ASSEMBLING OF A SUPERCRITICAL FLUID EXTRACTION EQUIPMENT TO OPERATE IN CONTINUOUS MODE

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Abstract. Supercritical fluid extraction (SFE) of bioactive compounds from vegetal matrices in continuous mode presents the advantage of reducing the process setup time and increasing the productivity. The exchange of batch process to continuous process might be performed adding two or more extractors operating in parallel mode to the process line. This allows the system to operate continuously in spite of the exhausting of the solute in the fixed bed. The solvent percolation occurs in n-1 extractors, at each extraction cycle, while the remaining extractor is on process setup. The assembly of a SFE equipment SFE-2×1L containing two 1 L extractors, was therefore done aiming to operate in continuous mode; while one extractor is at operation procedure, the other can be charged with raw material to subsequent operations, and vice versa. Extractor 1 has height to internal diameter ratio (Hb/Db) of 7.1, while Extractor 2 has Hb/Db=2.7, both supporting 60 MPa. The use of different Hb/Db ratios is to analyze the influence of the extractors geometry on the overall extraction curves (mass of extract versus time of extraction). The interference of the tubing length on each extractor output was minimized by maintaining the same distance from the output of the extract+solvent mixture to the separator. The equipment was assembled considering the possibility of coupling a co-solvent in the system. Furthermore, the SFE-2×1L equipment is multipurpose, because it will be also applied for the fractionated separation of extract. The validation of this equipment will include experimental assays using clove, fennel and rosemary.

Keywords: Supercritical fluid extraction (SFE), continuous mode, bed geometry.

1. Introduction

Researches in the area of supercritical technology are increasingly moving forward because this technology possesses a green label. Due to the globalization, the access to specific equipment which supports high pressures was facilitated. The referred access provides different alternatives, not only of types as well as of prices, to the ones interested in assembling an extraction plant using supercritical fluids.

In this field, the extraction of bioactive compounds with supercritical CO_2 in continuous mode is of great importance, since this configuration allows the continuous obtaining of product by intercalating the charge/discharge time of the *n* extractors in a plant. Thus, the continuous extraction in a system containing *n* extractors is characterized as follows: while one extractor is in charge/discharge step, the *n-1* extractors are in extraction process step.

The assembling of equipment that can operate in continuous mode is necessary. This operation mode improves the technical extraction feasibility and enhances the process productivity. So, the objective of this study is to describe the assembling of a laboratory equipment which involves supercritical technology. The design, the difficulties and the solutions during the development of the home-made system are pointed out.

2. Assembling of a SFE equipment to operate in continuous mode

Supercritical fluid extraction is a process that allows operating in continuous mode. The choice of CO_2 as solvent for the respective process is linked to its advantages: moderate critical temperature, non-flammable, high availability and easiness of separation from the extract. The last characteristic makes the obtained products free of solvent [1]. Thus, the techno-scientific development of SFE (Supercritical Fluid Extraction) in research centers is rising. However, implanting an industrial SFE plant depends also of economic aspects, mainly related to the high cost of investment. In this sense, a scientific investigation focused in the process optimization is needed. In such case, the continuous mode of extraction is profitable because it can reduce the cost of manufacturing (COM) smaller when compared to the batch mode process. So, the return time of the invested capital can be reduced. As cited by Brunner [2], the amount of raw material manufactured in a continuous mode process at a fixed time is higher than the amount processed in batch mode in the same time.

Generally, SFE from solid matrices is performed in batch mode. In this situation, the target compounds are extracted by percolating a solvent in a fixed bed, where the filling material inside the extractor is composed by the vegetal matrix. The filling material is exchanged after the extraction time and the extract collecting is interrupted. This system configuration is characterized as a discontinuous process, being industrially undesirable because the process interruptions lead to high operational times and less productivities [3].

The scale up process and the capacity of operating in continuous mode need to be considered in extraction plants design. Several extractors disposed in parallel system can be utilized [4], as schematized in Figure 1.

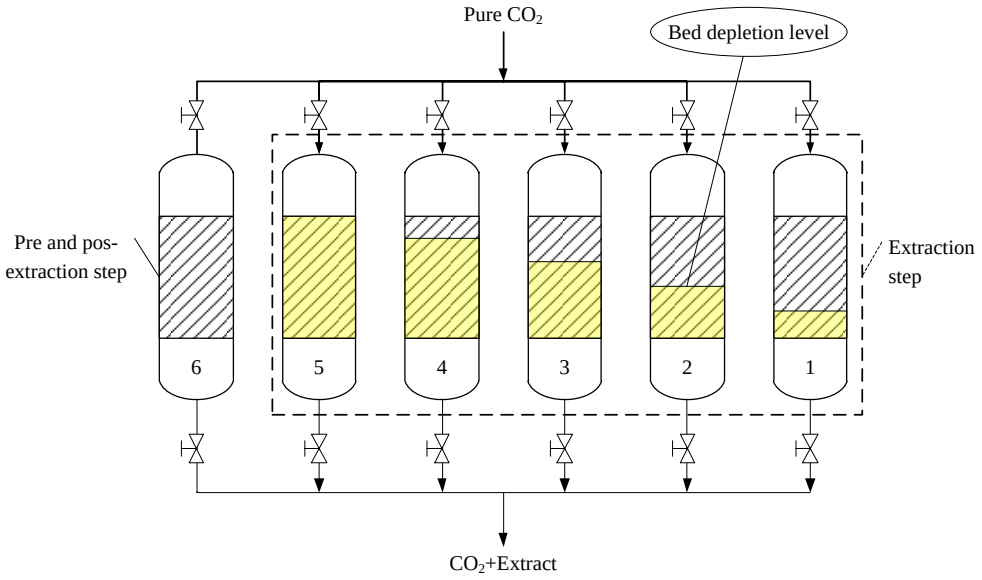


Figure 1. Schematic diagram of a continuous mode process with extractors disposed in parallel system.

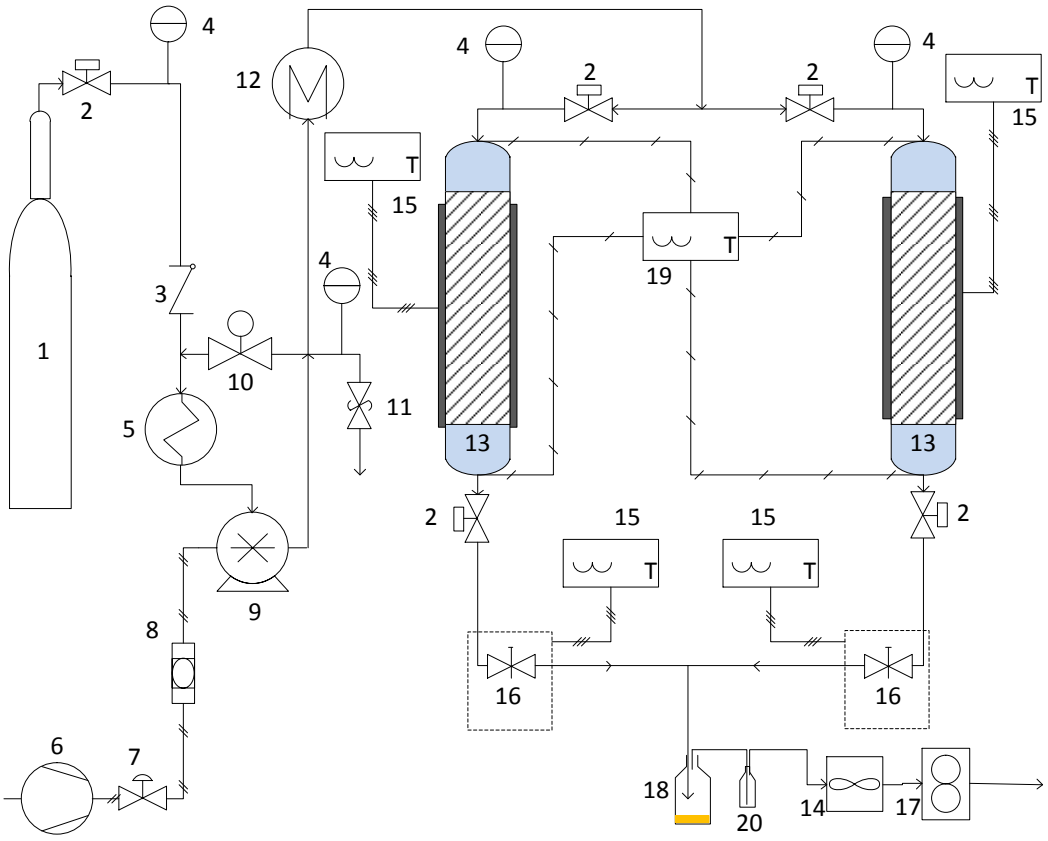
A process in continuous mode is performed with two or more extractors. This is the minimum quantity of extractors involved. A range of six extractors is presented in Figure 1. The extraction bed is maintained fixed while the solvent moves inside the extractor continuously extracting the bioactive compounds. The referred system is a modification of "Shanks" system described by Treybal [5]. The continuous mode proposed in this study operates as follows:

I) Supposing that the system is running in a certain time, the extractors 1-5 are in extraction step and the extractor 6 is in charge/discharge step. The process was started by extractor 1, where the bed depletion is finishing, and the extractor 6 is the last to be charged. After this cycle, another cycle is initiated;

II) After preparing the extractor 6 (charge/pressurization/static time), this extractor is inserted to the running process. Now, the extractors that are in extraction step are 2-6 and the extractor 1 is in post-processing step, as depressurization, discharge and cleaning process. After it, the extractor 1 begins the pre-processing step again;

III) Considering *n* extractors disposed in parallel in a system, at least *n-1* extractors are in extraction step, while the rest of extractors are in pre and post-processing step.

Figure 2 presents the flow diagram designed for assembling the SFE-2×1L equipment. Two 1 L extractors were inserted. Futurely, more extractors can be added to the equipment. The PDSA (Plan, Do, Study, Action) cycle was used as a tool of process improvement to organize and optimize the stages during the assembling. It also helped in planning and performing the experimental assays.



Eletric
Extract/CO_2
Pneumatic
Thermal signal

List of equipments	
1	CO_2 reservoir
5	Cooling bath
6	Air compressor
9	Air-driven CO_2 pump
12	Heating bath
13	Extraction cell

List of valves/instruments	
2	Blocking valve
3	Non-return valve
4	Pressure gauge
7	Control valve (air flow)
8	Air filter
10	Back pressure regulator
11	Safety valve
14	Flowmeter
15	Temperature controller
16	Micrometering valve
17	Flow totalizer
18	Extract collecting vessel
19	Temperature indicator
20	Residual extract collecting vessel

Figure 2. Flow diagram for the SFE-2×1L experimental apparatus.

3. Results and discussion

3.1. Equipment assembling

Figure 3 shows the SFE-2×1L equipment assembled by the LASEFI's researchers. A safety valve was added in the system for immediately releasing the solvent if the system unexpectedly reaches pressure higher

than that supported by the extractors (60 MPa). The instruments were placed in its appropriated locals, facilitating the extract collecting and the control of temperature, pressure and solvent flow rate values during an experimental running. The interference of the tubing length on each extractor output was minimized by maintaining the same distance from the output of the extract + solvent mixture to the separator.

Figure 3. Photo of the SFE-2×1L equipment.

Some difficulties were found during the assembling of the equipment to operate in continuous mode. PDSA cycles were done to identify these difficulties and to solve them. The troubles can be avoided, so the mainly points are listed below.

I) For multipurpose SFE equipment, a detailed literature review should be done in this field. It is interesting to obtain an estimative of extraction yields of the botanic matrices group to be used. Thus, the equipment should be designed for the limiting conditions, as the higher mass extracted or the higher pressure. The separation process is generally a limiting factor. In this case, the separators should not be sub sized.

II) A SFE equipment should be assembled for allowing futurely the coupling of more extractors. In short extraction times, the use of only two extractors is operationally difficult.

III) The pressurization of the system needs to be properly designed. An efficient solvent cooling before entering in the pump should be done. High solvent flow rates demand high thermal exchanges. In this aspect, the heat exchanger should be correctly designed for avoiding troubles in the pump. It is important to avoid the pump to work with gaseous fluid.

IV) The bed of the extractors should be wholly filled with raw material or the remainder volume should be completed with an inert material, as glass beads. The use of filters and baskets of at least 80 mesh in laboratory or pilot extractors is recommended to facilitate the charge/discharge step.

V) The extractors and separators should be preferentially heated by an indirect contact of a fluid in double jacketed material. Electric resistances for heating are not recommended because it generates heterogeneous points of temperature and it consumes expressive amount of energy.

VI) A small quantity of extract, mostly the volatile oil, can be dragged with the solvent stream. A trap should be positioned before the rotameter and flow totalizer instruments for avoiding obstructions or contaminations with oil residue.

VII) The solvent can leak out through the extractor during the pressurization step if the lids are not rightly closed. The gasket system should be tested before the extraction process.

VIII) The heat exchangers should be switched on in a defined period before starting the experimental running. In the case of SFE-2×1L equipment, the thermostatic baths should be switched on 1 h earlier of starting the process.

IX) The extractors' pressurization without any filling material is not advisable, because it can cause damages if the extractors are not rightly dimensioned.

3.2. Temperature profiles inside the extraction beds

Table 1 - Experimental design randomized in blocks

Sort order	Run order	Extractor	Position	Temperature in °C (blocks)
8	1	E-2	High	40
10	2	E-1	High	40
1	3	E-1	High	40
9	4	E-1	Medium	40
14	5	E-2	Medium	40
35	6	E-2	Low	40
17	7	E-1	Medium	40
30	8	E-2	Medium	40
23	9	E-2	Low	40
19	10	E-2	High	40
33	11	E-1	Low	40
22	12	E-1	Low	40
32	13	E-1	Low	50
24	14	E-2	Medium	50
18	15	E-2	Low	50
13	16	E-2	Low	50
11	17	E-1	Medium	50
34	18	E-2	Medium	50
5	19	E-2	High	50
4	20	E-1	Medium	50
31	21	E-2	High	50
16	22	E-1	High	50
21	23	E-1	High	50
29	24	E-1	Low	50
28	25	E-1	Low	60
6	26	E-2	High	60
25	27	E-2	Medium	60
27	28	E-1	Medium	60
2	29	E-2	Low	60
12	30	E-1	High	60
36	31	E-1	Medium	60
15	32	E-1	Low	60
20	33	E-2	High	60
3	34	E-2	Low	60
26	35	E-2	Medium	60
7	36	E-1	High	60

Temperature values of the bed during the period of static time was collected for both extractors belonging to SFE-2×1L equipment before validating the respective equipment. The factors investigated were: extractor geometry, position inside the extractors and temperature of the extractors' external surface. The positions

evaluated contemplated three axial levels (high, medium and low). The temperatures levels of the extractors' external surfaces were 40°C, 50°C and 60°C. The extractors geometry was tested in two levels (E-1 and E-2), where E-1 has 0.407 m of height/0.057 m of internal diameter (H_B/d_B = 7.1) and E-2 has 0.212 m of height/0.078 m of internal diameter (H_B/d_B = 2.7). The experiment was performed in replicate, totalizing 36 assays. An experimental design randomized in blocks was done, where the blocks were the temperatures of the extractors' external surfaces. Table 1 displays the experimental design used.

The solid residue of SFE process of clove (*Eugenia caryophyllus*) extract was applied for investigating the temperature profiles in the bed. On each axial position, five radial points (center, front, right, left and back) were collected. Figure 4 exhibits some of the obtained results for the static process tested.

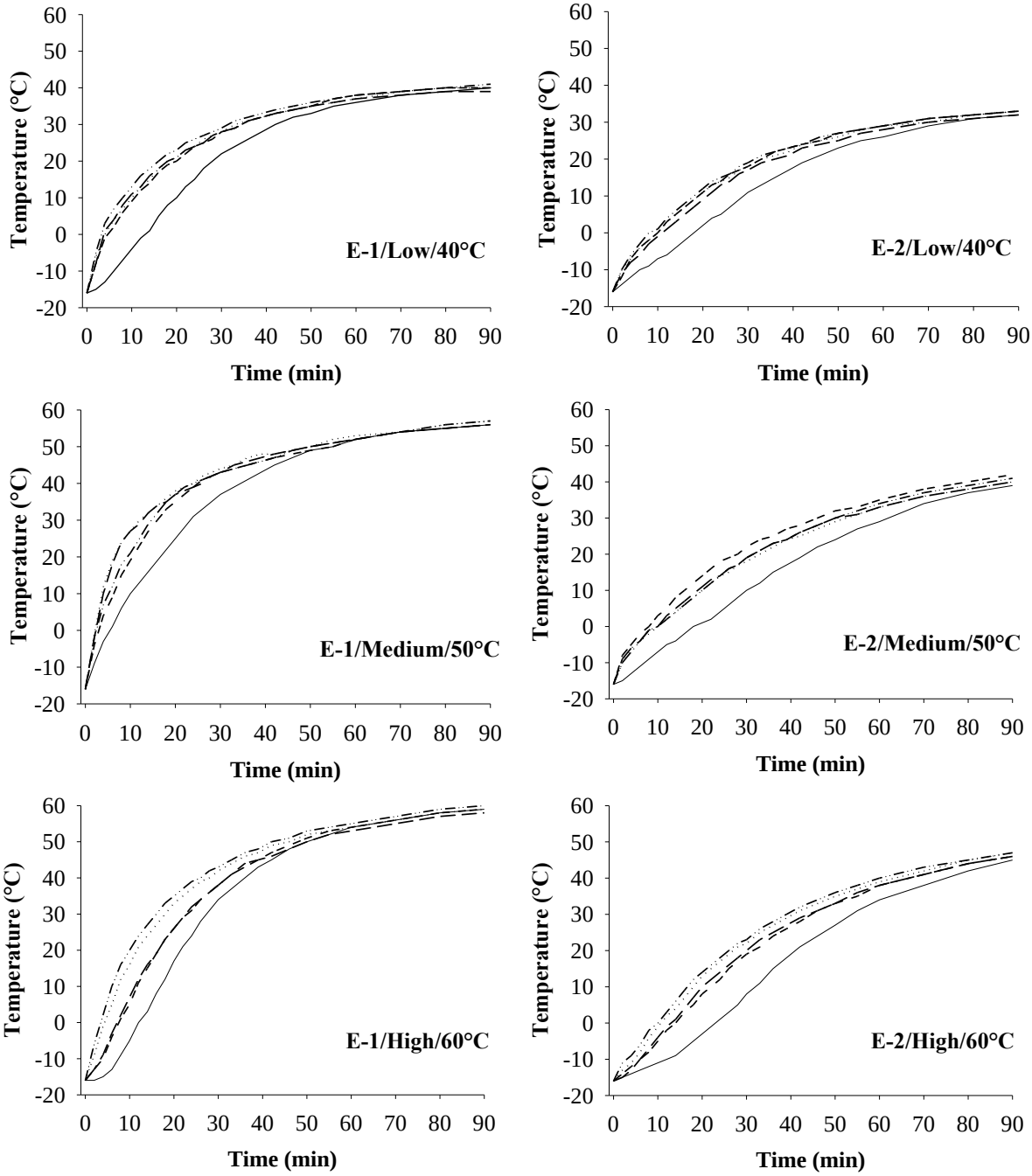


Figure 4. Control graphics of bed temperatures at different positions inside the extractors and at different temperatures of the extractors' external surface. (——) center; (•••) front; (— -) right; (—··) left; (– –) back.

Seeing Figure 4 as a table, the columns represent different extractors while the lines represent different temperature of the extractors' external surface and axial positions. Comparing the temperature profiles between the two 1 L extractors, the temperature increments are more accentuated in E-1, because this extractor has an H_B/d_B ratio of 7.1. This configuration allows an improvement of heat transfer. Fixing the process time, the positions of the beds reach different temperatures. Therefore, this study is important to obtain information about the temperature inside the beds. In such case, it is necessary to change another factors, as the thermostatic bath, to attain similar temperatures for both extractors. This characteristic allows obtaining uniform extracts. The intercalation of the extractors should not interfere in extract properties.

Concerning these aspects, the temperature of the extractors' external surface should be different configured. In E-1, it needs to be 45°C, while in E-2 it needs to be 52°C. In a dynamic process, with a defined period of static time of 20 min (for the equilibrium of pressure and temperature), the bed reached satisfactorily the desirable temperature of process (40°C).

3.3. Validating of SFE-2×1L equipment

For validating the SFE-2×1L equipment, the commercial equipment, known as Spe-ed (Applied Separations, model 7071, Allentown, USA) equipped with one 0.1 L extractor, was used. The selected criterion of scaling change was the maintenance of the S/F (mass of solvent/mass of raw material) ratio and the extraction time constants. The other parameters as pressure, temperature, bed porosity, bed density and raw material lot were maintained the same. The three kinetic curves obtained in E-1, E-2 and Spe-ed are visualized in Figure 5.

Clove was used for this process. The operational conditions were set: pressure of 15 MPa, temperature of 40°C immediately after the extractors output and solvent (CO_2, 99.0% of purity, Gama Gases Industriais, Campinas, SP) mass flow rates of 17 g/min for both 1 L extractors and 1.7 g/min for 0.1 L extractor (Spe-ed equipement). For obtaining the standard deviation of the mean, the kinetic curves were performed in duplicate.

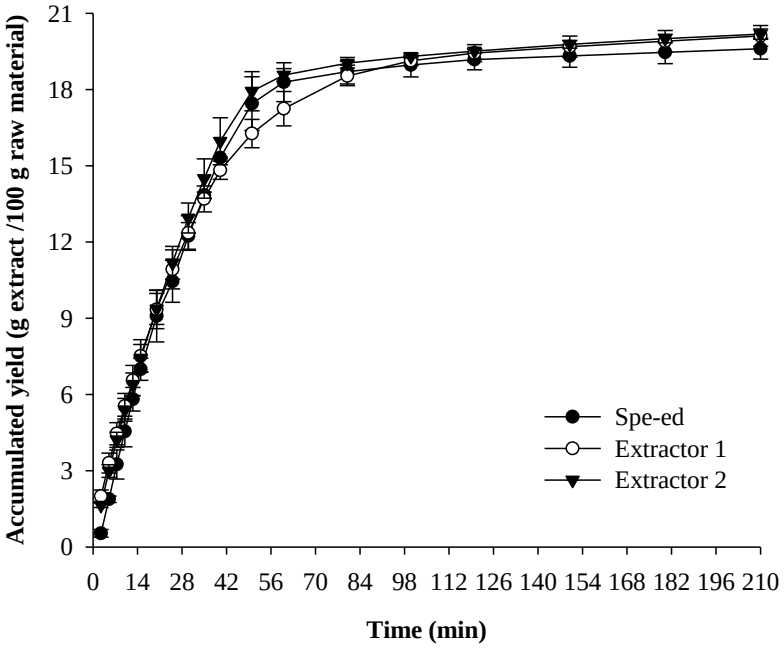


Figure 5. Kinetic curves for validating the SFE-2×1L equipment. (–●–) Spe-ed, (–○–) Extractor 1 and (–▼–) Extractor 2.

Figure 5 shows a superposition of extraction curves. There is an overlapping of the standard deviations in all of the kinetic points for both curves. Thus, there is no evidence of significant difference among the kinetic yields, which validates the SFE-2×1L equipment.

Since the assembled equipment was validated, Figure 6 was elaborate to show the planning of operational steps using two extractors for obtaining extract in continuous mode. At least one extractor should be extracting.

4. Conclusion

The assembled equipment to operate in continuous mode using supercritical fluids is suitable for extracting bioactive compounds from vegetal matrices. The results obtained with clove were satisfactory. Tests using other raw materials, as fennel and rosemary, still needs to be performed to see if the different vegetal species interfere on the selected operation mode. Prospective tests also will gather the investigation of fractioned separation of the extracts in this referred equipment.

Acknowledgments

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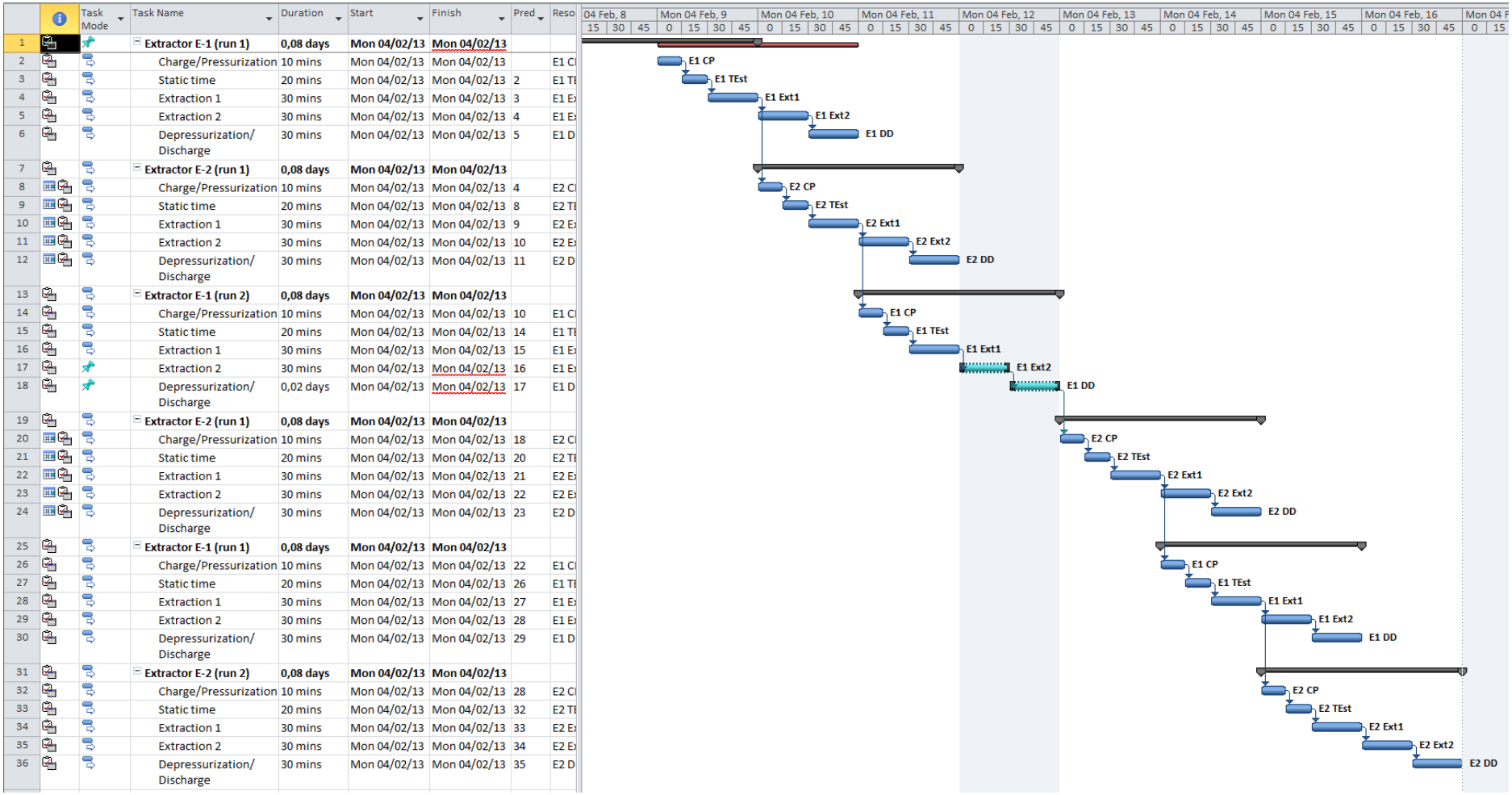

	Task Mode	Task Name	Duration	Start	Finish	Pred	Reso
1		**Extractor E-1 (run 1)**	**0,08 days**	**Mon 04/02/13**	**Mon 04/02/13**		
2		Charge/Pressurization	10 mins	Mon 04/02/13	Mon 04/02/13		E1 C
3		Static time	20 mins	Mon 04/02/13	Mon 04/02/13	2	E1 T
4		Extraction 1	30 mins	Mon 04/02/13	Mon 04/02/13	3	E1 E
5		Extraction 2	30 mins	Mon 04/02/13	Mon 04/02/13	4	E1 E
6		Depressurization/ Discharge	30 mins	Mon 04/02/13	Mon 04/02/13	5	E1 D
7		**Extractor E-2 (run 1)**	**0,08 days**	**Mon 04/02/13**	**Mon 04/02/13**		
8		Charge/Pressurization	10 mins	Mon 04/02/13	Mon 04/02/13	4	E2 C
9		Static time	20 mins	Mon 04/02/13	Mon 04/02/13	8	E2 T
10		Extraction 1	30 mins	Mon 04/02/13	Mon 04/02/13	9	E2 E
11		Extraction 2	30 mins	Mon 04/02/13	Mon 04/02/13	10	E2 E
12		Depressurization/ Discharge	30 mins	Mon 04/02/13	Mon 04/02/13	11	E2 D
13		**Extractor E-1 (run 2)**	**0,08 days**	**Mon 04/02/13**	**Mon 04/02/13**		
14		Charge/Pressurization	10 mins	Mon 04/02/13	Mon 04/02/13	10	E1 C
15		Static time	20 mins	Mon 04/02/13	Mon 04/02/13	14	E1 T
16		Extraction 1	30 mins	Mon 04/02/13	Mon 04/02/13	15	E1 E
17		Extraction 2	30 mins	Mon 04/02/13	Mon 04/02/13	16	E1 E
18		Depressurization/ Discharge	0,02 days	Mon 04/02/13	Mon 04/02/13	17	E1 D
19		**Extractor E-2 (run 1)**	**0,08 days**	**Mon 04/02/13**	**Mon 04/02/13**		
20		Charge/Pressurization	10 mins	Mon 04/02/13	Mon 04/02/13	18	E2 C
21		Static time	20 mins	Mon 04/02/13	Mon 04/02/13	20	E2 T
22		Extraction 1	30 mins	Mon 04/02/13	Mon 04/02/13	21	E2 E
23		Extraction 2	30 mins	Mon 04/02/13	Mon 04/02/13	22	E2 E
24		Depressurization/ Discharge	30 mins	Mon 04/02/13	Mon 04/02/13	23	E2 D
25		**Extractor E-1 (run 1)**	**0,08 days**	**Mon 04/02/13**	**Mon 04/02/13**		
26		Charge/Pressurization	10 mins	Mon 04/02/13	Mon 04/02/13	22	E1 C
27		Static time	20 mins	Mon 04/02/13	Mon 04/02/13	26	E1 T
28		Extraction 1	30 mins	Mon 04/02/13	Mon 04/02/13	27	E1 E
29		Extraction 2	30 mins	Mon 04/02/13	Mon 04/02/13	28	E1 E
30		Depressurization/ Discharge	30 mins	Mon 04/02/13	Mon 04/02/13	29	E1 D
31		**Extractor E-2 (run 2)**	**0,08 days**	**Mon 04/02/13**	**Mon 04/02/13**		
32		Charge/Pressurization	10 mins	Mon 04/02/13	Mon 04/02/13	28	E2 C
33		Static time	20 mins	Mon 04/02/13	Mon 04/02/13	32	E2 T
34		Extraction 1	30 mins	Mon 04/02/13	Mon 04/02/13	33	E2 E
35		Extraction 2	30 mins	Mon 04/02/13	Mon 04/02/13	34	E2 E
36		Depressurization/ Discharge	30 mins	Mon 04/02/13	Mon 04/02/13	35	E2 D

Figure 6. Gantt chart of operating in continuous mode in SFE-2×1L equipment