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Estimation of the Process Parameter for High-Pressure (supercritical fluid) Carbon Dioxide Extraction of Natural Products

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Abstract

The objectives of this work were to find a useful concept for the design of high-pressure extraction (HPE) plants and to carry out a parameter analysis of various influences on construction and design. To evaluate the influence of each parameter on the process better, the parameters were subdivided into five groups. Experiments were made to determine the solubility and mass transfer of neutral products in CO_2. These results were tested with models in order to establish the possibility of a mathematical description of HPE processes.

INTRODUCTION

Since high-pressure extraction (HPE) is important for the production of natural extracts (for example, decaffeination of green coffee beans, production of hop extracts), useful concepts for plant design can reduce the economic risks of a new process.

The numerous parameters which influence the process and the design of a plant must be evaluated by many experiments on a laboratory plant. This paper tries to reduce this extensive experimental work by a subdivision of the main problems (*1*). In an extraction experiment, all parameters act together and it is difficult to recognize the influence of one parameter to the process.

The main problem areas are:

Nonalterable material specific basic data
Thermodynamic conditions in the extraction and separation steps
Mass transfer
High-pressure extraction process in the *T*,*s* diagram
Special problems in the separation step

DESCRIPTION OF THE EXPERIMENTAL PLANT

Figure 1 shows a general flow sheet of a high-pressure extraction plant as used in our laboratory. The experimental plant consists of the following main items: extraction vessel, separation vessel, liquid gas storage vessel.

The cycle of the solvent CO_2 is as follows: A pump draws off liquid CO_2 from the storage vessel (1) and compresses it to extraction pressure (2). Then the CO_2 is heated up to extraction temperature by a heat exchanger. In the extraction vessel, the highly compressed supercritical or liquified gas dissolves the soluble substances from the raw material. In the throttle

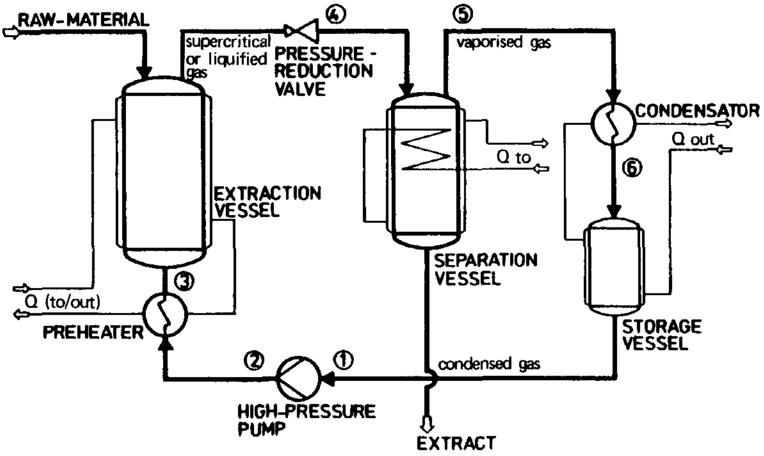

FIG. 1. Flow sheet of the experimental plant.

section (4) the temperature and/or pressure of the loaded solvent are changed. Usually, the pressure is reduced from 150 to about 40–60 bar.

The remaining liquid CO_2 is evaporated by means of another heat exchanger. At separation conditions the solubility of the extract is completely depressed, the solute and the solvent are separated, and the extract can be drained off through a valve. The nearly extract-free gaseous CO_2 is completely liquified in a condenser (6) and fed back into the storage vessel, completing the cycle.

It is also possible to use a compressor instead of a pump to increase the pressure. In this case the evaporated CO_2 gas flows directly to the compressor, and no condenser or storage vessel is needed. However, investment costs and energy demand for the compressor are considerably higher.

BASIC DATA

The first main parameters needed for a HPE process are properties of the raw material and the required production rate as well as the concentration of the extractable substances in the feed, kind of raw material for extraction, specific volume of the prepared feed, and the mode of operation. For extraction of natural substances, usually only the preparation of the raw material and the specific volume can be varied to some extent. For example, it is possible to change the specific volume by milling or pelletizing the raw material. This parameter influences mainly the volume of the extraction and separation vessels.

THERMODYNAMIC CONDITIONS

The next parameter to be considered is the estimation of the thermodynamic conditions in the extraction and separation steps. In the range at the critical point or in the supercritical region the influence of pressure, temperature, and density of the solvent on the distribution equilibrium are much more important than in conventional extraction. Therefore, it is possible to vary the solvent properties of a compressed gas by changing the pressure and temperature. In the extraction step it is desirable to reach a high solubility and therefore a low solvent consumption. In the separation step a very low concentration of the extract in the solvent is required to guarantee a good regeneration of the solvent.

Useful models for the description of the experimental equilibrium concentrations are necessary to enable a fast optimization of this parameter. The well-known models in the literature are based on three equation systems:

Empirical equations of state
Half-empirical equations of state
Derivations from the association laws and/or from the entropies of the components

Half-empirical equations of state are used to fit binary systems, and thermodynamic data of the solute and the solvent have to be known. For systems with more than two components, the mathematical solution is very difficult. A useful equation of state for the description of simple binary systems is the Peng-Robinson (*2*) equation. This equation is applicable for large pressure and temperature ranges.

For unknown solvent data, derivation from the association laws is used to adjust experimental results. The most popular equation of this type was published by Chrastil (*3*).

Figure 2 shows the correspondence of measured and, according to Chrastil, calculated equilibrium data for rapeseed oil in CO_2. The dominating influence of gas density on CO_2 loading is significant. This

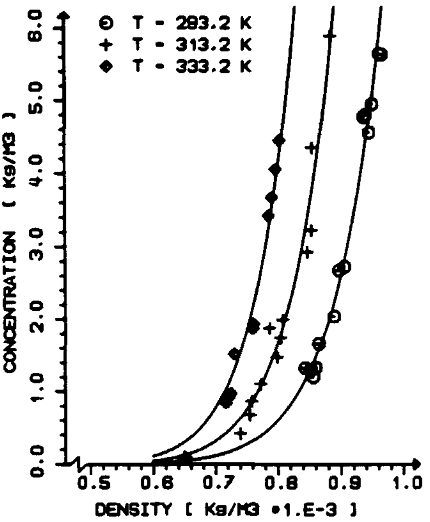

FIG. 2. Equilibrium of rapeseed oil in CO_2.

equation is very useful to describe the equilibrium distribution of natural substances in compressed gases.

MASS TRANSFER

The objective of this investigation is to determine the optimum flow rate. The energy consumption is linearly dependent on the mass flow rate of the solvent in any case, involving complete solvent recirculation.

In order to study the mass-transfer behavior, several experiments were made to measure the loading of the solvent as a function of extraction time and the height of the bed. All experiments were made in the same laboratory plant. The flow sheet of this plant is shown in Fig. 1.

Flaked rapeseed and milled press cake of rapeseed were used as feed. To exclude the influence of different feed properties, preparation of the raw material was done in the same way for all experiments.

The same thermodynamic conditions were used for all mass transfer investigations:

Extraction pressure 290 bar, extraction temperature 40°C
Separation pressure 50 bar, separation temperature 25°C

Some results of these measurements are shown in Figs. 3 and 4.

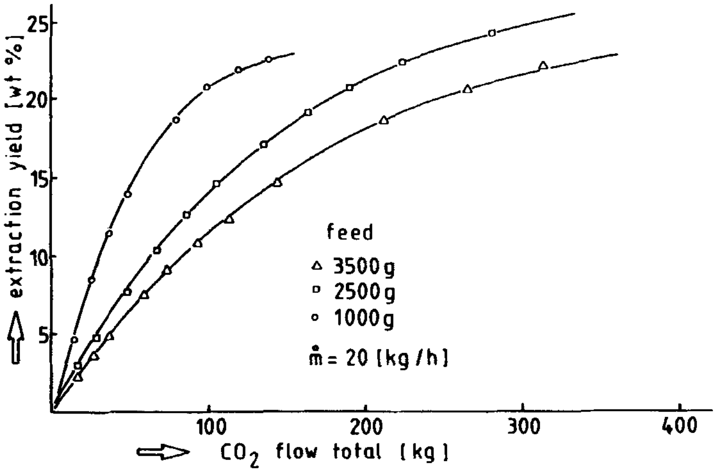

FIG. 3. Extraction of rapeseed oil as a function of total CO_2 throughput.

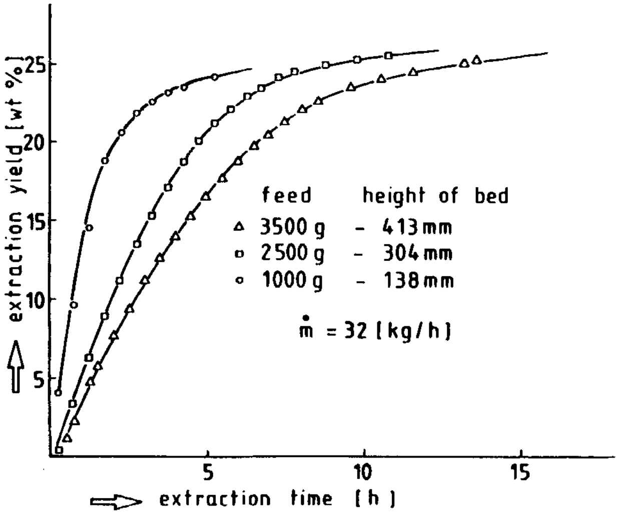

FIG. 4. Extraction yield as a function of extraction time.

Because it is not possible to get solid samples out of the extraction vessel, it is necessary to make separate experiments for each height. This means that it is possible to determine the concentration distribution versus time in one experiment, but it is not possible to determine the concentration distribution versus the height of the bed at the same time. The extraction time is very long because of the small solvent velocity in the extractor.

At the beginning of an extraction process or at low absolute CO_2 throughput, high solvent loadings are obtained because of the great concentration differences as shown in Fig. 5.

Extraction in the lower layer is finished after a flow of 120 kg CO_2. Then the mass-transfer area moves to the upper layers. The mass-transfer area is that part of the extractor where the concentration gradient is high enough to get an economical mass transfer.

Extraction is complete when the boundary of the mass-transfer area reaches the top of the extractor. Knowledge of the motion and expansion of the mass-transfer area is very important for optimization of mass transfer.

For low solvent throughput the mass-transfer area is much smaller than the height of the bed. Therefore, the mass-transfer area is much smaller than the height of the extractor and the extraction time increases. For high solvent throughput the mass-transfer area is larger than the

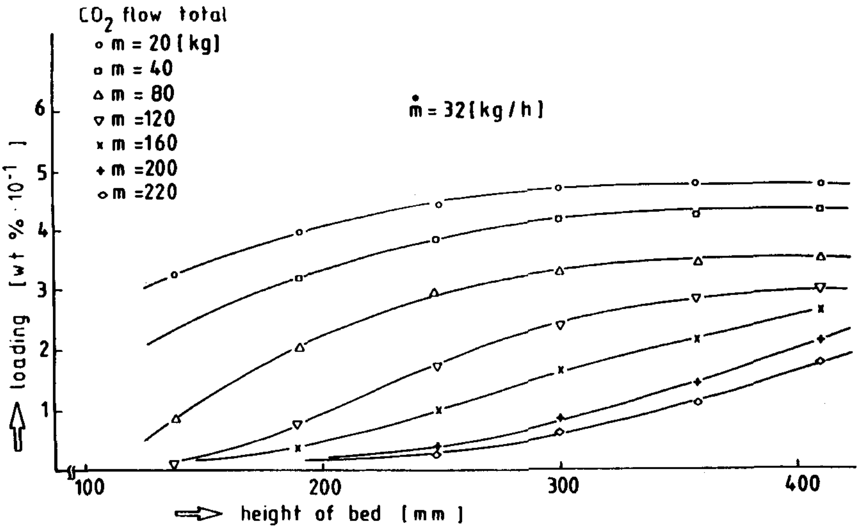

FIG. 5. Concentration distribution versus height of bed.

height of the bed, the solvent is not completely loaded, and process costs increase.

Figures 6 and 7 show the extraction yield versus the height of the bed and the extraction time. The logarithmic plot of the extraction time in Fig. 7 shows the motion of the mass-transfer area from the bottom to the top of the extractor. A three-dimensional projection of Fig. 7 in Fig. 6 gives a three-dimensional dependence of the extraction yield on extraction time and the height of the bed. These relations are important for modeling the mass transfer.

MODELING OF MASS TRANSFER

The most popular models for describing mass transfer in high-pressure extraction were published by Brunner and King (*4*, *5*).

Because of the analogy of high-pressure extraction and drying processes, we transformed a drying model into a high-pressure extraction model.

There are two main relations between drying and HPE: the solubility equilibrium depends on the thermodynamic properties of the solvent and the mass transfer is divided into two sections. In the first section the substances to be extracted are removed from the particle surfaces just as in the first drying section. In the second part mass transfer is controlled

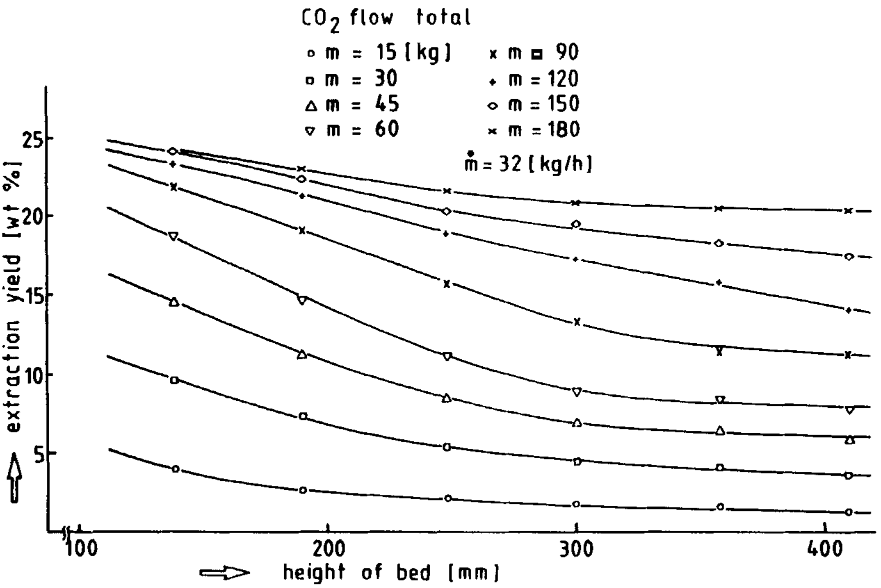

FIG. 6. Extraction yield as a function of the height of bed for different total CO_2 throughputs.

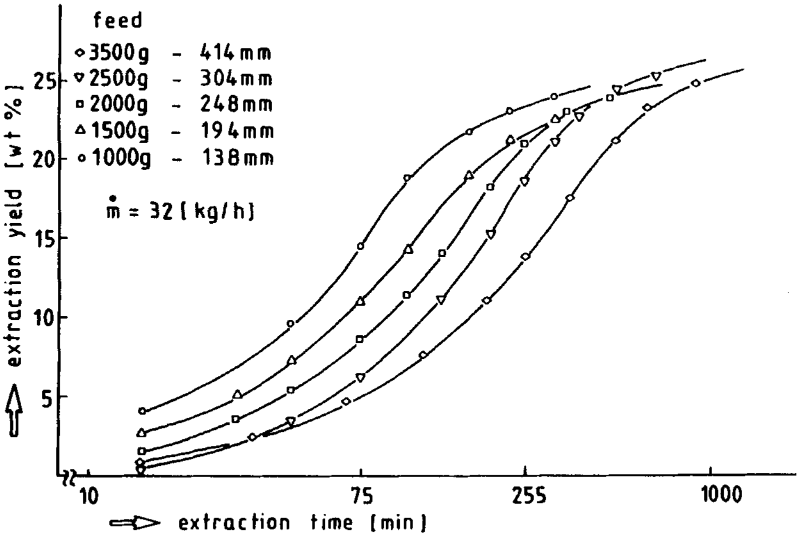

FIG. 7. Extraction yield as a function of extraction time for five feed amounts or height of bed.

by diffusion or other properties which reduce the mass-transfer velocity (for example, adsorption bondings). A computer program was established to calculate the mass transfer by means of the transformed drying model. The results of the calculation show a good correspondence to the experimental results of Fig. 8.

THE HPE PROCESS CYCLE IN THE *T,s* DIAGRAM

The fourth main parameter is the estimation of the best process cycle in the *T,s* diagram. Because of the various possibilities offered in the supercritical region, it is difficult to find the process with the lowest energy consumption as shown in Fig. 9. To determine the best process cycle, we used a computer program that enabled us to calculate several process variations.

About 250 processes were evaluated with this program. The program uses the thermodynamic conditions in the extraction and separation steps as starting points to give the two limits of the process in the *T,s*

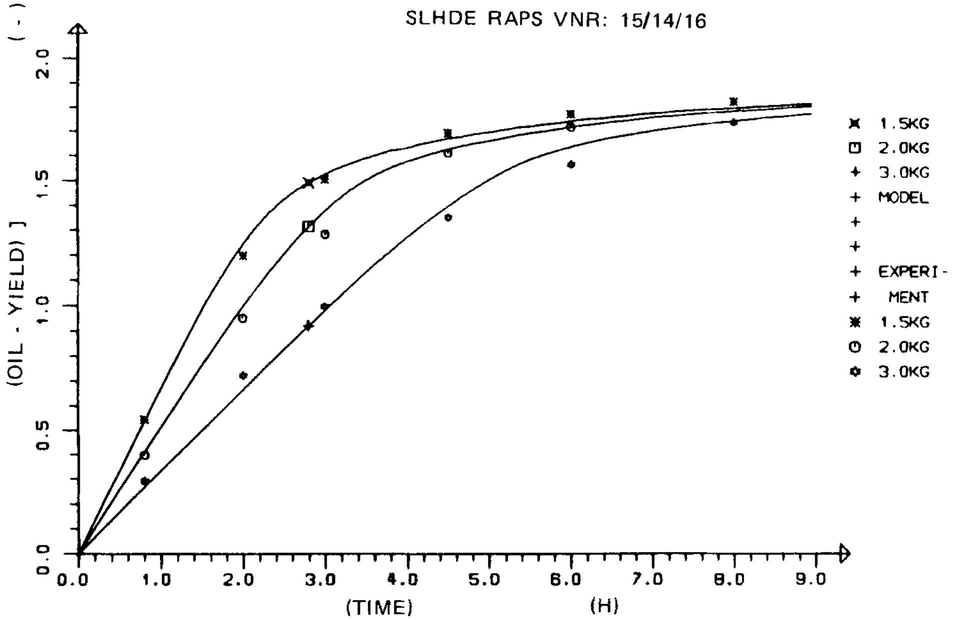

FIG. 8. Extraction of rapeseed based on the drying model.

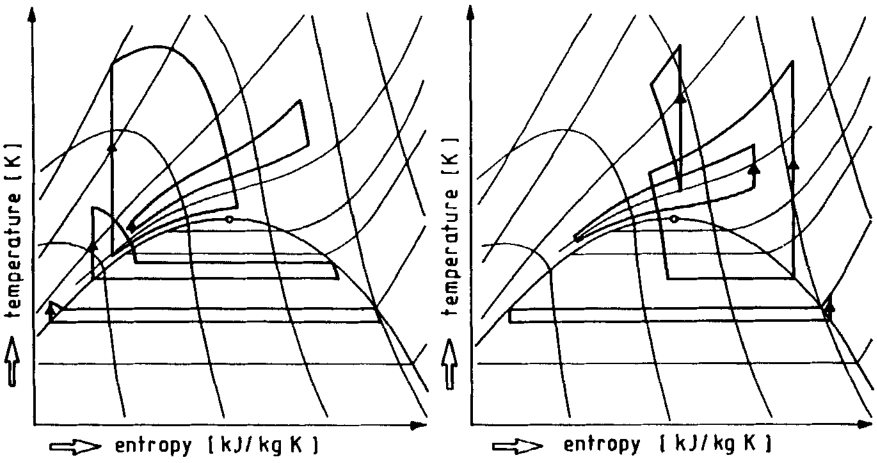

FIG. 9. Different possibilities of a process cycle in the HPE extraction.

diagram. The program then calculates the pump and compressor processes. The thermodynamic conditions of CO_2 in each stage of the process are calculated from the JUPAC equation of state. The two types of energy required during the process are electric energy for all mechanical equipment, such as pump, compressor, and refrigerator, which is needed for condensing the gaseous CO_2, and thermal energy for the preheater.

The energy costs are calculated for 1000 kg CO_2 passing through the process cycle in the *T,s* diagram. The costs for the two types of energy are 0.055 US$ for 1 kWh electric energy and 0.025 US$ for 1 kg of steam with a thermal energy of 2150 kJ/kg.

Analysis of the Pump Processes

The main energy consumers of pump processes are the refrigerator for condensing the gaseous CO_2, the circulation pump, and the preheater between the pump and the extractor. The electric power consumption of the refrigerator depends only on the separation conditions. The cost for the refrigerator varies between 0.1 US$ for a separation pressure of 60 bar and 1.2 US$ for a separation pressure of 30 bar.

There is only a small rise in temperature in the pump for low extraction pressures. Therefore, the preheater needs more energy. When the temperature of the solvent at the delivery side of the pump corresponds to the desired temperature in the extractor, the energy demand is minimized. The area of minimum energy costs is situated between 150 and 300 bar, and depends on the extraction temperature.

For low separation pressures, as shown in the three-dimensional curve of Fig. 10, the cost level is very high. This is due to high energy consumption by the refrigerator. Minimum process costs are achieved for a separation pressure of about 60 bar and an extraction pressure of 200 bar (about 0.45 US\$/t CO_2).

Analysis of the Compressor Process

Plotting of a three-dimensional cost curve is not possible because higher extraction pressures involves more than one compression step. The maximum compression ratio for one compression step is about 3.5.

The compressor accounts for nearly the entire energy consumption of the process. Compressor processes have a low energy consumption for low extraction and separation pressures. For a separation pressure of 30 to 40 bar and up to 300 bar extraction pressure, the compressor processes need less energy than the pump processes because of the high costs for the refrigerator.

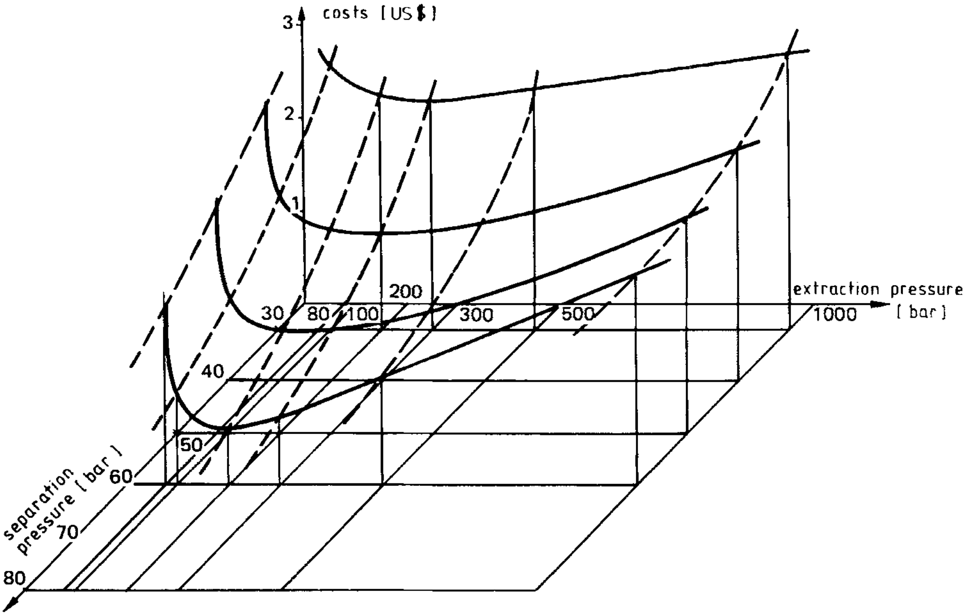

FIG. 10. Process costs as a function of extraction and separation pressures for a constant extraction temperature (40°C).

PROBLEMS OCCURRING IN THE SEPARATION STEP

The next group of problems refers to the separation step. As mentioned before, energy costs are low if the separation pressure is about 50 to 65 bar. But with higher pressure and temperature the concentration of extracts in the CO_2 phase in the separation vessel increases. Extracts which contain essential oils and waxes can be fractionated with multistage separation (Fig. 11). In the first separation stage, waxes are enriched, and in the second one, which takes place at lower pressure and temperature, a concentrated extract of essential oil is obtained.

Significant problems arise when highly volatile substances at low concentrations must be separated. To reach a quantitatively high separation in one step, a very low separation pressure and temperature is necessary. This involves high energy consumption and the risk that solid material (e.g., ice) will block the pipes and the valves.

Separation in a multistage distillation column may be a solution to these problems. Such columns can operate with a temperature above the freezing point of water. The degree of purification is determined by the height of the column and the reflux.

Another field of application is the regeneration of activated carbons.

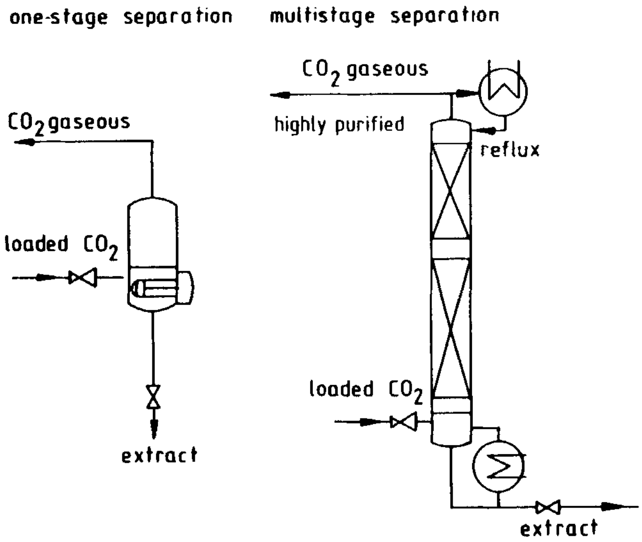

FIG. 11. Two examples for separation processes (6).

The degree of regeneration depends on the purity of the CO_2 after separation.

SUMMARY

Finally, we discuss the influence of the main parameters on the various parts of the plant. Process design data, such as plant capacity, extraction yield, specific volume of the feed, preparation of the feed, mode of operation, etc., mainly influence the volume of the extraction and separation vessels.

The thermodynamic conditions determined give the temperatures and pressures in all steps of the process, taking into consideration the desired quality of the product.

The optimized mass transfer determines the mass flow of the solvent. The HPE process in the *T,s* diagram determines the change of state in the process steps and therefore the energy level. A way of determining the influence of the main parameters on the economy of the process is to combine the results of the mass transfer investigations with the energy demand of the process cycle. Determining the extraction yield curves for a defined feed amount and for different solvent flow rates versus extraction time and total throughput of CO_2 enables the extraction time and CO_2 mass flow required for a desired extraction efficiency to be obtained.

By multiplying the investment costs of the plant for about 1 h by the extraction time for a desired extraction efficiency and for a constant specific CO_2 mass flow rate, one point of the investment cost curve is evaluated. Then, a fixed cost curve can be plotted for several specific CO_2 flow rates. The same procedure can be used for the evaluation of the operation costs.

For given thermodynamic conditions in the extraction and separation steps, one point of the operating costs curve can be evaluated by multiplying the costs for 1000 kg of CO_2 required for the process cycle by the total throughput of CO_2 required for the desired extraction efficiency.

The same can be done for several specific CO_2 flow rates. The operating costs curve can then be plotted. The addition of the investment costs curve and the operating costs curve yields an approximate answer for the process costs of the desired product.

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