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Process Simulation Tools for the Assessment of Biorefinery Process Intensification by Ultrasound Technology

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In the present work, on the basis of literature and experimental data, some correlations for ultrasound-assisted dissolution of lignin and hemicelluloses from the lignocellulosic raw material were defined in Aspen Plus® as function of the applied power and length of the ultrasound treatment. The dissolution yield of these biomass components was represented against the applied acoustic energy, taking into account the volume of solvent-solid treated in each case, making possible the scale-up of US-power consumption in a simulated biorefinery pretreatment process. The proposed ultrasound-assisted process was techno-economically evaluated in terms of process yield and utilities requirement. Furthermore, energetic and exergetic analyses were performed in order to evaluate the profitability of the simulated ultrasound-assisted biomass fractionation processes.

1. Introduction

The implementation of process intensification in biorefinery processes aims mainly to improve yields, to achieve time and energy savings and to enhance products purity/quality. In this sense, the intensification of biorefinery processes has been focused on the successful improvement of heat/mass transfer mechanisms and separation/purification technologies (Sanders et al., 2012). Heat or mass transfer intensification in biorefineries could be reached through alternative designs of the reactors and heat exchangers (Reay, 2008). For example, the use of microwave radiation has been proven as a powerful and efficient tool to improve different catalytic reactions or thermal conversions in biorefinery processes (Nikolic et al., 2010). Furthermore, ultrasound irradiation has been successfully applied for the lignocellulose treatment, as it achieves both heat and mass transfer improvements (Shirsath et al., 2012).
The ultrasound (US)–assisted treatments have been widely investigated in order to enhance mass transfer and dispersion phenomena (Alupului et al., 2009). Among the available newer energy sources for process intensification, the use of sound energy can result in significant process intensification because the occurrence of cavitational events.

2. Methodology

2.1 Correlations for the ultrasound-assisted dissolution of hemicelluloses and lignin

Based on literature data (see Table 1) and previous experimental results (García et al., 2011) some correlations for the ultrasound-assisted dissolution of lignin and hemicelluloses from the lignocellulosic raw material were defined. The dissolution yield of these biomass components was represented against the applied sonochemical energy (Dhar et al., 2012), taking into account the volume of solvent-solid treated in each case, applied power and duration of the treatment. Therefore, it could be possible to scale-up the US-power consumption in a simulated biorefinery process. In this way, the applied volume-specific acoustic energy (EV, kW/s·L) was defined as:

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$$EV = \frac{P \cdot t}{V} \cdot 60 \quad (1)$$

where P is the applied acoustic power (W), t the sonication time (min) and V (mL) the treated volume during the applied ultrasound experiment.

Table 1: Operation conditions applied in the literature used for the construction of hemicelluloses and lignin dissolution correlations.

Raw material	Solvent	Range of sonication power (W) and time (min)	Reference
Olive tree pruning	NaOH solution	420 W, 30 - 120 min	García et al., 2011
Wheat straw	KOH solution	100 W, 5 - 35 min	Sun and Tomkinson, 2001a
Wheat straw	KOH solution	100 W, 5 - 35 min	Sun and Tomkinson, 2001b
Sugarcane bagasse	NaOH solution	400 W, 5 - 50 min	Velmurugan and Muthukumar, 2012

The US-treatment yield, referred to the achieved lignin and hemicelluloses dissolution percentage for the diverse specific US energy applied, was statistically processed using OringinPro 8 SR0 v8.0724 software, and it was found to successfully fit the Stirling model. The mathematical model that represents these correlations resulted as follows:

$$y = a + b \cdot \frac{e^{k \cdot x} - 1}{k} \quad (2)$$

where y represents the dissolution yield (%) and x the specific energy EV (kW/s·L). The parameters a, b and k for hemicelluloses and lignin dissolution correlation are displayed in Figure 1a and 1b.

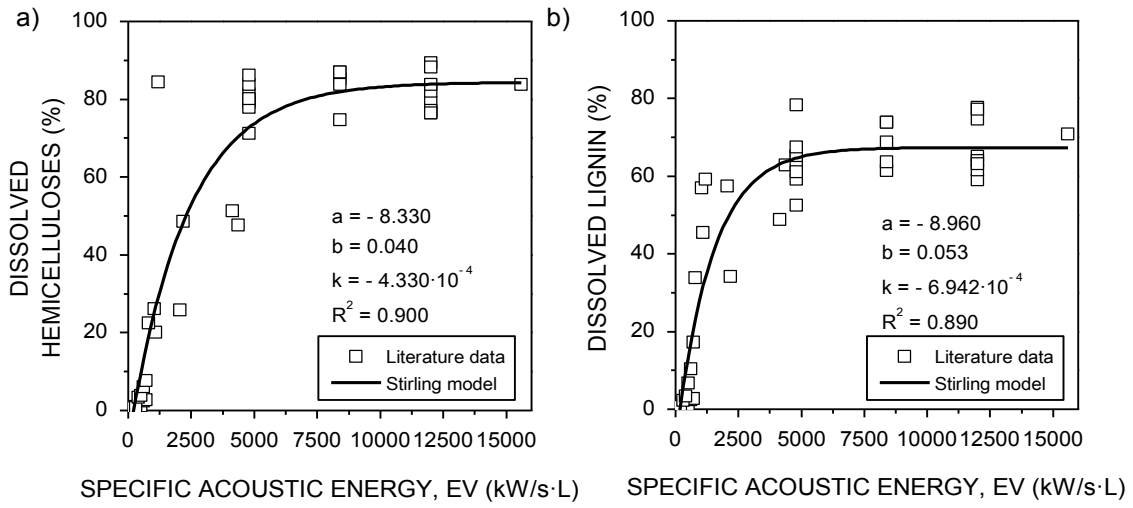

Figure 1: Dissolved hemicelluloses (a) and lignin(b) yields from literature data and their Stirling correlation vs. the applied specific US energy.

2.2 Design and simulation of the ultrasound-assisted treatment

For the design of the US-assisted pretreatment of lignocellulosic material (Figure 2) in Aspen Plus 2006 (Aspen Technologies Inc., 2006) a US-REACTOR was defined (RStoic module), where the previously detailed dissolution correlations were specified for lignin and hemicelluloses. The reactions extent was determined with the aid of the Calculator tool of Aspen Plus (using Fortran calculation method), where the previous Stirling correlations were introduced.

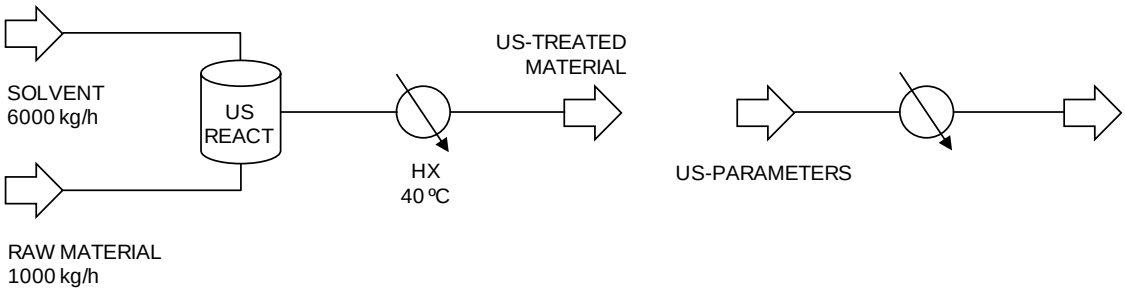

Figure 2: Flowsheet of the US-assisted pretreatment of the lignocellulosic material.

In order to manipulate the US-treatment parameters in the simulation, two fictitious components were defined for easy access of these parameters during simulation: TIME and POWER, represented in a separated stream (US-parameters). An additional module (Heater) was used in order to force the calculation of this specification stream. In the Calculator tool, the specific energy EV was calculated according these sonication parameters and, later, the dissolution yields. As reported in the literature (Gogate et al., 2011), a significant portion of the energy applied during the sonication process is irremediably lost as heat. This DUTY (established as 20 % of the applied total acoustic energy) was assigned as the heat duty in the US-REACTOR, increasing the temperature of the sonicated slurry. For cooling purposes, a heat exchanger HX was also simulated. The US-assisted reaction was performed at 1 bar and the applied acoustic energy was determined as the product of the previously calculated EV and the treated lignocellulosic feedstock mass (1000 kg/h, 25 ºC). The raw material was treated with 7.5 % w/w NaOH (25 ºC) at a solid to liquid ratio of 1:6.

2.3 Energy and exergy evaluation

The methodology applied for exergy calculations has been previously described (García et al., 2012). For a process stream, the specific physical exergy ē (kJ/mol) is determined as follows:

$$\bar{e} = (h - h_0) - T_0 \cdot (s - s_0) \quad (3)$$

where *h*, *T* and *s* are the enthalpy (kJ/mol), temperature (K) and entropy (kJ/K mol). The subscript 0 denotes the property under standard conditions (298.15 K and 1 atm). Taking into account the molar flow of each stream, *N* (mol/s), the exergy flow of a stream can be determined:

$$Ex = N \cdot \bar{e} \quad (4)$$

The exergy destruction associated to a process or equipment (Ex_{dest}, kW) is determined from the balance

$$\sum Ex_{in} + \sum Q \cdot \theta = \sum Ex_{out} + Ex_{dest} \quad (5)$$

where the exergy input and output flows (Ex_{in} and Ex_{out}, respectively, in kW) are considered. The term $Q \cdot \theta$ (kW) describes the exergy involved in reaction and heat exchange process, being *Q* the duty or heat exchanged (kW) and θ the Carnot factor, that depends on the outlet temperature from the process (*T*, ºC) and the temperature at standard conditions (T_0, ºC):

$$\theta = 1 - {}^{T_0}/_{T} \quad (6)$$

The exergy balance involved the analysis of input and output streams and the simulated equipment (US-reactor and heat exchanger).

3. Results and discussion

3.1 Simulation of the ultrasound-assisted treatment

The simulation of the above described US-assisted process consisted in the evaluation of hemicelluloses and lignin dissolving ratios, of the US-reactor provided duty (kW) and of the energy required for the slurry cooling to 40 °C, taking into account the mathematical correlations used during the design of this process. The sonication time (min) and the US equipment power (W) were considered as process variables. For this purpose, a Sensitivity analysis was carried out in Aspen Plus, varying the duration of the ultrasonic

treatment from 5 to 120 min and the power applied to the system by the US probe (between 1,000 and 8,000 W). The range choice of this parameter was done considering commercial specifications for this type of equipment. It was found that, for the treatment of big inputs, 500 to 4,000 W powered US or immersible transducers would be required. Therefore, for the sonication of 1,000 kg/h of lignocellulosic feedstock with water in a solid to liquid ratio of 1:6, between 2 and 4 US modules would be needed.

In Figure 3, the results of the performed sensitivity analysis are displayed. The hemicelluloses and lignin dissolution extent tendencies (Figures 3a and 3b), with sigmoidal behaviour for low US-parameters values and hyperbolic conduct for the severer sonication conditions, showed maximum values of 82.9 % and 67.3 %. These values resulted for the longest and strongest sonication conditions (120 min, 8,000 W). However, not much different yields were observed for somewhat milder treatment conditions (from 60 min of US irradiation with 5,000 W of power). For these operation conditions, medium duty values were applied to the US-reactor (between 1,300 and 1,800 kW) and less cooling energy consumptions (1,400 - 2,000 kW) would be required (see Figures 3c and 3d). Therefore, the mentioned ranges should be considered as the optimum operation conditions for the simulated US-assisted fractionation process.

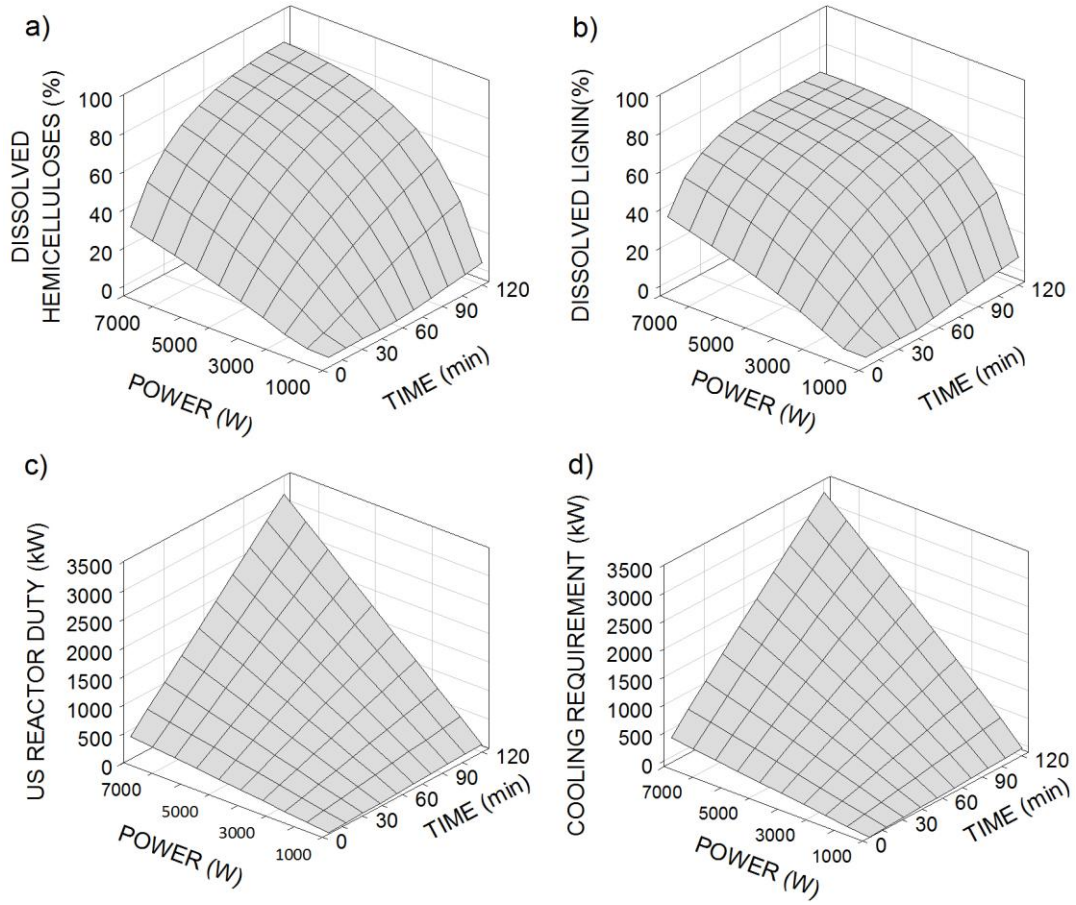

Figure 3: Influence of the sonication time (min) and the applied US power (W) on some parameters during the simulated ultrasound-assisted treatment of lignocellulosic raw material: a) hemicelluloses dissolution extent (%), b) lignin dissolution extent (%), c) acoustic energy (kW) provided to the US-reactor and d) energy required for cooling down the sonicated slurry (kW)

3.2 Exergy balance

For the evaluation of the exergy loss in the proposed ultrasound assisted process, the streams of raw material, solvent and US-treated material were considered (see Figure 2). Input streams (raw material and solvent) did not contribute to the performed exergy balance because both streams were introduced to the process at 25 ºC and, therefore, according to Eq(3), no associated exergy changes occurred. Thus, exergy input to the process only occurred due to duty and heat requirements in the simulated equipments.

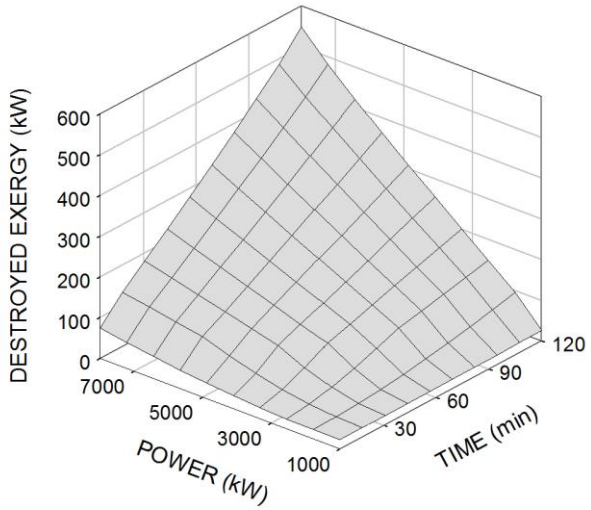

Figure 4: Destroyed exergy (kW) for the proposed ultrasound assisted treatment.

Furthermore, by applying a sensitivity analysis in Aspen Plus for different sonication conditions (1,000 – 8,000 W, 5 - 120 min), the exergy variation in the US-treated material stream due to change in stream composition during the treatment, was determined. A range of related exergy flow of 19.25 - 23.88 kW was found for this output stream.
Similarly, performing the sensitivity analysis allowed the determination of exergy flows associated to the equipment in the range of the studied process parameters, resulting in exergy values from 0.14 to 682.27 kW for the sonoreactor and from 4.16 to 157.30 kW for the simulated heat exchanger. The results displayed in Figure 4 show a clear influence of the energy requirements during the process, resulting in a tendency quite similar to that observed for duty and heat requirements of the simulated equipments (see Figures 3c and 3d).

4. Conclusions

In the present work, an ultrasonic reactor was designed and simulated in Aspen Plus according to literature data. The hemicelluloses and lignin dissolution yield, the acoustic energy supplied to the US-reactor and the energy required for cooling down the resulted sonicated slurry were evaluated under different time and power conditions of the sonication process. Subsequently, the operation conditions for the optimum hemicelluloses and lignin dissolution were established (60 min and 5,000 W). Medium energy requirement were associated to these optimum conditions, resulting in consumption 1,048 kW for cooling in the heat exchanger. Finally, using simulation tools, an exergy assessment was performed for the simulated process. This study indicated an almost linear correlation between the destroyed exergy of the process and the applied sonication power and time. At the operation conditions established for the optimum lignocellulose dissolution yield (60 min, 5,000 W), an exergy destruction of 178 kW was found.

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