostrictive transducers (50-55%). This problem was encountered when we tried to scale up chemical processes that gave outstanding results in the laboratory. Two eloquent examples are the degradation of asbestos fibres from water suspension [19, 20] and vegetal oil extraction and its transesterification [21]. First we checked our laboratory procedure with the classic industrial US-batch reactors equipped with mechanical stirrer. In both cases the low energy density required long sonication times with an overall high energy consumption. This made this approach inefficient and not economically viable. Thus the aim of the current work is focused on the design of a reliable system for an efficient scale up of sonochemical process, a key requirement for practical and credible applications in sonochemistry.

Among the common chemical reactions of industrial interest, the transesterification of vegetal oils for biodiesel production is probably at the top of the list, given the demand for a rational use of biomass under environmentally-friendly conditions (Scheme 1).
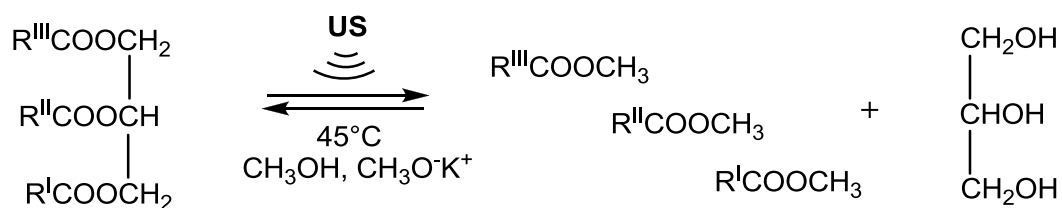
Scheme 1. Base-catalyzed transesterification of triglyceride with methanol under US irradiation.

Maeda, Vinatoru and associates demonstrated that low frequency US can be efficiently applied for this transformation, offering economical advantages over the conventional procedure even in large scale production [22]. Working at room temperature the reaction time was four times shorter than under mechanical stirring, the quantity of required catalyst was 2 or 3 times lower and the molar ratio of alcohol/oil used is only 6:1. Actually the transesterification is strongly temperature dependent, and the industrial production is usually performed at 60°C. Room-temperature sonochemical treatments are hardly competitive so far with thermal conditions in terms of energy consumption. Several authors studied the competitiveness of US-promoted processes for biodiesel production [23-28]. We have studied the process from lab scale to industrial scale in 100 L-batch reactors usually employed for plant extraction. Actually the energy density in the tank exerted by four emitting surfaces (180 x 300 mm; 22.5 kHz, 200 W) it is relatively low for such application and a complete transesterification took place in about three hours at 35°-40°C. In this paper present a new pilot flow-reactor for high-intensity US irradiation well suited for such an application. It should be finally mentioned that flow reactor systems have gained increasing popularity for the synthesis of fine chemicals and for small-scale production, and they can eventually be scaled-up. They often enable access to target compounds in high purity avoiding time-consuming work-up and purification steps [29, 30]. In addition, other non-conventional techniques, especially microwaves, can synergistically be combined with continuous flow conditions, thus allowing access to chemical transformations via a more expedient protocol [31]. Similarly, combining the unique characteristics of ultrasonic irradiation with a flow reactor will further enhance many synthetic processes that have been hitherto considered unpractical or sluggish, providing future opportunities in both academia and industry.

2. Experimental

2.1. Materials and Methods

All reagents and solvents were purchased from Carlo Erba Reagenti. Soybean oil was kindly provided by BF Pharma Spa Italia (Fossano, Italy). The course of transesterification reaction was followed by thin layer chromatography (TLC) on Fluka F254 (0.25 mm) plates, which were visualized by heating after spraying with molybdic acid. The purity of biodiesel was confirmed by 1H NMR (Bruker Avance 300 spectrometer), FT-IR (Shimadzu FT-IR8001 spectrometer) and GC/MS (Agilent 6850 gas-chromatograph equipped with a 5973 MS detector).

2.2. Technical Equipment

The flow US-reactor is constituted by three transducers (21.5 kHz) lodged in the bottom of the chamber and cemented to a high-quality titanium alloy plate (100 x 325 x 0.9 mm) (Fig. 1 and 2). Transducers consist of high-efficiency pre-stressed piezoelectric (PZT) rings (planar PZT Morgan Electronics, diameter of 50 mm) compressed between two ergal blocks (Fig. 3).
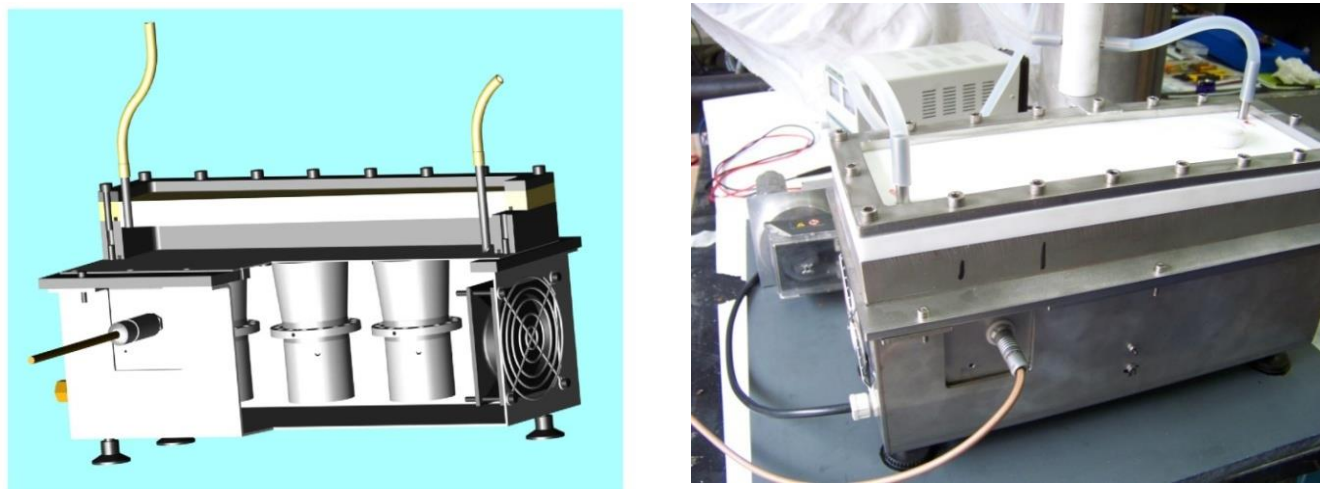

Figure 1 and 2. 3D section and external view of the flow reactor respectively.

The frequency is tuneable between 17 and 45 kHz with an optimal efficiency at 21.5 kHz. Power can be varied up to a maximum of 900 W, corresponding to a mean value of 3 W/cm^2 at the emitting surface (Fig. 4). and is monitored by a true reading wattmeter.
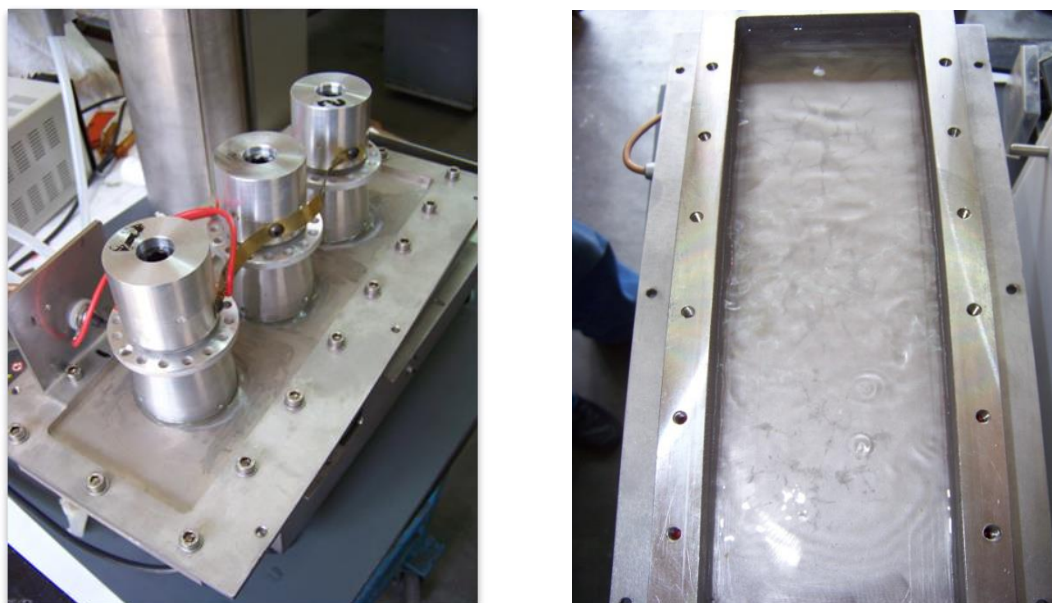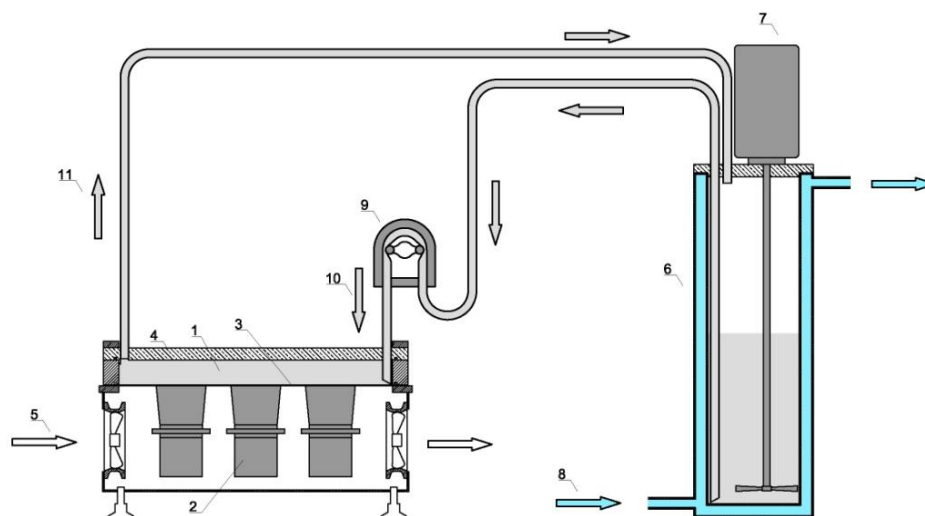
Figure 3 and 4. Both sides of the emitting titanium plate, from the bottom (transducers) and from the top without the cover.

The whole circuit entail a tank with mechanical stirrer and a peristaltic pump (Fig. 5).

Figure 5. Complete view of the flow reactor with tank, thermometer and mechanical stirrer on the right.

The flow reactor operates in the following manner (Fig. 6):

1. Sonication chamber	7. Mechanical stirrer
2. US transducers	8. Thermostatting liquid
3. Titanium plate	9. Peristaltic pump
4. Screwed cover	10. Inlet
5. Air cooling	11. Outlet
6. Tank	

Figure 6. Detailed scheme of the system

A peristaltic pump (power: 30 W) circulates the reacting mixture (oil, methanol, sodium methoxide) contained in the 5 L-cylindrical tank through the sonication compartment. The cylindrical tank is thermostatted (temperature range 0-90°C) by a flow of silicone oil through the external jacket and the internal coil. In the working system, the 0.5 L gastight sonication chamber is completely full of circulating liquid, while the 5 L tank can work up to a minimum volume of 0.1 L as the aspiration pipe ends very close to the bottom. The peristaltic pump draws fluid from the tank and propels it through the sonication compartment. We observed a linear dependence between the scale in Volt and the corresponding flow up to 15 V (200 mL/min), then the slope of the line increases slightly.

The reaction was studied at different flow rates in the range of 25 to 100 mL/min that corresponds at about 5 - 20 min residence time. Optimal flow rate was at about 55 mL/min that corresponds at about 9 min residence time. The mechanical stirrer can be regulated in height in function of the level of the liquid in the tank (optimal position of the propeller). Two thermocouples monitor the temperature at different points of the system: 1) at the outlet from the sonication chamber and 2) in the tank. The temperature of the thermostatted silicon oil is controlled by an external thermostat system.

Keeping the flow rate constant at 55 mL/min, the transesterification was performed at three different power namely 500, 600 and 700W. At 700 W the temperature of the reaction mixture measured at the outlet reached the 58-59 °C while at 600 W the maximum temperature was 50-51 °C. The former was too close to the boiling point of methanol, condition that dramatically reduce the cavitation and the efficiency of the reaction. On the base of this set of experiments the best ratio power/conversion was observed at 600 W that gave total conversion to methyl esters after 1 h flow.

The total energy consumption is a sum of three components:

(i) The energy to heat the oil (1.6 L) from 20 °C to 45°C

(dT = 25 K). L = Cs_m_dT = 2000 J/kg K_1.6 L 0.916 kg/L°25 K =73.28 kJ = 20.35 Wh (1 Wh = 3.6 kJ).

(ii) The energy to heat methanol (0.4 L) from 20 °C to 45°C

(dT = 25 K) L = Cs_m_dT = 2500 J/kg K 0.4 L 0.79 kg/L_25 K =19.75 kJ = 5.5 Wh.

(iii) The energy to sonicate the mixture for 1 h at 600W is

L = P_t = 600 W;1 h = 600 Wh.

Therefore the total energy consumption was about 625 Wh. The whole reactor absorbs a total of 1520 W, namely 900W for the sonication chamber (300W each transducer), 100W for the pump, mechanical stirrer and fans, 20W for the electronics and 500W for the thermostat system.

2.3. Experimental Procedure.

a) The first set of experiments was carried out in the flow reactor at about 45 °C (40–41 _C at the inlet and 49–50 °C at the outlet). 2.0 L of reaction mixture constituted by 1.6 L of oil, 360 mL of MeOH, and 40 mL of MeOK, was prior mixed with a domestic hand blender (Minipimer MR4050HC Braun) for 1 min. The mixture was poured in the tank and maintained at 45 _C under mechanical stirring for 1 h. Then the peristaltic pump draws the mixture from the tank (flow rate was 55 mL/min) and propels it through the US reactor (600 W, 200Weach transducer). Samples were taken out of the reactor at regular intervals of 5 min, cooled to 5 °C and quenched by the addition of few drops of 5% acetic acid solution in methanol. Overall energy consumption was about 0.70 kWh. b) The second set of experiments entailed a two-step process where US irradiation (35 min) was applied only after 30 min conventional heating under mechanical stirring at 45 °C. It is evident that with a halftime sonication (30 min vs 1 h) also the energy consumption was cut by half (only 300 Wh). Overall energy consumption was about 0.45 kWh corresponding to 0.28 kWh per L.

2.4. Analysis.

The layer of fatty acid methyl ester was separated by centrifugation at 8000 rpm and analyzed by TLC with hexane:EtOAc 19:1 as eluent, FT-IR and 1H NMR. After purification the biodiesel was analyzed by GC/MS analyses using an Agilent 6850 gas-chromatograph equipped with a 5973 MS detector and fitted with an HP-5 MS fused silica column (length 30 m; i.d. 0.25 mm; film thickness 0.25 lm).

3. Results and discussion

A new pilot flow reactor for high-power US irradiation, has been developed to test and scale up synthetic procedures and chemical transformation, which have been the subject of interest in our laboratories. Based on the previous experience of a US flow reactor where we combined two different frequencies (20 and 300 kHz) [32], we designed a more powerful system with a closed sonication compartment. Preliminary tests showed a wide potential applicability for organic synthesis, advanced oxidation processes (polluted water, sulphur-containing oil) and even extraction of powderised plant material. We present here the transesterification of soybean oil (1.0 L) for biodiesel production. This equilibrium involves the reaction of triglycerides with volatile, lower alcohols, usually methanol (Scheme 1). Recently, Moholkar et al. showed that the influence of US on transesterification reaction is of a purely physical nature [33]. Colucci et al. demonstrated that rate constants of US-promoted transesterification of soybean oil in methanol were 3–5 times higher than those reported for mechanical

agitation [34]. The formation of a fine emulsion between oil and methanol enhances the interfacial area promoting the reaction. Apart from the cost of the oil, the main factors that influence the competitiveness of the process are: energy consumption, the amount of methanol and catalyst. The last also determines the amount of glacial acetic acid (relatively expensive) necessary in the end to neutralize the biodiesel. In our conditions the molar ratio of alcohol to oil was about 6:1, and the quantity of catalyst was 0.5% of a MeONa 30% solution that corresponds to 0.15% (wt/wt) to the oil. Sonication (600 W) for 1 h at 45–48 °C with a flow rate of 55 mL/min brought the reaction to completion, as confirmed by TLC, GC/MS, and NMR analysis. In terms of energy consumption the best conditions involve a two-step treatment: first only thermal under mechanical stirring (30 min), followed by the ultrasound irradiation (35 min). The kinetics of the base-catalyzed transesterification shows an equilibrium at the end of the reaction when a residual amount of mono- and di-glycerides (10–20%) is hardly converted into methyl esters. At this stage the base (sodium methoxide or KOH) is much more soluble in glycerol losing activity. A common approach to bring the reaction to completion is an intermediate centrifugation to remove the glycerol. An efficient sonication of the reacting mixture at this point strongly promotes full transesterification that otherwise requires a higher amount of catalyst and longer reaction times. Cavitation mainly affects the mass transfer rates and ensures uniform distribution of the reactants, as one concludes from the fact that the significant effect on both reaction rate and equilibrium conversion is only observed in the later stages of the reaction when heterogeneity sets in. The energy consumption under the most favourable conditions was about 0.28 kWh per L that roughly corresponds to 50 eurocents per 10 L of biodiesel (in Italy1 kWh costs about 20 eurocents)

4. Conclusions

The application of US to chemical process intensification hinges on in the development of large-scale multiple transducer sonochemical reactors operating in a continuous mode. A new stop-flow US reactor was efficiently applied to the transesterification of soybean oil for biodiesel production with an extremely low ratio of methanol and catalyst, moderate energy consumption and a short reaction time. Considerable energy saving could be achieved by a two-step process where US irradiation (35 min) was applied only after 30 min conventional heating under mechanical stirring at 45 °C.

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