Basic Economic Analysis for Sonochemical Processes

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Abstract: Ultrasound (US) and other non-traditional energy sources (for instance microwave (MW)) are widely used to increase the rate of chemical reactions, to prepare nanoparticles, to extract natural products etc. In all such cases, the scaling-up of the process must have a defined economic constraint, which generally can be reduced to the evaluation of the parameter R_C, which is the ratio between the raw energy cost to produce US (or MW) and the total production cost for unit mass of product. The paper gives a basic correlation among the different parameters to evaluate R_C both for processes using only US (or MW and other not traditional sources) and those with mixed energy sources.

Keywords: Economic analysis, Ultrasound, Scale-up, Energy, Microwave.

1. INTRODUCTION

Ultrasound (US) and Microwave (MW) are energy sources largely studied to improve the efficiency of several chemical reactions, material preparations or industrial processes [1]. For example, several researches have been published proposing US as tools to promote oxidizing reactions to mineralize organic pollutants in wastewater [2]. Assisted synthesis of quinolones compounds have been reported using both MW and US to improve the yields or the selectivities [3]. The preparation of innovative heterogeneous catalysts using US in their synthesis procedure have been proposed, for example, for iron based catalysts for Fischer-Tropsch process [4]. US have been also applied to increase the performance of sorption-desorption processes [5-7].

Nevertheless, in almost all these researches and publications, the attention is placed on the chemical effects of the application of ultrasound, while little is said about the actual energy consumption and the consequent economic evaluation. On the other side, technical and sustainability analysis is a fundamental step to develop new technologies addressed to industrial applications [8, 9]. The economic analysis is often difficult in laboratory stage because the scheme and the size of the final industrial application is not clear in these embryonal new technologies. The scale up process and design will be defined only if the proposed technology will be considered by a company, or if the academic research will go on, with specific aims to design the possible industrial layout. Basic and simple methods to evaluate the economic conse-quences of the application of US and MW should estimate these important aspects in the first step of these researches and address the selection of the most important operative parameters, as first of all the ratio between US and MW power and the volume of the reactor for the different processes.

The economical incidence of the energy cost over the total cost of a chemical process is a fundamental topic in the industrial economy. In the processes in which ultrasound are applied, this evaluation is of particular importance due to the energy consumption of the US apparatus. This incidence can be of high impact over the total process cost, especially in case of low efficiency of the sonochemical sources. In this paper, a general calculation scheme is shown that is applicable to every energy consuming source. Selected numerical examples are reported using the data deriving from literature. Some hypotheses have been made and discussed both to simplify the calculations in a first approach and to uniform the data available in the US literature.

2. DISCUSSION AND RESULTS

The parameter R_C indicates the ratio between the incidence of US energy cost over the cost for the total process, both referred to the same amount of product (in the case of a chemical process producing a substance). Such a parameter can be evaluated using the following equation:

$$R_C = W_S \left(\frac{a}{b} \right)$$

(1)

being: R_C = money for US generation (€ for total process)$^{-1}$; W_S = kWh withdrawn from the electrical net for US generation (kg produced)$^{-1}$; a = € (kWh)$^{-1}$; b = Total € (kg produced)$^{-1}$. Obviously:

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$$W_S = W_S' / \eta \tag{2}$$

where: W_s' = (kW emitted at the tip) (process time (h)) (kg of substance produced)$^{-1}$; η = efficiency of US apparatus = kWh emitted at the tip (kWh withdrawn at the electrical net)$^{-1}$. Then:

$$R_C = \left(\frac{W_S'}{\eta}\right) x \left(\frac{a}{b}\right) \tag{3}$$

We can consider as example: W_s' = 10^{-3} kWh kg^{-1}; η = 1 (then W_S = 10^{-3} kWh kg^{-1}); a = 0.1 € (kWh)$^{-1}$; b = 5 € kg^{-1}, then from equations (1) and (2) it can be derived: R_C = 2 x 10^{-5}. But if the efficiency of the sonochemical apparatus is η = 0.5 then W_S = 10^{-3}/0.5 = 2 x 10^{-3} kWh kg^{-1} and E_C = 4 x 10^{-5}. These examples are exceptionally favourable to the use of US because only a quite negligible part of the total process cost is dedicated to US. Instead, if the total process cost is dedicated to the production of US (i.e. R_C = 1) then from equation (1), with the same values of a and b as previously reported, it can be derived: 1 = W_S x 5/0.1 then W_S = 50 kWh is withdrawn from the net to produce US (kg processed)$^{-1}$. Due to the fact that the value of W_S can change in a very large range, it is more convenient to express the equation (3) on logarithmic scale:

$$-\log R_C = -\log\left(\frac{W_S'}{\eta}\right) - \log\frac{a}{b} \tag{4}$$

For example, the halogenation of aromatic hydrocarbons was studied by Mason, Lorimer and Lindley [10] using copper (II) bromide on alumina in silent and US (20 kHz) conditions. After 60 min of US irradiation, the conversion of naphthalene (A) into mono (B) and disubstituted (C) bromoderivates was complete with a ratio B/C = 97/3; the same total conversion, in silent conditions, was reached after 180 minutes with a ratio B/C = 91/9. The other experimental conditions were: US 42 W (cm)$^{-2}$; end diameter of the horn 6 mm (section 0.283 cm^2); (A) weight 1.152 g, corresponding to a total weight of 1.8832 g ((B)+(C)), at 97/3 (B)/(C) molar ratio, when (A) is totally converted.

Therefore: W_s' = [42 W cm^{-2} x 0.283 cm^2] x 1 h /1.8832 g = 6.312 Wh g^{-1} or kWh kg^{-1}.

Considering equation (3) with, η = 30%, a = 0.1 € (kWh)$^{-1}$; b = 5 € kg^{-1}, the parameter R_C is R_C = (6.132 / 0.3) x (0.1 / 5) = 04088 € US (€ total production)$^{-1}$.
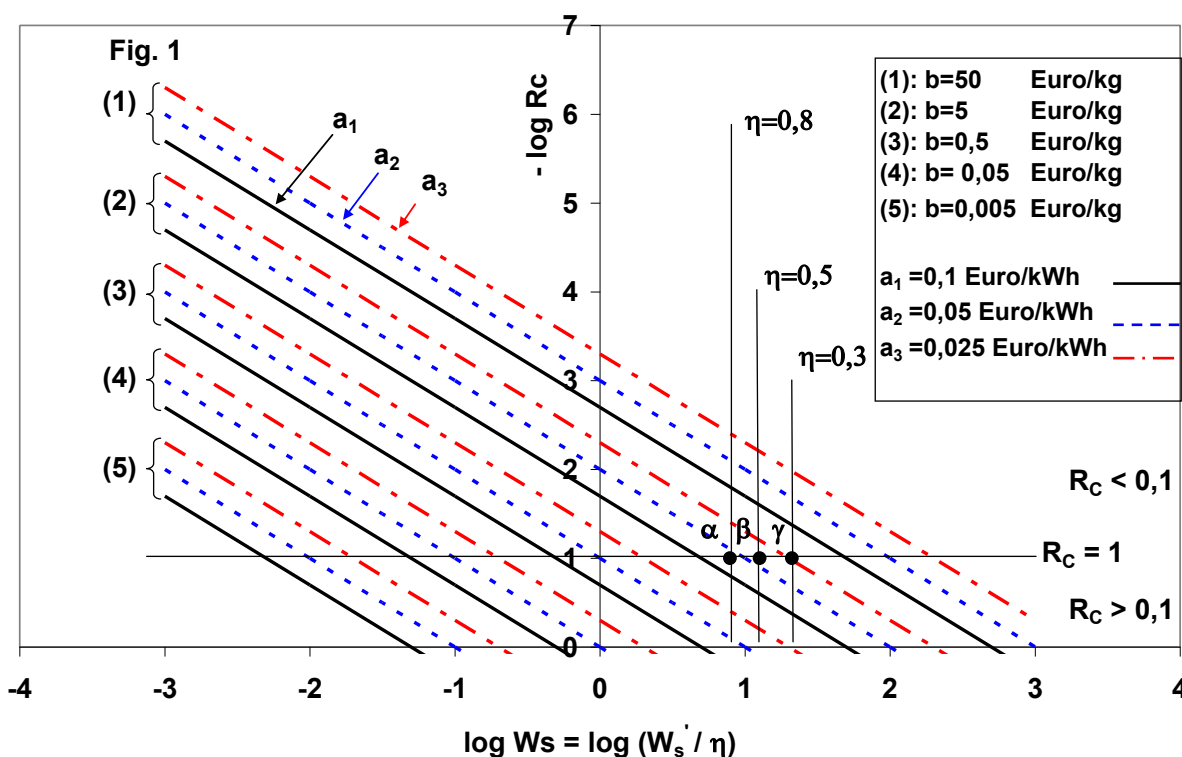

Figure 1: Graphical correlation among parameters R_C, W_S, W , η, a, b as defined in the text.

Obviously if the efficiency of US apparatus changes also R_C values are different.

Therefore, it is possible to plot equation (4) for each process (i.e. for each value of $W_s^{'}$) at different values of the efficiency η and different values of a and b. Such results are shown on Figure **1**.

For instance, by assuming $W_s^{'}$ = 6.312 kWh kg^{-1}, according to the calculations previously reported, and η = 0.8, 0.5, 0.3, the vertical lines with such values were drawn. Taking from the literature the data for W_s (assuming η = 1), Table **1** is derived.

Obviously, the majority of the data reported in the cited literature (Table **1**) is on a small scale, therefore the pertinent unit for W_s is Wh (g)$^{-1}$. Therefore, the equivalence a [Wh (g)$^{-1}$] = a [kWh (kg)$^{-1}$] is absolutely correct from a formal point of view, but if applied to a chemical process, it implies that there is a linear scale-up factor that is not always correct. However, there are no indications in the literature of a scale factor at present for these kind of processes.

The reactions considered until now are character-ized by a continuous emission of US or MW. Other processes can be considered in which US are used alternatively with other energy sources, or in a pulsed mode. Many of such processes are applied in indus-tries, for example during oil extraction from the wells [18].Taking in consideration this process, it is possible to show (Figure **2**) how the quantity of oil Q (kg) is extracted as a function of time; usually Q decreases with time due to the effect of solid deposits or very viscous hydrocarbons at the bottom of the pipes located down inside the wells.
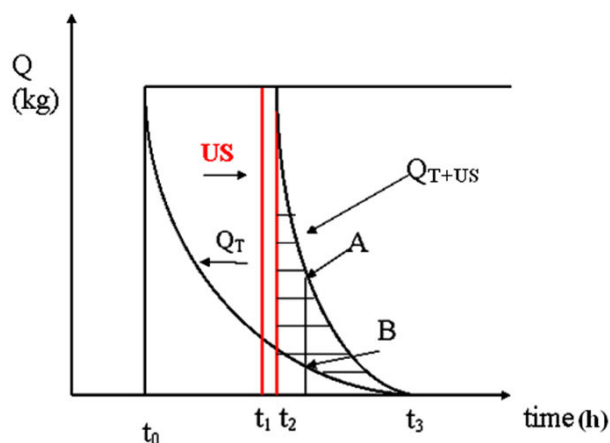
Figure 2: Productivity Q as a function of time (t). Q_T is the production applying traditional energetic sources (for instance pressure, as explained in the text), Q_T+US is the production after application of US energetic source for a very short time between t_1 and t_2.

If US are emitted with a power E_{US}, near the occluded end of the pipe for a very short time, between t_1 and t_2, then the solid-viscous deposit is removed and the extraction quantity comes back to the original value. Therefore, Q_{US} is the quantity extracted after the US treatment by using the traditional power (i.e. a source of pressure, of power E_T). Then, it is possible to calculate the parameter W_S as:

$$W_S = \frac{\int_{t_0}^{t_3} E_T(t)dt + \int_{t_1}^{t_2} E_{US}(t)dt}{\int_{t_0}^{t_3} Q_T(t)dt + \int_{t_2}^{t_3}[Q_{T+US}(t) - Q_T(t)]dt} \quad (5)$$

US could be used only when Q_T = 0 (Figure **3**) from t_1 to t_2.

Table 1: Some Examples of Specific Energy Consumption (WS, kWh kg^{-1}) in Ultrasonic Processes Based on the Nominal Power Collected from the Net

Reaction	US Frequency (kHz)	W_s (kWh kg^{-1})	Reference
Alogenation of aromatic hydrocarbon	20	6.31	[10]
Glucose oligomerization	20	6.67	[11]
Furoin alkylation	25	22.7	[12]
Condensation between nitrobenzaldehyde and acetone	59	483.9	[13]
1,4-dihydropyridines synthesis	25	284	[14]
Extraction of phenolic compounds from coconut	25	5.83	[15]
Synthesis of nanocrystalline HgS, HgSe, HgTe	20	HgS: 219.6 HgSe: 184.8 HgTe: 160.8	[16]
Decomposition of Volatile Solids (VS) in waste activated sludge by US followed by biodegradation	31	0.1 (Average value)	[17]
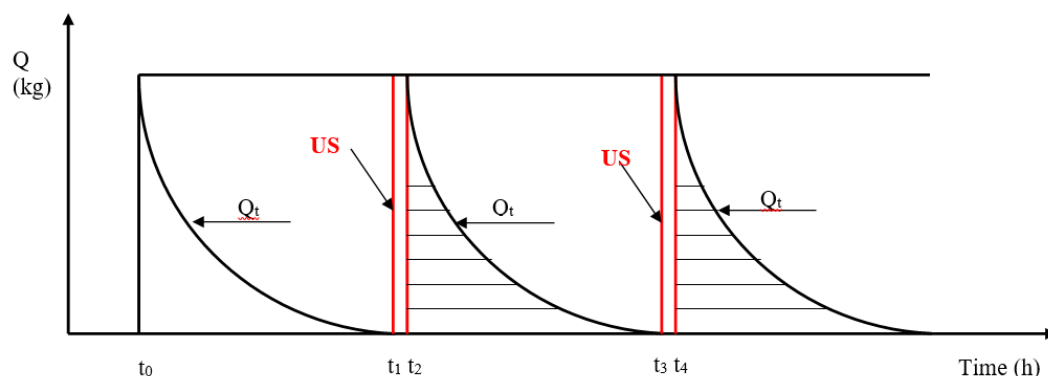
Figure 3: Cycles of productivity Q by applying US for a short time between t_1 and t_2 only when the productivity QT is quite zero.

Such a treatment can be repeated cyclically in the steps II, III and so on. In this case, W_S can be calculated as follows:

$$W_S = \frac{\int_{t_2}^{t_3} E_T(t)dt + \int_{t_1}^{t_2} E_{US}(t)dt}{\int_{t_2}^{t_3} Q_{T+US}(t)dt} \qquad (6)$$

The integrals in equations 5 and 6 can be solved by interpolating with a polynomial equation, the experimental data Q_T and $Q_{T,US}$ vs. t.

Table **1** shows that the data of literature are extremely dispersed in order to calculate the specific energy consumption of US, W_S (kWh $(kg)^{-1}$), as this value ranges from 9.0×10^{-3} to 2.5×10^{-5}. Such values are referred to very different processes and are calculated both without considering a scaling-up factor, as previously discussed, and assuming an efficiency of sonochemical apparatus $\eta = 1$.

As regard to the mathematical model illustrated in the paper, the relevant parameters W, W_s', a, b, η, which appear in the equations 1 and 2, are easily correlated with the important economic parameter R_C in a graphical form shown in Figure **1**. This monogram can be used to calculate the range of flexibility of a chemical process in different forms. For instance, if R_C = 0.1 is fixed (i.e. only 10% of the production cost is dedicated to the energy– Consumption to produce US) then, according a total production cost (b), only some combinations of the electric energy cost (a_1, a_2, a_3) are allowed each having a value of W_S, then of the efficiency of the US apparatus if a value of W_s' is required.

On the other hand, if W_s', η and b are known, the energy cost has a range of variability. In Figure **1**, such costs are indicated with a_1, a_2, a_3 for W_s' = 6.312 kWh

kg^{-1} and η = 0.8; 0.5; 0.3 respectively, for R_C = 0.1. Although the above mentioned conclusions are qualitatively obvious, Figure **1** gives "quantitative" correlations among the different parameters: the lower the US apparatus efficiency is, the lower the cost of electric energy must be at a value of W_s'. Conversely, in such situations (η low) the higher is the production cost, the lower is the value of R_C.

For hybrid processes, i.e. those using US and traditional energetic sources, the energy consumption for unit mass of the product (W_S) should be determined on the basis of an elaboration of the experimental production data according to the equations (5) and (6).

3. CONCLUSIONS

Several processes and reactions are promoted by coupling with energetic sources such as ultrasound and microwave. A balance between the promotion given from these sources and their cost should be considered to evaluate the real economic sustainability of these processes. A simple method was proposed on the basis of the parameter R_C, which is the ratio for unit mass of product, between the raw energy cost to produce US or MW and the total production cost. The application of this parameter in different case-studies taken from literature was discussed and the main principles to define the most convenient operative parameters were suggested.

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