Comparison of Processes for the Supercritical Carbon Dioxide Extraction of Oil from Soybean Seeds

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Three different process alternatives for the production of soybean oil by supercritical carbon dioxide extraction were analyzed. The first two processes were organized according to the classical scheme, based on high-pressure extraction followed by separation induced by pressure reduction. Different techniques were used to recover the solvent in these two schemes, in the liquid and in the gas phases, respectively. The third alternative was based on an isobaric scheme—the oil, extracted at high pressure, was separated by changing the temperature in the separator. In a further improvement, a technique for the heat transfer network integration was added to all the process schemes. The different schemes were used to establish the process configuration that can produce a lower operating cost for soybean oil extraction. Operating costs were considered on an industrial scale to carry out a screening of the different alternatives. The operating cost of these plants were then compared with the hexane extraction process. A substantial reduction in the specific costs was obtained in the case of heat transfer integration, and the operating costs fell in the same range as conventional extraction plants.

KEY WORDS: **Carbon dioxide, cost comparison, processes, soybean oil, supercritical extraction.**

Seed oil extraction is traditionally based on the use of organic solvents. The product consists of a solution that has to be further processed to yield an oil of the required purity. The effect of solvent residues in the final edible product is an extensively studied argument, and presence of the solvent is deemed negative. For this reason, many countries have introduced regulations to limit the presence of organic solvents in the products. The reduction to the maximum allowable quantity of residues strongly affects production costs.

Supercritical carbon dioxide (SC-CO_2) extraction can overcome the negative aspects of the traditional techniques; the oil produced is guaranteed solvent-free. Moreover, by modifying the pressure and the temperature of the extractor, it is possible to change CO_2 selectivity. Therefore, different compound families can be extracted. Unfortunately, the SC-CO_2 technique is not yet widely used because operation at high pressure requires a high investment and high operating costs. Thus, although it is possible to obtain an improved product, the technology is still not widespread.

Only a few studies exist in which systematic analysis has been performed on investment and/or on SC-CO_2 operating costs (1–3). On the other hand, the lack of information on the solubilities in SC solvents makes the development of such an evaluation even more difficult. The SC-CO_2 of soybean oil is one of the rare cases in which the equilibrium solubility data are available in a wide range of temperatures and pressures (4,5). Therefore, this process could be considered an interesting model to evaluate supercritical fluid extraction (SFE) costs. The oil contains more than 80% of linoleic acid esters and, thus, can be modeled as a pure compound (6). Moreover, the characteristics of soybean oil–hexane extraction are well known (7). Therefore, it is possible to compare the SC-CO_2 product and the operating costs for its production.

This work aims at evaluating the operating cost of the SC-CO_2 of soybean oil for different process configurations. Three process schemes were hypothesized in which different methods were adopted to precipitate the solute and/or to recover the solvent: (i) separation based on pressure reduction and CO_2 recovery based on compression from the gas phase; (ii) separation based on pressure reduction and CO_2 recovery realized by pumping from the liquid phase; and (iii) separation based on temperature reduction without changes in pressure.

The study of each scheme was extended by performing an optimization of the energy required; the process integration technique (8) was used for this purpose. Our calculations indicated that the operating costs of two of the adopted SC-CO_2 schemes can be competitive with traditional hexane extraction.

Development of SFE process alternatives. Soybean oil is widely used; therefore, conventional plants based on hexane extraction have large capacities and can operate 24 h per day. On the contrary, for SC-CO_2 plants, continuous operation is not yet available on an industrial scale. An example of continuous feeding has been proposed for soybean oil production on a pilot-scale; and a little feeder has been designed and tested (9,10). Quasi-continuous operation has also been reached for caffeine extraction from coffee (11). Although the continuous feeder has to be tested on an industrial scale, to compare the SC-CO_2-based processes to hexane extraction, we hypothesized that the feeder can be scaled up and that continuous SC-CO_2 operation is possible on an industrial scale.

An SC-CO_2 apparatus is basically made up of an extraction and a separation block. In the extraction section, high oil solubility is required, whereas the opposite is required in the separation block. In principle, this second goal can be obtained by reducing the pressure as well as by changing the temperature. The effect of pressure is stronger and has largely been utilized in all SC-CO_2 plants. The temperature effect, however, has to be tested case by case. Figure 1 shows that for soybean oil, besides pressure, temperature also significantly affects the oil solubility in SC-CO_2. Therefore, on an industrial scale, thermal energy instead of mechanical power can mean great advantages.

Solubility values can be used to define the maximum yield of the process in the hypothesis of an infinite contact time. But thermodynamic equilibrium cannot be reached in an industrial extractor because of the finite contact time of the solvent and the solute. Therefore, a reasonable extraction rate can be obtained when the oil concentration in the SC phase is lower than the equilibrium value. This constraint means selecting an extraction stage efficiency (12). In our calculation, we hypothesized an efficiency of 60% with respect to the equilibrium value, according to the suggestions of Stahl *et al.* (6).

Based on the above hypothesis, three different SC-CO_2 process alternatives, named A, B and C, were considered.

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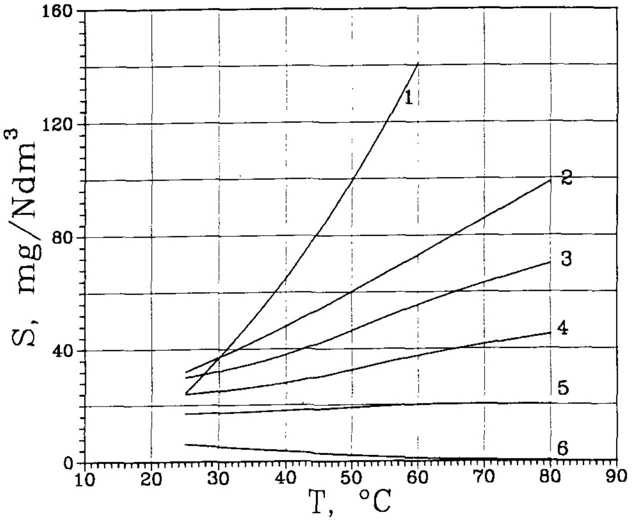

FIG. 1. Soybean oil solubility in high-pressure carbon dioxide as a function of temperature [adapted from Quirin (4)]: 1, 1000 bar; 2, 600 bar; 3, 500 bar; 4, 400 bar; 5, 300 bar; 6, 150 bar.

Alternatives A and B used a separation process based on pressure reduction and differed in the physical state of CO_2 at the exit of the separator:liquid CO_2 in A and gaseous CO_2 in B. Process scheme C was based on the isobaric separation of the soybean oil obtained by reducing the temperature in the separator.

The calculation model. Mass and energy balances were performed at various extraction pressures. If the extractor and the separator behave as equilibrium stages of known efficiency, the global and solute mass balance on the separator can be written as:

$$E = S + P \qquad [1]$$

$$\eta_E \cdot x_E \cdot E = \eta_S x_S \cdot S + (1 - \eta_s) \cdot x_P \cdot P \qquad [2]$$

where E is the solute-rich stream at the inlet of the separator, (kg/h); S is the solute-poor stream at the outlet of the separator, (kg/h); P is the produced oil (kg/h); x_E is the oil mass fraction in stream E (dimensionless); x_s is the oil mass fraction in stream S (dimensionless); x_p is the oil mass fraction in stream P (dimensionless); η_e is the extractor efficiency (dimensionless); and η_s is the separator efficiency (dimensionless). x_E, x_S and x_P can be calculated, when pressures and temperatures are fixed from the soybean oil solubility data reported in Figure 1.

When temperature, pressure and efficiencies of the extractor and of the separator are given for a fixed plant capacity, Equations 1 and 2 can be used to determine the CO_2 flow rate. The product was assumed to be only soybean oil ($x_P = 1$).

The energy balance was obtained by fixing the temperature and pressure in the extractor and in the separator. The enthalpy variations and vapor liquid equilibria were evaluated through the thermodynamic functions. Moreover, we hypothesized that the solute had a negligible effect on CO_2 enthalpy and entropy behavior. This hypothesis was supported by the consideration that the maximum oil concentration in the SC-CO_2 is less than 1% by weight. For this reason the calculation has been performed on pure CO_2.

The following additional hypotheses were used: Heat and mass losses are negligible; pumps, compressors and valves are adiabatic: the energy put into the equipment is entirely transferred to the fluid, as mechanical work and as heat.

The evaluation of the various alternatives can be performed if the effects of the temperature and pressure on enthalpy, vapor–liquid equilibria and the transfer parameters are known. This information was obtained by using the following submodels: (i) CO_2 enthalpies were calculated by using the Lee-Kesler equation of state (EoS) (LK) (13), because in the range of temperature and pressure of interest it has been demonstrated that such an EoS approximates the experimental data well (14). (ii) CO_2 liquid-vapor equilibrium was calculated by using the Soave–Redlich–Kwong EoS (SRK) (15), which shows a good agreement with the literature data (16). (iii) CO_2 liquid density was evaluated according to the API method (17), and gas density was calculated from the SRK EoS (15). (iv) The electrical power supplied to the compressors was evaluated at constant entropy by using the enthalpy of the fluid upstream and downstream in the equipment. The adiabatic efficiency was fixed at 75%. (v) The electrical power supplied to the pumps was evaluated according to the relationship used for liquids (18). The efficiency was fixed at 75%.

In each process alternative, the following set of operating conditions was adopted: (i) Extraction temperature at 80°C—during extraction, higher solubilities were required, and, thus, according to Figure 1, a high temperature value was chosen. Similarly to the hexane process (7), temperatures over 80°C were avoided, because they can lower the quality of soybean oil. (ii) Separation temperature at 20°C—this temperature corresponds to a low soybean oil solubility in SC-CO_2 at any pressure. (iii) The separation pressure was fixed at 55 bar for A and B, starting from the estimation developed in a previous study (19). In process C, pressure in the separator is equal to the one in the extractor minus the pressure drop due to the flow of SC-CO_2 in the equipment. The pressure drop was set at 0.5 bar.

The three process schemes are shown in Figures 2–4. Plant A (Fig. 2) has one extractor (EXT-1) and one separator (S-1). The pressure reduction is obtained by two valves, and a part of the Joule Thomson effect is recovered by heat exchanger E-1. Downstream to the separator, the CO_2 stream is condensed and subcooled to avoid cavitation (E-2), and then it is pumped up to the extractor pressure. At last, in heat exchanger E-3, the temperature is increased up to the value set for the extractor. An auxiliary cooling circuit (K-1, E-4, valve, E-2) is necessary to obtain a stream that can condense the CO_2 stream.

In alternative B (Fig. 3), CO_2 is recovered as a gas, and some compressors are required to increase the pressure of the recycled solvent; cooling units are inserted to improve the compression efficiency. The number of compressors is determined by the maximum allowable CO_2 temperature at the outlet of each compressor, i.e., 80°C.

Process C is shown in Figure 4. It is organized to obtain the oil recovery in an isobaric process. The CO_2 stream is cooled by using water and a cooling circuit in series, CO_2 is then pumped (P-1) and heated (E-3).

The utilities required in all schemes are electric power, cooling and heating fluids. The heating fluid in all schemes is hot water, obtained by burning methane in a boiler at 90%

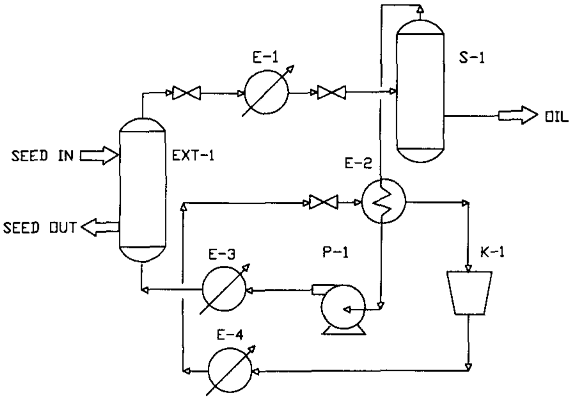

FIG. 2. Process flow diagram for scheme A. EXT-1, extractor; S-1, separator; P-1, high pressure pump; E-1, CO_2 heater; E-2, CO_2 condenser; E-3, CO_2 heater; K-1, compressor cooling medium, and E-4, cooler cooling medium.

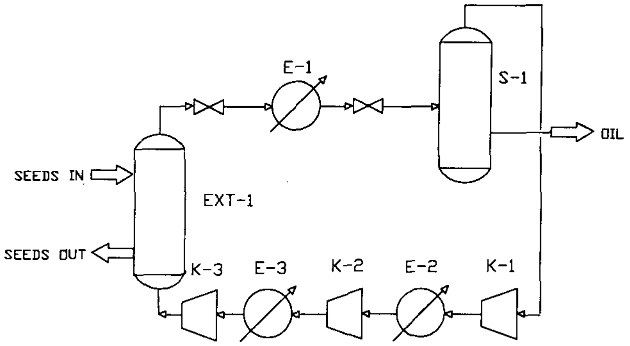

FIG. 3. Process flow diagram for scheme B. Abbreviations as in Figure 2, except E-2, E-3, CO_2 coolers; K-1, K-2, K-3, CO_2 compressors.

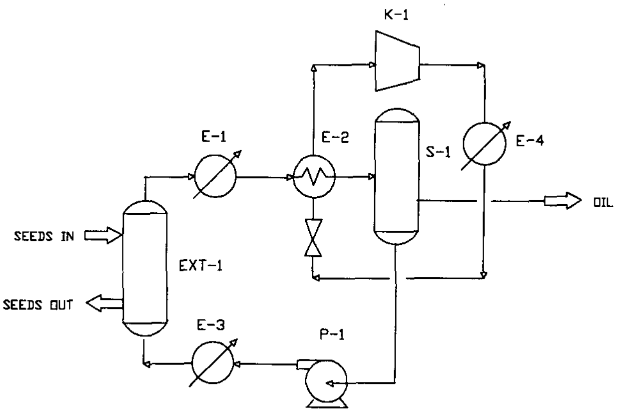

FIG. 4. Process flow diagram for scheme C. Abbreviations as in Figure 2, except for P-1, recycle pump; E-1, E-2, CO_2 coolers; E-4, cooler cooling medium.

of thermal efficiency. Cooling is carried out by water for temperatures above 35°C, and by a cooling circuit filled by freon for lower temperatures.

RESULTS AND DISCUSSION

The simulation was performed at various extraction pressures. Table 1 shows the material balance (CO_2 flow rate) and the duties of each equipment unit for the analyzed alternatives. Table 2 summarizes the overall consumptions. These are divided into electric power and thermal energy used to cool and to heat the process streams.

Because the aim of this work was to make an economical comparison of plant consumptions, it was necessary to indicate an economical equivalence for the energies involved. Therefore, the results of Table 2 were processed by supposing the following cost index in arbitrary units (AU) per kW: fuel, 1; electric power, 4.6; and cooling water, 0.0008.

These indexes were calculated on the basis of 1993 costs for a medium-large factory in Italy. The cost of cooling water included pumping, chemicals consumption, make-up water and the use of a cooling tower.

On this basis, the operating costs data have been obtained for alternatives A, B and C. In Figure 5, these costs are reported as a function of the extractor pressure. All costs fell with a decrease of the pressure in the extractor. This is not a trivial result; one would expect that the operating costs increase as a consequence of higher pumping costs. On the contrary, the decrease in CO_2 flow rate, caused by the higher solubilities of soybean oil at higher pressures, induced a lower cost despite the increase of the specific consumption of CO_2.

The costs of alternative C were evaluated by starting from an extractor pressure of 400 bar. At lower pressures it is not possible to have any isobaric precipitation of the soybean oil (see the solubility diagram in Fig. 1). Whereas A and B show similar trends and absolute values of the costs, alternative C seemed more attractive.

Costs evaluated for alternatives A, B and C were compared to those of extraction and purification of soybean oil in a conventional hexane extraction plant. It is known from the literature (7) that, for this kind of extraction, 123 kW of electrical power and 1155 kW of thermal energy are required for each ton of oil product. Adopting the cost index, the resulting cost is about 1950 AU/ton, which is significantly lower than those proposed in Figure 5. Thus, the operating costs of the proposed process scheme are not competitive with the traditional extraction process. But, the SC-CO_2 processes can be further improved by reducing the use of energy by integrating a heat exchanger network. This procedure can minimize the external energy demand for the plants.

Heat transfer optimization methods for generic processes have been described by several authors. Particularly, Linhoff *et al.* (8) developed a technique based on the pinch point concept. This technique is based on simple rules that allow the identification of the hot and cold streams to be coupled. Moreover, the authors (8) demonstrated that, in a heat exchange network, the minimum external energy requirement is achieved when there is no temperature difference between hot and cold streams, i.e., the pinch point has been obtained. Therefore, the pinch point represents the limit condition at which the required heat transfer can be obtained with an infinite exchange surface. For practical uses, a minimum temperature difference between the hot and the cold stream is required.

TABLE 1

Energy Balances

Extraction pressure bar	CO_2 flowrate (T/h)	Duty E-1 (kW)	Duty E-2 (kW)	Duty E-3 (kW)	Duty E-4 (kW)	Duty P-1 (kW)[a]	Duty K-1 (kW)[a]
Process scheme A							
300	163.4	3194	-8310	3410	-10037	1706	1727
400	72.5	1653	-3737	1019	-4514	1065	777
500	46.7	1072	-2371	415	-2864	884	493
600	33.0	763	-1676	148	-2024	765	348
Process scheme B							
300	163.4	3209	-7340	—	1850	2281	—
400	72.5	1595	-2140	-1613	779	573	806
500	46.7	1073	-1716	-965	529	445	634
600	33.0	763	-1319	-723	374	371	534
Process scheme C							
400	282.7	-7029	-1405	8424	-1699	10	294
500	114.9	-2718	-542	3256	-656	4	114
600	66.5	-1523	-304	1825	-368	2	64

[a] Evaluated at an adiabatic efficiency of 75%.

We fixed the minimum temperature difference between heating and cooling streams at 10°C.

In alternative A (Fig. 2), three process streams have to be warmed—the solution at the exit of the extractor (cold stream 1, ST1), the cooling fluid entering the vaporizer (ST2) and the circulating solvent to be vaporized and superheated (ST3). The process also contains two streams to be cooled—the solvent to be liquified (hot stream 1, H1) and the cooling stream at the exit of the compressor (H2). Streams ST2 and H1 are already coupled in the CO_2 condenser. The other couplings are affected by the temperature of the cooling medium at the exit of the compressor. Referring to Figure 6, two possible pinch points can thus be obtained, the first one in exchanger E-2 and the second one in exchanger E-1. Because the cooling stream has always been hypothesized at saturation conditions, the pinch points determine the suction and discharge pressures corresponding to minimum energy requirements. With respect to the pinch point, if the minimum temperature difference of 10°C is fixed, a minimum temperature of 90°C is required at the compressor outlet of the cooling circuit, K-1. Thus, as shown in Figure 6, the freon can be cooled in heat exchangers E-1, E-3 and E-4. This alternative, derived from scheme A, has been called A.1.

The same procedure can be applied to scheme B, producing alternative B.1, which is shown in Figure 7. The stream to be warmed (H1) is the SC solution at the extractor outlet after the first pressure reduction. The streams to be cooled are those at the exit of the CO_2 compressor stages (ST1, ST2). By coupling those streams and imposing the temperature difference of 10°C between the two streams, it is possible to recover heat from the solution containing the soybean oil up to 70°C. Further

TABLE 2

External Duty Requirements

Extraction pressure bar	Hot utilities (kW)	Cold utilities (kW)	Electric Power (kW)
Process scheme A			
300	6604	-10037	3433
400	2672	-4514	1842
500	1487	-2864	1377
600	911	-2024	1113
Process scheme B			
300	3209	-7340	4131
400	1595	-3753	2158
500	1073	-2681	1608
600	763	-2042	1279
Process scheme C			
400	8424	-8738	304
500	3356	-3374	118
600	1825	-1891	66

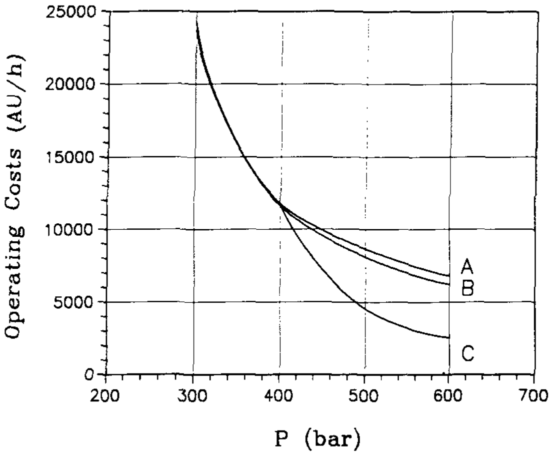

FIG. 5. Operating cost in arbitrary units (AU) as a function of extractor pressure (P). Scheme A, scheme B and scheme C are represented by curves A, B and C, respectively.

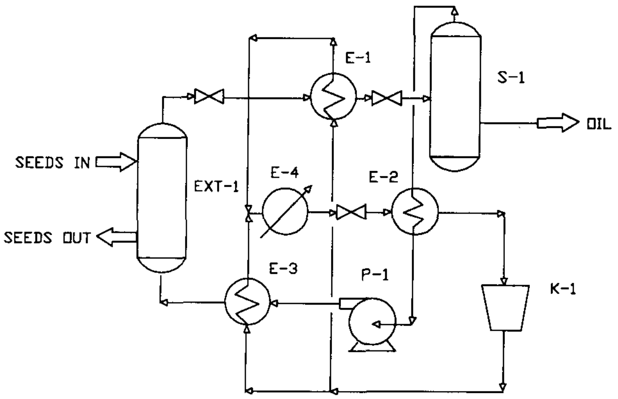

FIG. 6. Process flow diagram for scheme A.1. Abbreviations as in Figure 2.

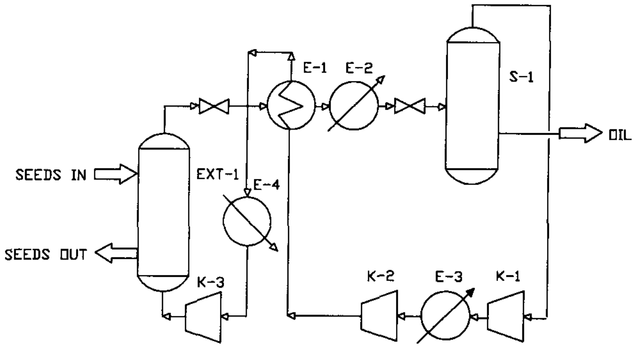

FIG. 7. Process flow diagram for scheme B.1. EXT-1, extractor; S-1, separator; E-1, E-2, CO$_2$ heater; E-3, E-4, CO$_2$ cooler; K-1, K-2, K-3, CO$_2$ compressors.

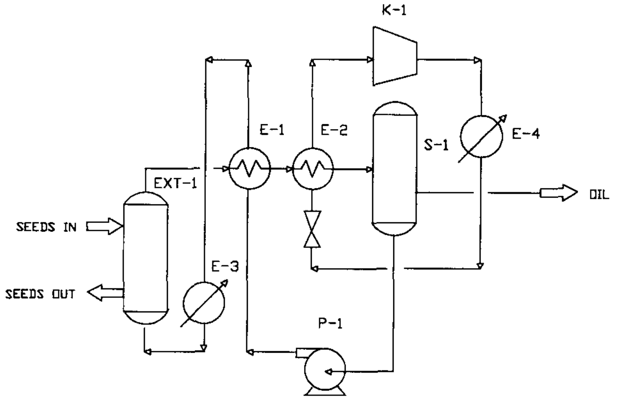

FIG. 8. Process flow diagram for scheme C.1. EXT-1, extractor; S-1, separator; P-1, recycle pump; E-1, E-2, CO$_2$ coolers; E-3, CO$_2$ heater; E-4, cooler cooling medium; K-1, compressor cooling medium.

heating requires the use of an external fluid. In a similar manner, the compressed CO$_2$ has to be further cooled by using an external fluid. With reference to Figure 7, the pinch point can be reached in the E-1 exchanger. This solution corresponds to elimination of exchangers E-2 and E-4.

Applying the optimization procedures to scheme C, alternative C.1 was generated (Fig. 8). In this scheme, the streams to be cooled are the one at the outlet of the extractor solution (H1) and the compressor outlet (H2). The streams to be heated are those at the separator exit (ST1) and the SC-CO$_2$ after the pump (ST2). It is easy to couple streams H1 and ST1. In this case, a pinch point can be obtained in exchanger E-1 (Fig. 8); this choice simplifies the network, limiting it to one single exchanger (E-1). The required minimum temperature difference results in a further heating of stream ST2 and in a final cooling of stream H1. Stream H2 is not sufficient to satisfy the heat requirements of E-3; thus, we preferred to reduce the number of heat exchangers rather than saving a little energy.

The energy requirements resulting from these new plant arrangements are reported in Table 3 as a function of the extractor pressure. Comparison of Tables 2 and 3 shows that the process arrangement after the optimization study has strongly reduced the heat and cooling requirements in all cases. In alternative A.1, no external duties are required.

Operating costs of alternatives A.1, B.1, and C.1 are reported in Figure 9 as a function of the extraction

TABLE 3

External Duty Requirements for Networked Heat Exchangers

Extraction pressure bar	Hot utilities (kW)	Cold utilities (kW)	Electric Power (kW)
Process scheme A			
300	—	−3433	3433
400	—	−1841	1842
500	—	−1377	1377
600	—	−1113	1113
Process scheme B1			
300	435	−4566	4131
400	906	−3064	2158
500	430	−2038	1608
600	309	−1588	1279
Process scheme C1			
400	1611	−1915	304
500	623	−741	118
600	350	−416	66

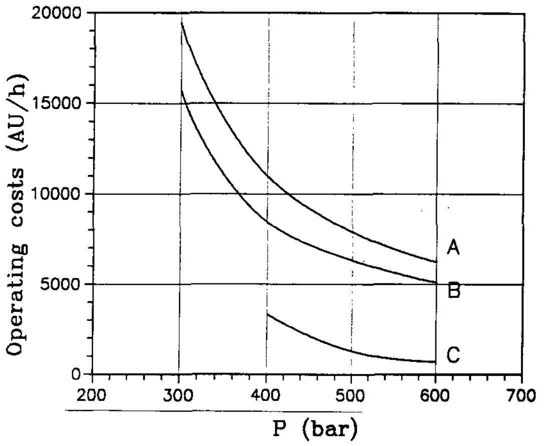

FIG. 9. Operating cost in arbitrary units (AU) as a function of extractor pressure (P). A, scheme A.1, B, scheme B.1, C, scheme C.1.

pressure. These curves show a similar trend to the one reported in Figure 5, but costs are greatly reduced. Particularly, the operating costs obtained in alternative C.1 were comparable with those for hexane extraction.

The analysis of operating costs is, of course, not sufficient to identify the optimum process; a plant cost analysis is also needed. This aspect is outside the scope of this work because it would require an extensive analysis of the costs linked to the main equipment used. Moreover, it is readily apparent that the traditional hexane technique requires less technology. Nevertheless, it is possible to perform a comparative analysis of plant costs related to the process schemes discussed.

Because the operating costs of the optimized schemes (A.1, B.1, C.1) are lower, it is interesting to compare their investment costs with the corresponding base schemes (A, B, C). The improved alternatives use an optimized heat transfer network but require more complex connections and, in some cases, more equipment. Therefore, one would expect that these plants are more expensive in respect to the base schemes. On the contrary, the optimized solution requires a lower overall power for heating and cooling, as shown by comparing the data in Tables 2 and 3. As a consequence, smaller boilers and coolers are required, and thus, a reduction of the heat transfer surfaces is obtained. This conclusion is supported by most of the cost analyses that compare unoptimized plants with those in which a heat exchanger network has been integrated (8). Therefore, alternatives A.1, B.1 and C.1 show more favorable plant and operating costs as compared to solutions A, B and C.

This analysis of different SC-CO_2 processes in soybean oil extraction has pointed out the possibility of a large reduction of operating costs by using techniques that integrate a heat transfer network. The best scheme analyzed (C.1) showed operating costs that are comparable to the conventional hexane extraction process.

Plant costs form the main disadvantage of the SC-CO_2 process as compared to hexane extraction units. Nevertheless, the continuous advances in SC-CO_2 technology will reduce this gap. Possible future changes in the purity standards of soybean oil could further encourage the adoption of SC-CO_2 technology for its processing.

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