STANDARDISED LOW-COST BATCH SFE – UNITS FOR UNIVERSITY EDUCATION AND COMPARATIVE RESEARCH

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ABSTRACT:

In the framework of the joined research project "Supernat" (CNPq, Brazil), equivalent to "BRA 098 / 78" (Ministry of Research and Education BMBF DLR-IB, Germany), the Technical University Hamburg Harburg (TUHH), Arbeitsbereich Thermische Verfahrenstechnik has designed and constructed identical screening units for Supercritical Fluid Extraction.

The units shall provide for each partner same (reproducible) process and working conditions for the screening of the natural product of interest, in different seasons, sites or regions of Brazil. The budget for the construction of each unit was limited to approximately 12.000 USD, all taxes included.

I OVERVIEW :

Brazil is one representative of the New Industrializing Countries with rich, unexploited and even undiscovered natural resources for new phytopharmaceuticals. The plants of the rain forest provide a wide research field for the development of new phytopharmaceuticals, whereas researchers as well as SME are faced with the drawbacks of the empirical design for Supercritical Fluid Extractions (SFE). Industrial users expect a standardised input for downstream processing, eventhough quality of botanical raw materials fluctuates considerably, due to regional conditions of nature, climate and harvesting period.

In order to transfer any type of technology from the University to the Industry it is mandatory to have tools that allow fast and sound estimations of technical and economical feasibilities. Since it entirely impossibly to generalize the knowledge to the entire Brazilian flora, the knowledge must be aquired and simple tools using minimum experimental information must be developed, which will permits some kind of generalizations, at least for large groups of vegetable raw materials, such as the aromatic, medicinal, and spice plants.

The research group SuperNat [1 – 6] congregates the following university institutions: TUHH (Germany), LASEFI – DEA / FEA – UNICAMP ,Campinas, LPN – IAC, Campinas, LAOS – DEQ / CT – UFPA, Belem, LESTE – DEQA / CT – UFSC, Florianopolis, AT – DEQ / CT – UEM, Maringa (all Brazil).

With the help of the identical screening units, reproducible and comparable experiments can be executed in different seasons, sites or regions of Brazil. An overview about the specifications is given in table 1:

Table 1 : *SFE-Screening Unit:Capacities*

Extractor Volume	100 mL
Extraction Pressure:	80 – 400 (600) bar
Extraction Temperature	40 – 100 °C
Mass Flow CO_2	0,1 – 2,5 kg/h

The supply of the solvent fluid CO_2 is maintained by commercial high pressure bottles (about 20-50 L inner volume), the inner bottle pressure at ambient temperature should remain in the range of 50 – 60 bar (monophase liquid or biphase liquid-gas fluid).
Auxiliary media are AC (220-230 V) and compressed air or nitrogen, either from university network, or from gas canisters (50 L). The gas supply pressure should not extent the limit of 4- 5 bar.

II. PRESENTATION OF THE UNIT

II.1 The Principle:

Figure 1 shows the flow sheet of the unit, including main parts, tubes and measurement equipment.

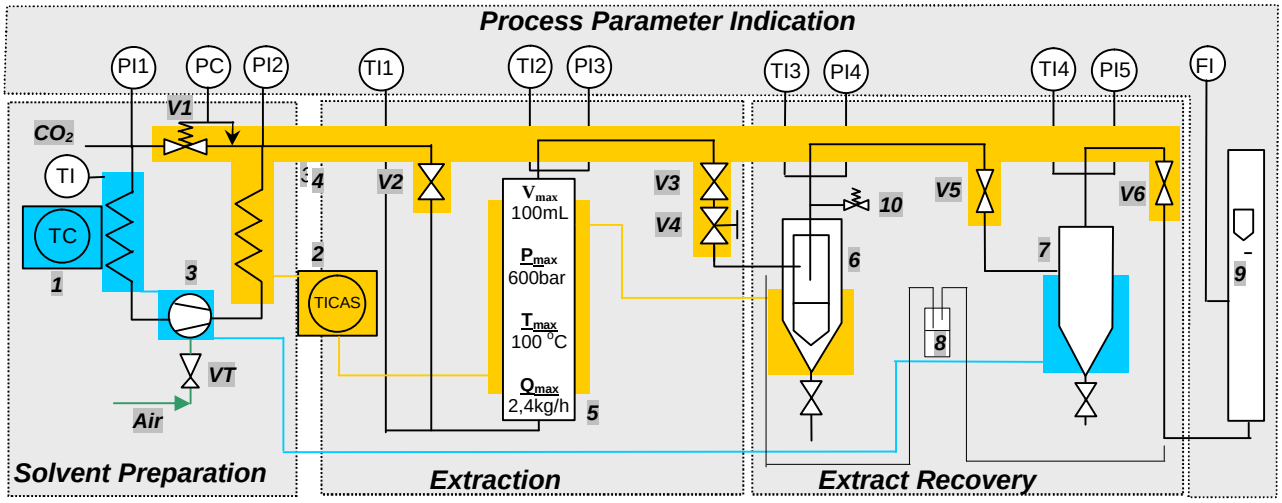

Figure 1 : *Flow Sheet of the Screening Unit*

1	Cooler (Condenser), CO_2 cooling loop	VT	Air Throttle → Booster Piston Frequency
2	Heater unit	V1	Back Pressure Regulator → Process Pressure
3	Air driven CO_2- Pump (“Booster”) 1:110	V2	Inlet I/O Valve for Extraction Autoclave
4	Water-heated box for expansion valves	V3	Outlet I/O Valve for Extraction Autoclave
5	Extraction Autoclave, 100 mL, heating jacket	V4	Micro Needle Valve→ Fluid Flow Rate
6	Cyclone with inner parts, heating jacket	V5	Regulation Valve → Cyclone Pressure
7	Separator with cooling jacket	V6	Regulation Valve → Separator Pressure
8	Alternative sampling line in glass tubes		
9	Flow Meter (kg CO_2 / h) at NPT		
10	Safety valve for cyclone and separator		
		PI 1	Pressure CO_2 Supply
TI 1	Flow Temperature at Autoclave Inlet	PI 2	Pressure CO_2 Solvent Preparation Cycle
TI 2	Flow Temperature at Autoclave Outlet	PI 3	Pressure Extraction Autoclave Outlet
TI 3	Flow Temperature at Cyclone Outlet	PI 4	Pressure Cyclone
TI 4	Flow Temperature at Separator Outlet	PI 5	Pressure Separator

To be able to use a pump for obtaining high pressures, the CO_2 has to be supplied in a liquid form. This requires the use of a heat exchanger (cooler) [1] in order to condense the gaseous fluid from the bottle outlet.
The air driven piston pump [2] may now compress the liquid CO_2 and produce a continuous flow of a high pressurized fluid: in order to avoid any malfunction risk (cavitation, gas bubble production), the pump head requires intensive cooling.
The oscillation frequency of the piston will be controlled by the throttle valve [VT]. The gear ratio of the booster piston is 1:110.

The system pressure itself will be controlled by the spring loaded back pressure regulator [V1]. The piston sensor opens when the required process pressure is reached. Then the preheated fluid flows from the valve box [4] back to the sucking section inside the condenser [1].Consequently, the pump produces continuously a compressed CO_2 flow in a closed loop. The closed loop assembly shall allow a constant solvent supply with low pressure fluctuation. In a wide range of experimental conditions, this assembly is therefore adapted for adsorption/ desorption processes as well as SF-Chromatography.
Due to the latent high pressure differences (up to 500 bar) before and behind the valves, the expansion-induced freezing of the CO_2 flow (Joule Thompson Effect) may lead to a complete blocking of the tubes by dry ice particles. Therefore, all relevant valves were placed in a tempered heating bath [4], which, is floated by the same heating liquid as the extractor unit [5].

A Crossing is fitted in the closed loop in front of the back pressure regulator [V1], from this position a part of the compressed CO_2 passes through the inlet valve [V2] into the extraction autoclave [5]. The thermocouple T1 may be replaced by a HPLC pump in order to introduce a modifier flow to the CO_2.

The section between inlet [V2] valve and the extractor outlet valve [V3] can be hermetically closed, in order to allow short term interruptions of the extraction experiment. Therefore, [V2] and [V3] were designed as “simple” shut off (I/O) valves. The flow itself may be adjusted by a high sensitive micro-needle valve [V4], which is fitted directly downstream of [V3].

Downstream of the [V3]-[V4] position, the extract flow may be expanded in one, two or three steps. In this pressure cascade, defined by the opening of the expansion valves [V5] and [V6], the extracted material may be collected or even fractionated in the separation units [6], [7], or [8].

The optimum choice for number and kind of separation methods, the inner cyclone parts, the separation parameters depend on the species of the natural product and should be adjusted with respect to the specified task.

Finally, downstream of the outlet valve [V6], the mass flow can be supervised by a flow meter [9] under Norm Conditions (1 bar, 20 ^{o}C).

II.2 The Construction

The following picture (figure 2) gives an overview about the complete unit and the most important details. The purpose of the design is a robust, easy to handle “low-end” screening unit for students and researchers. Therefore, the unit was constructed according a module approach.

The autoclaves and cyclones were set up on the front side, they are fixed by steel clamps. On the front right hand side, a supplementary steel clamp serves as place holder for an additional autoclave. In default, the place is used for the glass vials.
The autoclaves and cyclones may be tempered by a heating and a cooling jacket, and isolated by polymer coats. In the background of the front side, the pump is fitted under the extraction autoclave.

At the upper area on the right side, the isolated valve box (heating bath) is fitted. In the middle the whole connection between the autoclaves, the valves and the indicators for pressure and temperature is performed by a row of Swagelok Unions. The connecting lines are hidden under the perforated top metal plate.
The temperature values are indicated by a 2 - Channel Digital hand-held equipment on the left - hand side top plate. All pressure values are indicated by 5 manometers on the instrument bridge over the top plate. In the background, the two heat exchangers are fitted. The flow meter is connected with the hose pipe downstream of [V6] on the right hand side of the manometer bridge.

This assembly allows therefore an easy modification of the separation conditions (e.g. 1 cyclone, 2 cyclones, glass vials, cold trap, absorption unit), as well as a parallel or serial connection of two different autoclaves. The overall dimensions of the unit are 62 cm x 140 cm x 107 cm.

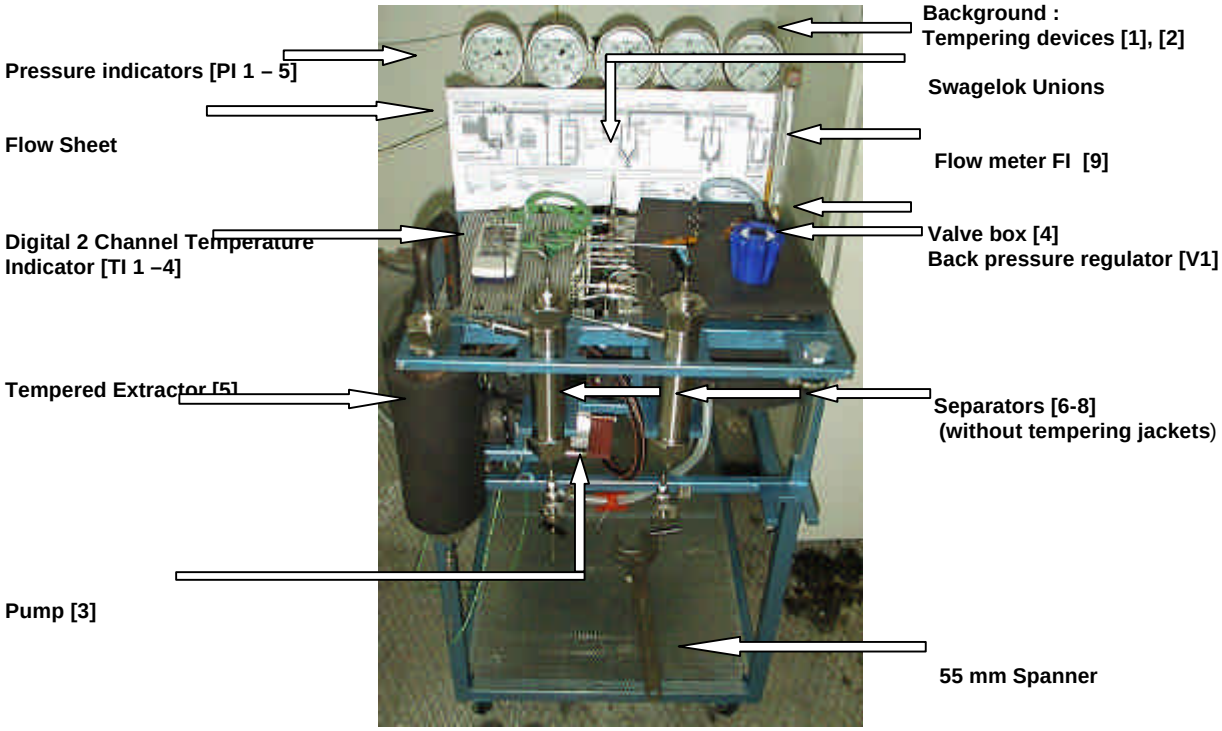

Figure 2: *Overview*

III. STANDARDIZED EXTRACTION PROCEDURE

The extraction procedure will be prepared with a characterisation of the solid particles. The following data are considered as essentially and will be noted: grinding and or sieving procedure, mean particle size and real solid phase densities.
The solute will be defined with respect to its accessibility (e.g. fixed or free solutes like essential or free oils) and in comparison with organic Soxhlet extraction.
Analytical actions are focused on Gas Chromatography, HPLC and Mass Spectroscopy, the results will be compared with literature data.
Information on solubility is collected by three methods. First screening results can be obtained when the system is considered as a pseudo-binary one (CO_2 and solute). Further, the operational solubility can be obtained from the slope of the initial extraction curve (dynamic method). Finally the system shall be represented by an adapted equation of state.

Modelling of the experimental results gives important information for understanding the physicochemical background as well as for estimating consumption and investment of subsequent up-scale applications. Desorption-diffusion based approaches as well as netto-solubility based models referring to solute-matrix interaction will be compared.
The organization of the collected data is shown in Table 2:

Batch Input		**Solute**	
Sample Preparation :	- grinding - sieving	Affinity	- fixed (glycerides) - free (essential oil)
Particle size	- Mean diameter	Conv. procedure	- Soxhlet - steam distillation
Solid density	- bulk density - porosity	evaluation	- active principles

Analytical Methods		**Solubility**	
Chromatography	- GC - HPLC	Mixture	- Pseudo binary system
		solid matrix	- operational solubility - dynamic method
Identification	- GCMS - Literature	Theory	- Equations of State

Results		**Yield**	
Substrate Name	- Common name - Botanical name	Diagrams	- Overall Extraction curve (extract vs solvent)
Laboratoy	- Research group - vresearch period		- Extraction rate (extract/time vs solvent/time)

References :

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