

Set-up and Mass Balances on Soxhlet Extraction Tests in “*Learning by Doing*” of Process Engineering Students

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A group of bachelor students undertaking a training in a chemical engineering lab class has been involved by the lecturer in the Soxhlet extraction of compounds of interest from agri-food residues. Beyond pursuing experimental practice and investigating solid-liquid extraction, the lab training received added value by the engineering objectives to which the students were oriented: 1) setting up and verifying the closure of the macroscopic mass balances – never reported in the literature according to the authors' investigation – on the Soxhlet apparatus; 2) quantifying the heat duty of a Soxhlet test as a function of the solvent choice.

Roasted hazelnut cuticles and tomato pomace from industrial food transformation processes were used for testing. Two cases were raised to the students' attention: I. the solvent and the solid to be extracted are perfectly anhydrous; II. water is present in both the tested solids and the extraction solvent. A scheme of the material flows in the Soxhlet experimental procedure was developed together with the trained students. Based on this, the mass balances were written, yielding three simple equations for dry solids, solvent and water. Their solution, after some simplifying assumptions, was quite straightforward and intuitive for the students. All in all, the Soxhlet experimental activity proved to be not only reliable and accurate, but also attractive and mind-opening.

1. Introduction

The Soxhlet extractor from Franz von Soxhlet (1848-1926) is well-known in chemical, pharmaceutical, environmental and food-related laboratories as an apparatus capable of separating, in batch mode, soluble components from an insoluble solid matrix using a volatile solvent. In particular, the Soxhlet apparatus allows the hot solvent extraction of “active compounds of interest” from a solid waste, either wet or dry, and works with polar, semi-polar or non-polar solvents according to the polarity of the active constituents to be extracted. The Soxhlet operation presents the foremost advantages of complete extraction and minimum amount of solvent, but requires heating for solvent boiling. Nowadays, in the context of Green Chemistry, the Soxhlet apparatus can play a relevant role in testing “greener” bio-based solvents like R-limonene and 2-methyltetrahydrofuran, obtained from crop's by-products, for more environmentally sustainable extraction processes.

The Soxhlet extractor has an important educational value. While it is well-known to students of chemistry (see the Project-Based Learning (PBL) approach for students of environmental chemistry by Davis et al. (2017)), pharmaceuticals, biotechnology, food science and technology, it is usually ignored or rarely approached by the students of chemical, environmental or food engineering. In turn, for these latter the Soxhlet apparatus is of great interest because it implements a studied unit operation, i.e., the solid-liquid extraction, and further lends itself to make practice with mass and energy balance calculations. The work carried out in the context of a laboratory of a process engineering course and reported here provides simple answers to some basic questions

that students of chemical, environmental or food engineering may ask themselves when approaching the Soxhlet apparatus for the first time or switching to a new solvent for extraction. The basic questions might be:

- Is it possible to set up mass balances on solvent, solids and water (if any)? Do they ensure “closure”?
- Is there any undesired solvent evaporation loss to atmosphere?
- When dealing with moist solids and hydrophilic solvents, how can the composition of the extracted liquid phase be determined as the initially pure solvent progressively mixes with water?
- How much is the energy demand of an extraction test?

According to the authors' investigation in literature, setting up macroscopic mass balances on the Soxhlet apparatus and verifying their closure was never reported (for instance, see Sicaire et al., 2015). To this end, the paper starts from the description of pre- and post-test manipulation, treatment, measurement (e.g., weighing of samples, analysis of moisture content in solids, mixing rule for determining density of miscible liquids, etc.) and data recording procedures in conventional Soxhlet extraction tests, at a prefixed liquid-to-solid ratio.

2. Materials and methods

2.1 Experimental

Roasted cuticles (perisperm) are residues of the industrial processing of hazelnuts in the food sector, e.g., for confectionery and pastry production. They have been kindly provided by Euronut Spa (Sperone, AV). Tomato pomace, i.e., a mixture of wet peels, seeds and small quantities of pulp, is a residue of the canning industry; it has been kindly provided by CMDO (Mercato S. Severino, SA).

First, the students under training received from the lecturer a schematic technical brochure on Soxhlet extraction available on Internet (Behr, 2004). The Soxhlet extractor available in the Dept. of Industrial Engineering at the Lab 104 is equipped with a 250 W electric oven, a 500 mL flask, an extraction chamber with a useful volume of 200 mL, which houses a 43x123 mm cellulose thimble, and a 300 mm long Graham condenser running water.

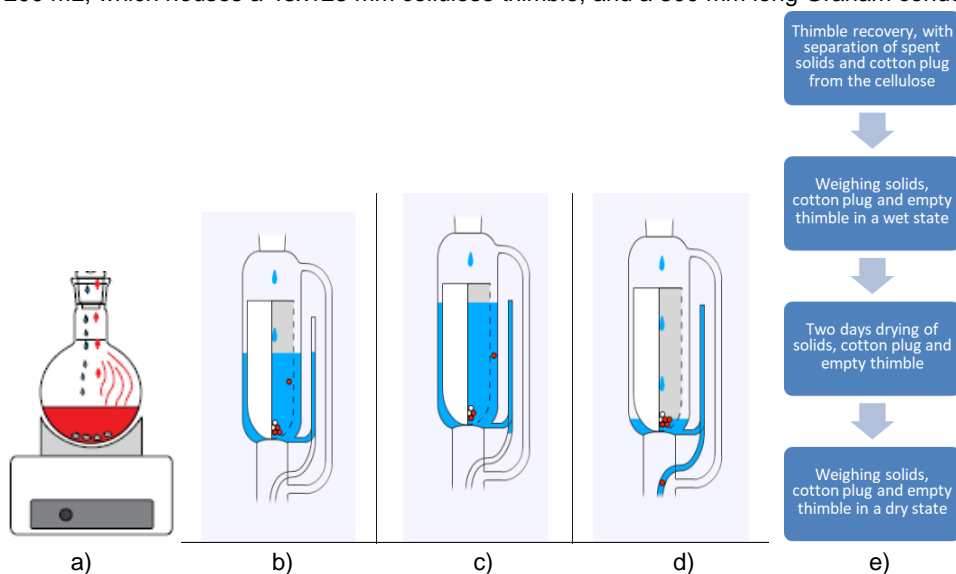


Figure 1: Representation of Soxhlet extraction (Behr, 2004) and processing of the thimble with spent solids:
 a) the solvent boils in the heated bottom flask while some condensed solvent returns as drops to it;
 b) a lateral arm allows the rise of the solvent vapors while the solvent, recondensed by the refrigerant, percolates out of the solid sample and the paper thimble;
 c) the solvent containing the extracted compound fills the extraction chamber below the siphon height;
 d) siphoning is triggered and the solution containing the extract falls into the bottom flask, where the extracted solids accumulate cycle after cycle in the solvent;
 e) block diagram of the processing of the thimble with spent solids at the end of the Soxhlet test

Then, the students attended a short demo session in the lab, which was aimed at showing operation of the Kern MLB Halogen Moisture Analyzer and of the Kern PFB 6K0.05 Technical Balance (Brachi et al., 2016). As a follow up, all the measurements of moisture content in solids as well as of weight of materials and glassware, before and after the extraction tests, were carried out by the students by means of the above instruments. Once the moisture content was determined for the first samples of cuticle and pomace, the students were prompted

to calculate mass and composition of water (w) and dry solids (DS) in them, as the two macro-components. Finally, the students attended the first Soxhlet test according to the procedure that is outlined in Figure 1. The Soxhlet flask is loaded with a pre-established quantity of solvent (e.g., 300 mL) and the thimble is loaded with a mass of sample, typically 15-30 g, which varies according to the humidity content of the raw sample, previously measured with the Kern Moisture Analyzer. The material in the thimble is subjected to repeated impregnation in the pure solvent cycle after cycle and this makes the process very efficient. The test duration depends above all on the solvent used while the efficacy is confirmed by the change in color of the extract in the flask (for example brown for hazelnut cuticles, yellow/orange for tomato pomace). The extracted solution, after cooling and weighing, is stored in a glass bottle away from light. At the test end, the processing of Soxhlet solids follows the separation and drying procedure schematically represented in Figure 1.e. Everything was dried by forced air circulation for two days in a laboratory fume hood and then reweighed. The difference between the initial and the final weight after drying gave the mass of liquid (i.e., solvent and/or water) retained in the spent biomass (SP) at the end of the extraction test. The density of the extracted solution was measured with the aid of a precisely graduated balloon. The students were trained to use the mixing rule for the density of miscible liquids, by which the masses of the two components (solvent and water) in the extracted solution can be determined by calculation.

2.2 Mass balance

The students were given by the lecturer a very rough scheme of the Soxhlet apparatus (see Figure 2(A)) and were asked to identify and locate on it the material flows, either at start-up or when running or terminating the test. After a group discussion and a check with the lecturer, they devised the streams that appear in Figure 2(B) and are described in the associated caption.

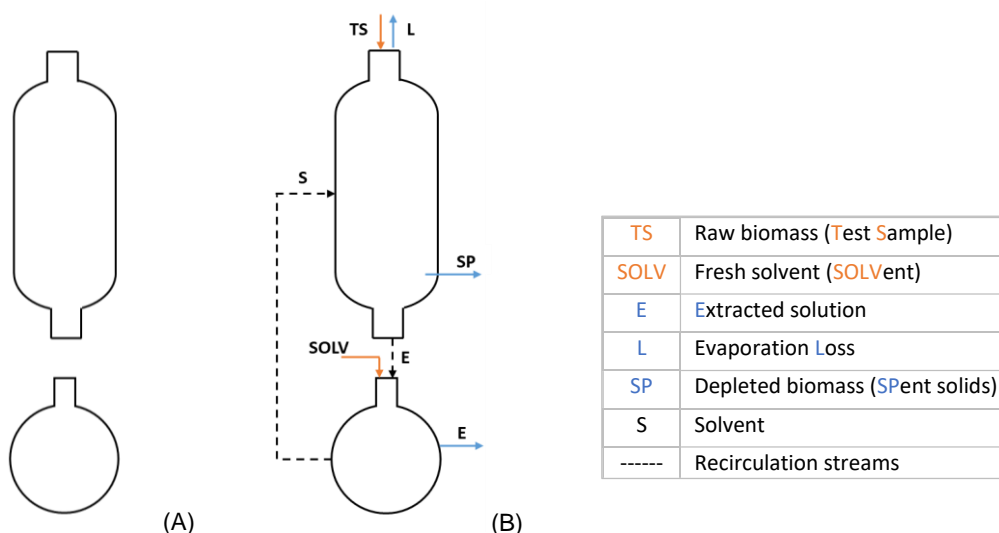


Figure 2: Schematic representation of (A) the Soxhlet apparatus and (B) the associated material flows

Then, the students were prompted to devise the macro-components that might reasonably represent the composition of the material flows for a development of simplified mass balances according to the general conservation law:

Input (at Soxhlet start up) = **Output** (at Soxhlet test conclusion)

After a group discussion and a check with the lecturer, the students proposed the solvent (S), the water (w) and the dry solids (DS), and, respectively, wrote the following material balance equations:

$$x_{S,SOLV} \cdot W_{SOLV} = W_{S,E} + W_{S,SP} + W_{S,L} \quad (1.)$$

$$x_{w,TS} \cdot W_{TS} + x_{w,SOLV} \cdot W_{SOLV} = W_{w,E} + W_{w,SP} + W_{w,L} \quad (2.)$$

$$x_{DS,TS} \cdot W_{TS} = W_{DS,SP} + W_{DS,E} \quad (3.)$$

when W_{TS} , W_{SOLV} , $W_{DS,SP}$ are the masses of the raw sample, solvent and dry solids in the spent biomass (SP), respectively, and are known by weighing at the start-up or at the end of the test. The mass of solvent and water in the spent biomass is determined by the difference in weight between the end of the test and the end of two-day drying under the hood:

$$W_{w,SP} + W_{S,SP} = \text{known value} \quad (4.)$$

Finally, the overall mass of the extracted solution (E) is simply determined by the difference in the weight of the flask that contains it at the end of the test.

$$W_{DS,E} + W_{w,E} + W_{S,E} = \text{known value} \quad (5.)$$

Then, the students were invited to consider a possible loss of vapors due to incomplete condensation in the Graham condenser. Therefore, they designated $W_{S,L}$ the solvent mass and $W_{w,L}$ the water mass lost by this way, which both represent unknown variables.

The students asked the lecturer how to consider the composition of the liquid phase that was wetting the depleted biomass (SP) at the test end and was then lost by evaporation as a consequence of two-day drying under the hood. After discussion, the students with the lecturer agreed upon the assumption that such a composition of the liquid phase is approximately equal to that of extracted solution (E); this leads to the following two further equations:

$$W_{w,SP}/(W_{w,SP} + W_{S,SP}) = W_{w,E}/(W_{w,E} + W_{S,E}) \quad (6.)$$

$$W_{S,SP}/(W_{w,SP} + W_{S,SP}) = W_{S,E}/(W_{w,E} + W_{S,E}) \quad (7.)$$

In the same discussion, the students noticed that the following equations of congruence reduce to 2 identities:

$$X_{S,SOLV} + X_{w,SOLV} = 1; \quad X_{DS,TS} + X_{w,TS} = 1$$

since the mass fractions relative to the fresh solvent $X_{S,SOLV}$ e $X_{w,SOLV}$ are known from its specification sheet; the mass fractions relative to the tested biomass (TS) $X_{DS,TS}$ e $X_{w,TS}$ are known from the Kern moisture analysis.

All in all, the above equations are in number $N_E = 7$.

The unknowns are $W_{w,SP}$ $W_{S,SP}$ $W_{DS,E}$ $W_{w,E}$ $W_{S,E}$ $W_{S,L}$ $W_{w,L}$, hence their number is $N_V = 7$.

Therefore, the degrees of freedom are in a number $N_{GL} = N_V - N_E = 0$.

2.3 Energy balance

The students were invited by the lecturer to move their attention to the energy-related aspects of the Soxhlet operation. Following a gradual approach to the subject, they were first asked to focus a generic extraction cycle. During a cycle, the thermal energy that is to be supplied to the bottom flask by means of the bottom heater (see Figure 1a) is equal to the latent heat of the evaporated liquid volume plus any heat dispersion:

$$Q_{HEATER} = Q_{EVAP} + Q_{DISP} \quad (8.)$$

For a first rough estimation of the heat duty, the students after a group discussion agreed upon the following simplifications: i. heat losses are negligible, that is: $Q_{DISP} = 0$; ii. the pure solvent vaporizes at its normal boiling point. Therefore, the previous Eq.(8) becomes:

$$Q_{EVAP} = V \rho_{SOLV} \lambda_{SOLV} \quad (9.)$$

where V = volume of solvent evaporated in one cycle [m^3]; ρ_{SOLV} = density of the solvent [kg/m^3]; λ_{SOLV} = latent heat of vaporization at atmospheric pressure [J/kg].

The students immediately realized that the total energy consumption for boiling during the complete Soxhlet test is simply obtained by multiplying the number of cycles:

$$Q = N_{CYCLE} \cdot Q_{EVAP} \quad (10.)$$

To move forward on the energy-related aspects, the lecturer reminded the students that another heat duty was to be considered and perhaps it was not negligible with respect to latent heat: the thermal energy required in the transient step preceding the triggering of cycle No.1, i.e., from ambient to boiling temperature. The students confirmed the assumption of negligible heat losses, and simply came out that such a thermal energy is equal to the sensible heat necessary to bring the solvent from room temperature to boiling. Accordingly:

$$Q_{TRANS} = W_{SOLV} C_{p,SOLV} (T_b - T_{amb}) \quad (11.)$$

where $C_{p,SOLV}$ is the specific heat at atmospheric pressure of the solvent [$J/(kg K)$].

While continuing their discussion, the students realized that in the above equations the volume V of solvent evaporated in one cycle is only a part of the whole solvent in the flask, having a mass W_{SOLV} . Therefore, they argued about a method to measure under cold conditions the actual volume siphoned, which exactly corresponds to that of evaporated solvent. After that, they experimentally found $V = 70$ mL.

3. Results

3.1 Case I

When the solvent is perfectly anhydrous and the sample to be extracted is perfectly dry, the mathematical problem of solving the mass balance closure simplifies. In fact, the water balance in Eq.(2) loses its significance, the Eq.(6) and Eq.(7) become identities: then, the number of equations reduces to 4; the same applies to the unknowns that appear highlighted in a green background in the Table 1.

Table 1: Closure of the mass balances for free-from-water Soxhlet tests: pure ethanol and roasted cuticles.

TEST ID		S38 [g]	S40 [g]	S42 [g]
Dry solids in biomass	$W_{DS,TS}$	15.05	15.2	15.45
Solvent	W_{SOLV}	236.7	236.7	236.7
TOTAL IN		251.75	251.90	252.15
Solvent evaporated during drying under hood	$W_{S,SP}$	39.65	42.00	55.75
Dry spent biomass	W_{SP}	13.95	14.20	13.65
Solvent in the extract	$W_{S,E}$	181.5	176.7	167.3
Solvent lost due to lack of condensation	$W_{S,L}$	15.58	17.96	13.68
Solids dissolved in the extract	$W_{DS,E}$	1.10	1.00	1.80
TOTAL OUT		250.65	250.90	250.35

Following a gradual approach to the problem, the students were asked to consider this Case I first. Hence, to solve the material balances and check the closure, they easily carried out hand calculations with the test data and the reduced system of Eq.(1, 3, 4 and 5). The results are reported in Table 1.

The students evaluated the relative error as $\Delta(TOTAL_{OUT} - TOTAL_{IN})/TOTAL_{OUT}$ to be in the range 0.1–0.2 %, that is a very good result. In this Case I, the solvent loss due to imperfect condensation turned out relevant as $W_{S,L}$ was calculated in the range 14–18 g.

3.2 Case II

In the case of wet tomato processing residues, two Soxhlet extraction tests were performed.

Table 2: Closure of the mass balances for Soxhlet tests with water: ethanol 70% v/v and wet tomato pomace.

TEST ID		S53 [g]	S68 [g]
H ₂ O in biomass	$W_{W,TS}$	53.45	33.01
Dry solids in biomass	$W_{DS,TS}$	6.55	17.0
Solvent	$X_{S,SOLV} \cdot W_{SOLV}$	165.7	193.3
H ₂ O in solvent	$X_{W,SOLV} \cdot W_{SOLV}$	89.8	105.0
TOTAL IN		315.51	348.10
Solvent evaporated during drying under hood	$W_{S,SP}$	33.19	49.97
H ₂ O evaporated during drying under hood	$W_{W,SP}$	32.41	36.18
Dry spent biomass	W_{SP}	7.05	18.1
H ₂ O in the extract	$W_{W,E}$	108.68	96.27
Solvent in the extract	$W_{S,E}$	111.32	132.95
Solvent lost due to lack of condensation	$W_{S,L}$	21.18	10.39
H ₂ O lost due to lack of condensation	$W_{W,L}$	2.18	5.34
Solids dissolved in the extract	$W_{DS,E}$	0.21	0.70
TOTAL OUT		316.01	349.20
$\Delta(TOTAL_{OUT} - TOTAL_{IN})$		0.50	1.10
$\Delta(TOTAL_{OUT} - TOTAL_{IN})/TOTAL_{OUT}[\%]$		0.16%	0.31%

Water was present in both the tested biomass and the extraction solvent, which had been selected as ethanol 70% v/v. However, the water content was known or measurable in both ones. Therefore, the students were asked to address this more demanding Case II where water turns out present in all material flows in Figure 2. The students prepared a MS EXCEL® spreadsheet in a group work under the supervision of the lecturer, implemented the calculations to solve the above system of Eq.(1 to 7), introduced the known or measured test data and obtained the results presented in Table 2.

Even in this case, the students reasonably found a very low relative error (see the bottom rows of Table 2).

In the Case II, the solvent loss due to imperfect condensation turned out relevant as $W_{S,L} = 21.18$ and 10.39 g, respectively. On the contrary, the water loss due to imperfect condensation was small (see Table 2).

3.3 Energy consumption in Soxhlet test

After retrieving the thermal-physical properties of solvents from textbooks, the students easily carried out hand calculations with the Eq.(9 to 11). The results are reported in Table 3, for two different choices of the number of cycles $N_{CYCLE}=10$ (i.e., the actual number of cycles in the test S38) and 20 (i.e., a double value). They noticed:

- the thermal energy required in the transient step is of the same order of magnitude as that required for the vaporization of the solvent in one cycle
- the use of water as a solvent, although greener and cheaper, is by far the most energy demanding.

Table 3: Heat duty required in the Soxhlet tests as a function of the solvent. The initial volume of solvent is 300 mL. All data are in kJ.

Solvent	Q_{EVAP}	Q_{TRANS}	Q		Q_{TOT}	
			$N_{CYCLE} = 10$	$N_{CYCLE} = 10$	$N_{CYCLE} = 20$	$N_{CYCLE} = 20$
Ethanol	46	31	469	500	939	970
Water	158	94	1577	1671	3154	3248
Ethyl acetate	23	27	227	254	454	481
n-hexane	15	20	153	173	307	327

4. Conclusions

The Soxhlet test methodology allowed lab-scale extraction of valuable substances from a low-value solid matrix constituted by a food processing residue; this was the case of polyphenols from roasted cuticles and lycopene from tomato pomace, the results of which, however, are not the focus of this paper.

The work done and reported here demonstrated the added value that the Soxhlet apparatus and technique may convey to training students of a chemical engineering lab class at bachelor level on the founding aspects of process engineering, from the concept of unit operation to the establishment of a conservation law. The students developed appropriate mass and energy balances for the Soxhlet extractor operation, carrying out all necessary measurements and taking care of both simplifications and uncertainties. The closure of macroscopic mass balances turned out successful, with a relative error in the range 0.1-0.3 %.

The calculation of the energy demand in a complete Soxhlet extraction test represented the basis for the trained students to think about the heat duty required by a possible industrial-scale application of the same unit operation and to develop the associated energy balance.

The developed activities and the way students actively participated represent a nice application of “hands on” practice and a good example of “learning by doing”.

Acknowledgments

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