Natural Essential Oils

Extraction Processes and Application to Some Major Oils

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The word natural essential oil means or covers all aromatic extracts from vegetable matter (flowers, leaves, branches, roots, gums, fruits) and extracts from animal secretion.

Several processes are used to obtain natural oils. These processes are developed in order to obtain the best aromatic substance to satisfy the needs of the perfumer and of the flavorist, in accordance with the worldwide legislation governing the use of these products.

"Essential oil" is a generic term and in fact may be

- *Concrete*—a fatty wax saturated with an aromatic substance
- *Absolute*—an alcohol-soluble liquid or semi-liquid oil saturated with an aromatic substance
- *Resinoid*—an alcohol or benzene direct distillation
- *Steam distilled oil*
- *CO_2 extracted oil*

METHODS OF EXTRACTION OF NATURAL ESSENTIAL OILS

Solvent Extraction

Production of Concrete

The static extraction vessel is filled with vegetable matter and covered with an organic solvent either hexane, benzene, toluene or other binary solvents. (See figure 1.)

The operation temperature varies with the solvent used and its boiling point (60 to 80°C). The duration of extraction and the number of possible successive extractions, i.e., how many times the vessel is filled with solvent, varies from one vegetable matter to another in general, and specifically according to the characteristics of the vegetable matter such as humidity or ripeness on a given day. This is why it has been said many times that the production of good natural oils is similar to good cooking.

After maceration the saturated solvent-containing aromatic substances is pumped to a "concentrator" and heated at the solvent boiling point. The solvent is recycled and the volume of the solution is reduced to one tenth. The product is then pumped into a vacuum "finishing concentrator." The product obtained after final concentration is the concrete, which resembles a fatty wax, more or less solid when at room temperature.

The concrete is rather liquid for lavender, lavandin, a little more viscous for beeswax and quite solid for clary sage. In addition to aromatic substances, the concretes contain wax and natural colorings. Most are easily stored at room temperature.

Transformation from Concrete to Absolute

In most cases solvent extracted products are used in an alcohol solution. Perfumers and flavorists usually require extracts that are com-

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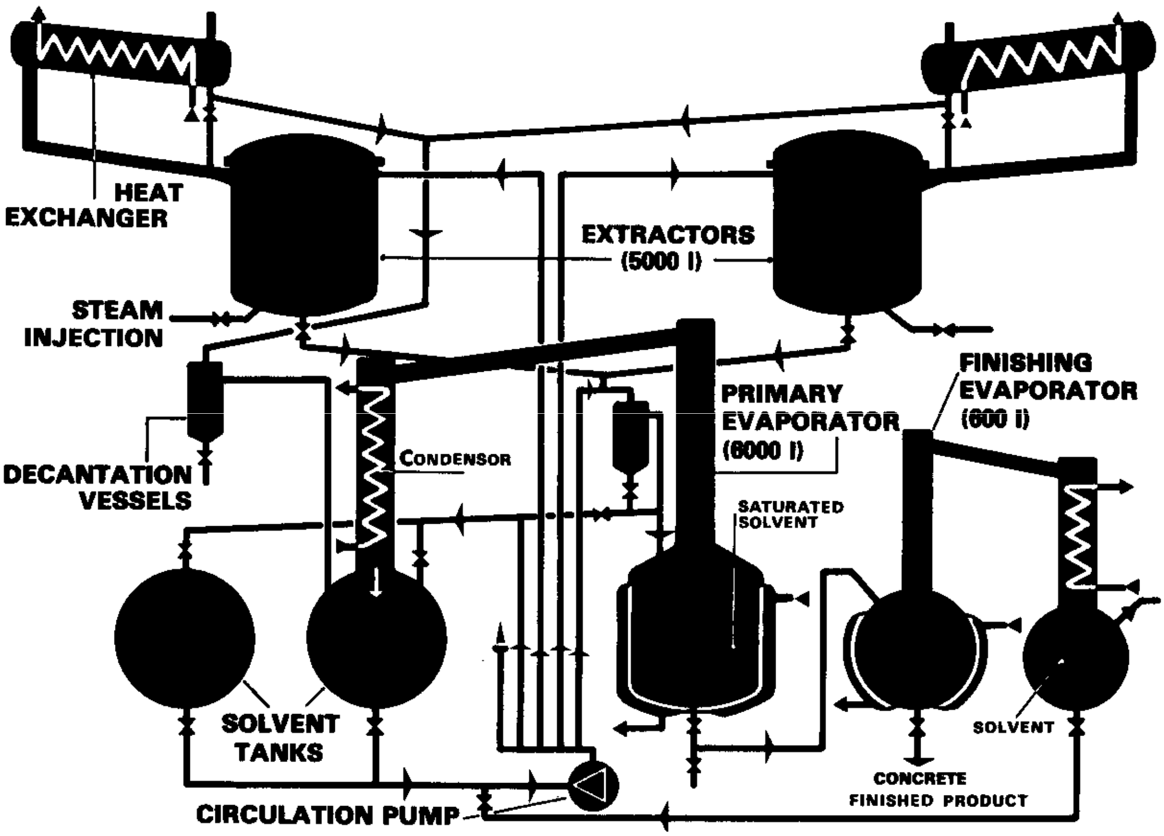
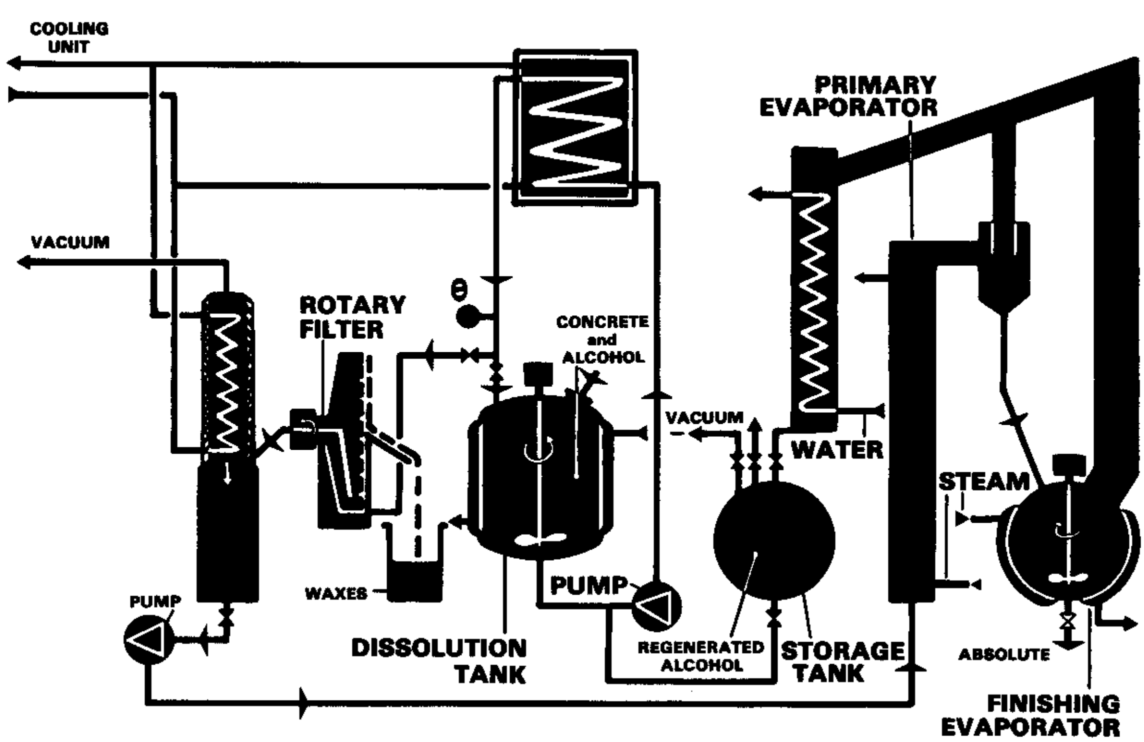


Figure 1. Solvent extraction unit

Figure 2. Transformation of concretes into absolutes



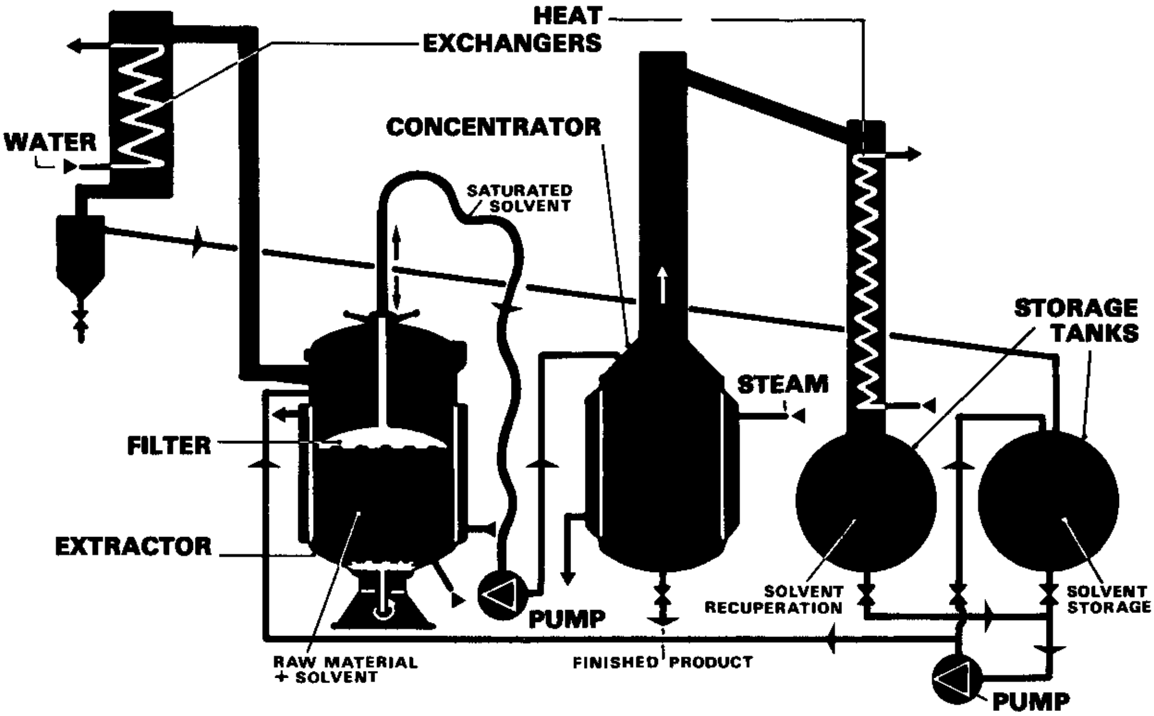
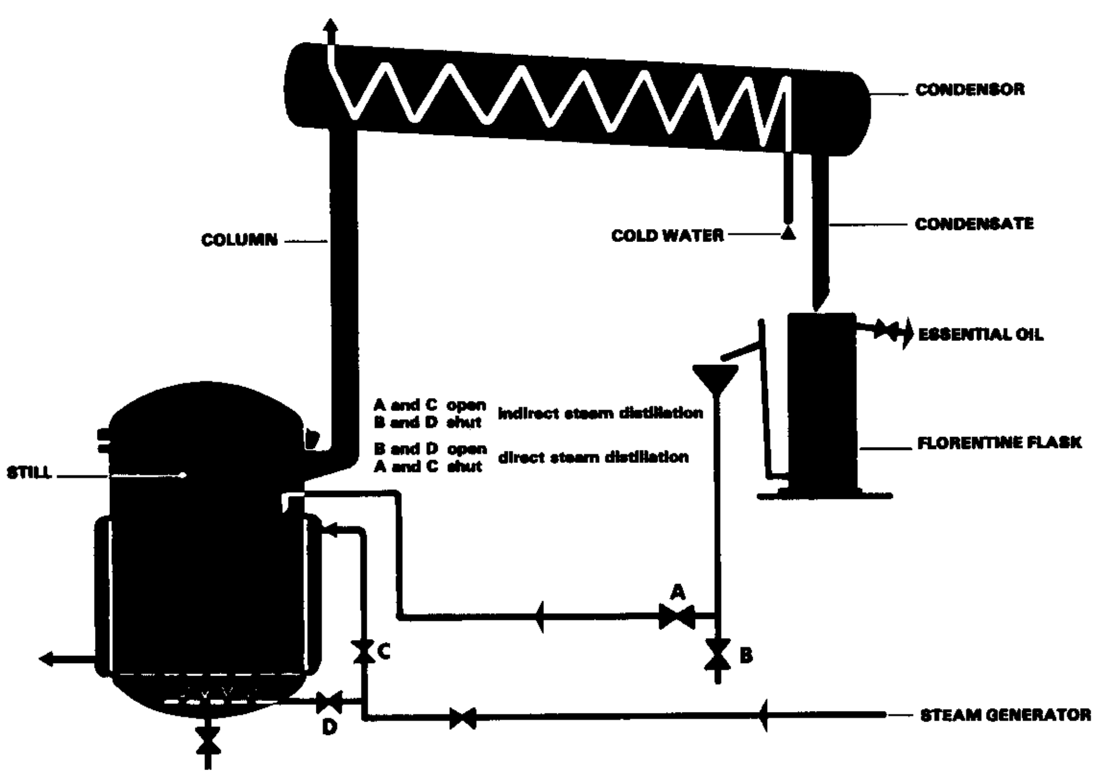


Figure 3. Resinoid extraction unit

Figure 4. Steam distillation diagram



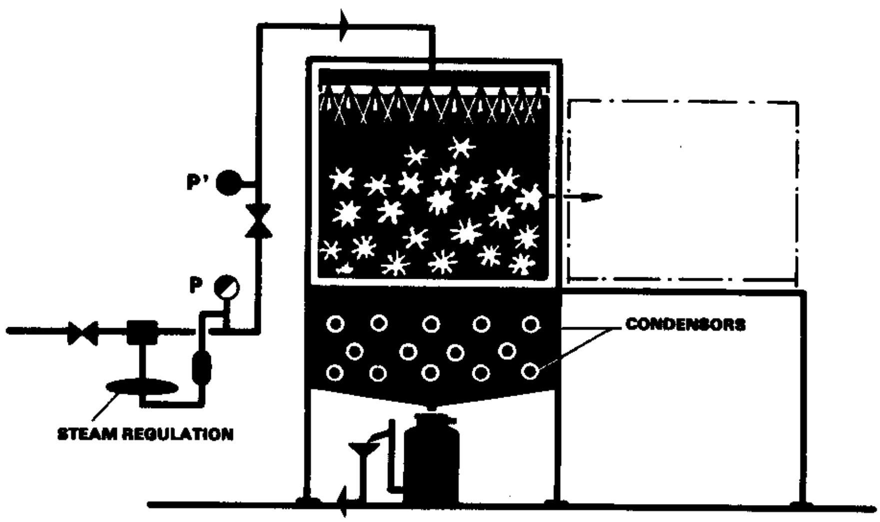


Figure 5. Hydrodiffusion diagram

pletely soluble in alcohol.

Waxes are not soluble in alcohol at low temperature (−1°C), therefore, a concrete is diluted in alcohol at 30 to 40°C and strongly agitated. When this alcohol solution is refrigerated at minus 5 to 10°C, waxes precipitate. Filtration is made through a rotary filter by adsorption. The obtained filtrate is vacuum concentrated and after alcohol elimination, the absolute remains. (See figure 2.) Absolutes are generally in liquid form though they may be viscous or "pasty."

Production of Resinoids

Resinoids are obtained in a floating filter extractor by filling the vessel with alcohol, chlorine solvents or even benzene, strongly agitating and then filtering. The filtrate is pumped into a concentrator where the solvent is evaporated. (See figure 3.) When no solvent remains, the obtained product is the so-called "resinoid." The solvent most frequently used is alcohol, but this may occasionally vary with the raw material processed.

Steam Distillation

Classic Steam Distillation

The "essence" or "distilled oil" is obtained by direct or indirect steam distillation as shown in figure 4.

For direct distillation, the vessel is filled with gum or vegetable matter. Steam is injected at the bottom, once saturated with aromatic oil particles, it is condensed in the refrigerator. The oil, being lighter than water, floats to the top in the Florentine flask and water is in the bottom.

For indirect distillation, a water suspension of the raw material is brought to boiling point; then the steam saturated with aromatic volatile substances is condensed in the refrigerator and oil is separated from water in the Florentine flask.

Most essences are liquid, but iris is not. They are more or less colorated and have a high percentage of volatiles.

Hydrodiffusion

In contrast to usual direct steam distillation, the steam enters from the top of the vessel. The resulting solution is condensed below the vessel and oil plus water are separated in the Florentine flask. (See figure 5.)

The main advantages of this method are in energy saving from reduced distillation time and therefore reduced steam consumption, as well as no hydrolysis because the vegetable matter is never in contact with water, only steam.

Hydrodiffusion is primarily used for seeds, but not for iris where the hydrolysis reaction is desirable, nor for gums that contain equipment-clogging solids.

Accelerated Distillation

This patented device (Aroma Process, 06 Mougins/France), shown in figure 6, accelerates distillation by rupturing the oil-containing plant cells through the grinder of a turbine.

Indirect heating by the walls gives a better

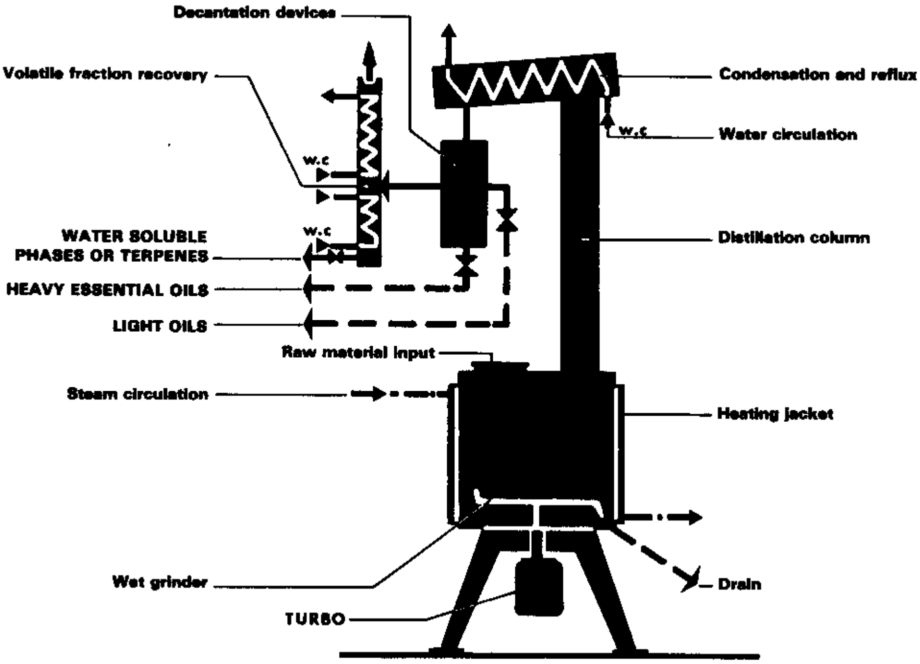
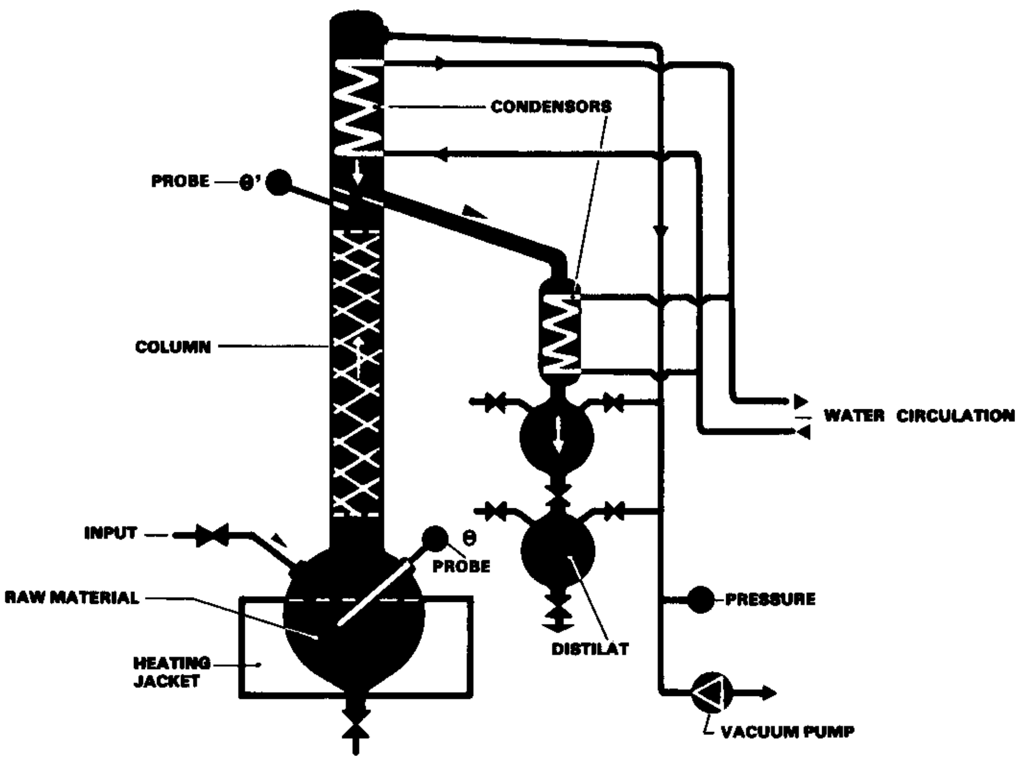


Figure 6. Accelerated hydro-distillation diagram

Figure 7. Vacuum distillation diagram



ratio of heat exchange without any possibility of having a "burnt" note in the solution. In addition, this process decreases distillation time and makes possible extraction of the most volatile notes in the saturated gas at the top of the condensor, which is not possible with the usual steam distillation process. The yields may also increase.

Special Selective Methods

Vacuum Distillation

In many cases the oil obtained either by solvent extraction or by steam distillation does not exactly fit the perfumer and/or the flavorist's needs. It is sometimes necessary either to eliminate certain constituents, for example, terpenes or heavy colorings, or to reinforce the percentage of major aromatic constituents such as irone, aldehydes, linalol, or cedrol.

Figure 7 shows a distillation column where according to their boiling point temperatures, various components can be isolated. The temperature gradually increases during the process in order to separate the volatiles first, then the other constituents. The better the vacuum is, the lower the distillation temperature which in turn saves the olfactive components of the product from degradation.

Molecular Distillation

Molecular or short-path distillation is used to obtain:

—colorless product
—more stable product because of the elimination of heavy constituents (acids, colorings)
—more delicate note because of the increase of the percentage of the aromatic parts of the oil

Because of the strong vacuum (from 10^{-3} to 10^{-6} PSI) the boiling point and extraction time are highly reduced, thus preventing the loss of some heat-sensitive notes in the oil.

The product to be processed is combined with a heavy and light solvent and then is passed through the short-path evaporator; the most volatile parts are condensed with light solvents on a so-called "finger" in the middle of the evaporator and then recuperated as a first distillate. (See figure 8.) The other parts are condensed on the walls of this first short-path evaporator and pumped into a second evaporator. There again, other parts of the oil are concentrated on the inner "finger" and recuperated as a second distillate. Residues and heavy solvent are condensed and recuperated in the residue tank.

We have developed a line of molecular distillation products called U.V. for Ultra Vacuum. Newly developed are essence Vetyver UV, Olibanum UV which enjoys a very good ratio quality/price, and Absolue Lavandin UV which enables the perfumer to obtain a good long lasting cheap lavender note when mixed with either essence Lavandin Abrialis or Grosso. Also available are Absolue Clove UV, Absolue Hay and Cyste UV which are colorless and more powerful than the normal absolute.

CO_2 Extraction

The advantages of this new method of extraction (see figures 9 and 10) are the following:

- no residual toxic solvents, which is particularly appropriate for materials used in flavors
- low process temperature, of importance when processing unstable and/or heat sensitive products
- important selectivity (caffeine extraction)
- non-flammable (no fire risk)
- energy saving (no loss of petrol or organic solvent such as hexane or benzene)

CO_2 extraction parameters can be varied according to the characteristics of the desired product, either by using liquid CO_2 or supercritical CO_2 (more than 1071 PSI and at 31°C or more). By changing the pressure and temperature parameters the characteristics of a given extract will change. CO_2 extraction will be a major process of natural aromatic raw material extraction for flavors and fragrances in future years.

The principle of the method is based on the good solubility in CO_2 of most constituents of aromatic vegetable matter and/or semi-finished products such as concrete or even essences.

The extractor is filled with vegetable matter and CO_2 is added. Pressure and temperature inside the vessel are regulated according to the manufacturing process developed.

Saturated CO_2 is then pumped into the separator vessel in which pressure and temperature are lower than in the extraction tank. The product is removed and the remaining CO_2 pumped into the charcoal trap tank to be purified and recycled.

APPLICATION TO SOME MAJOR OILS

The oils have been chosen because either they can be extracted by different routes (rose, iris, mosses, galbanum), they present some interesting points such as bitter orange, or they are special (blackcurrant buds, marigold). Most of all, I

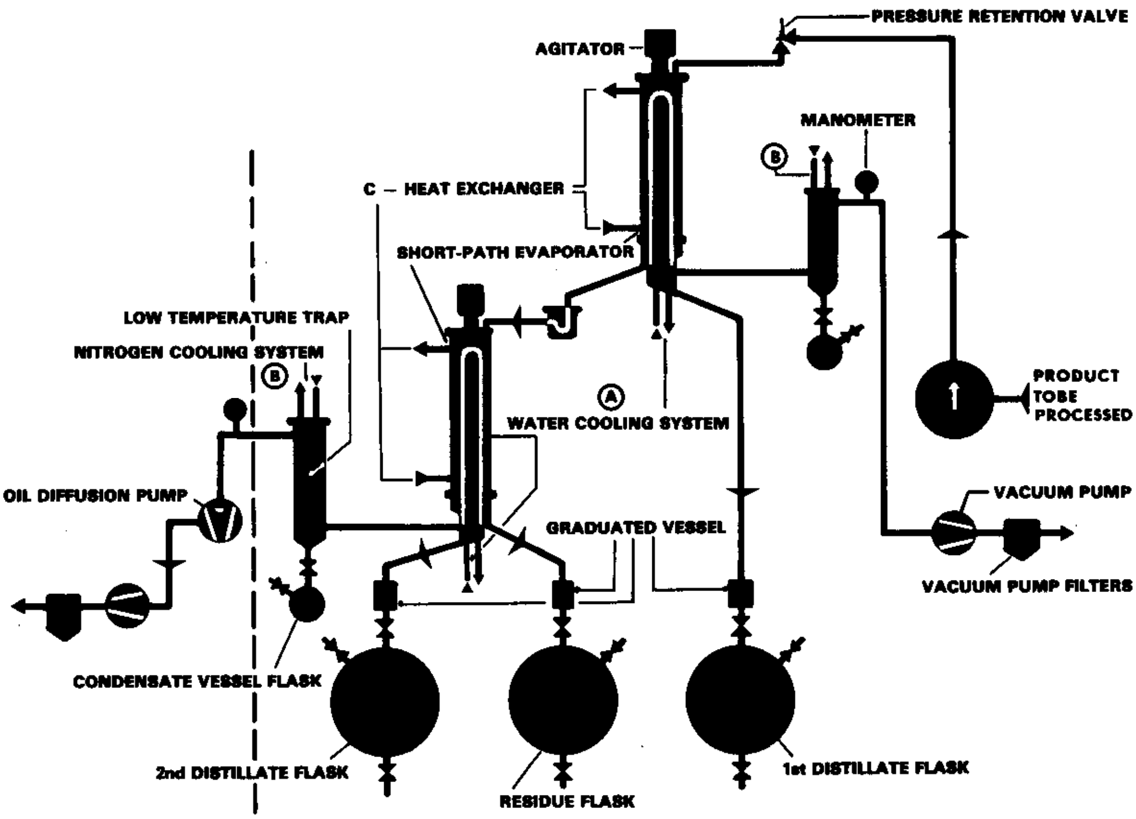
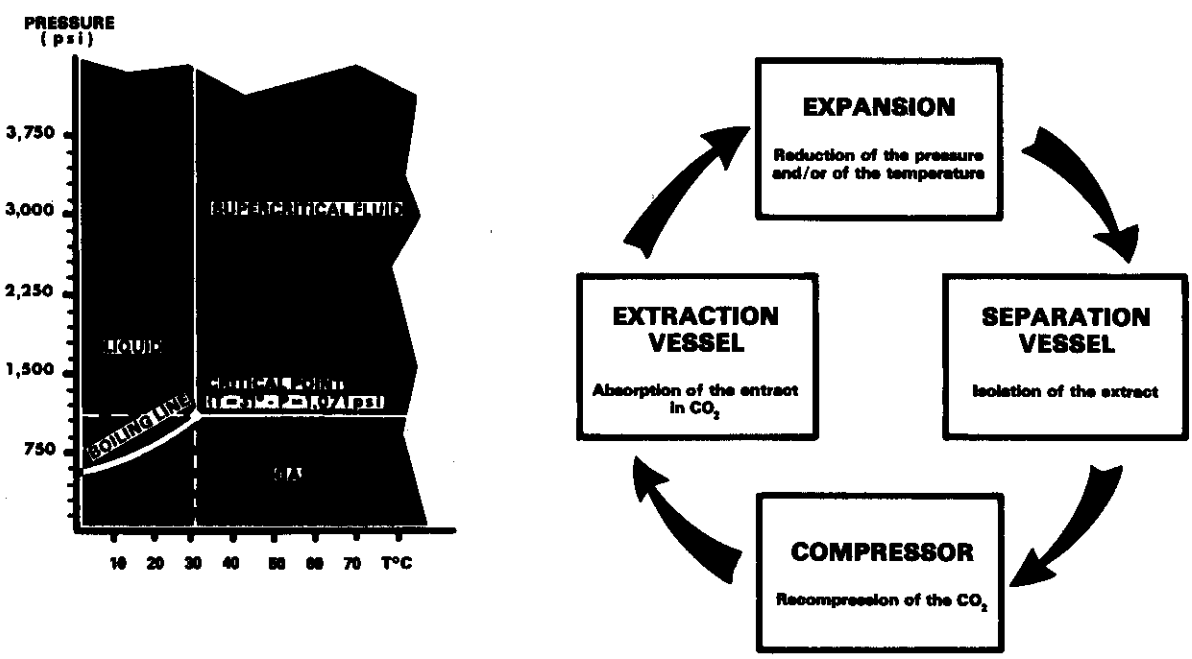


Figure 8. Molecular distillation unit

Figure 9. CO_2 extraction diagrams—physical states and process



PHYSICAL STATES OF CO_2

PROCESS DIAGRAM

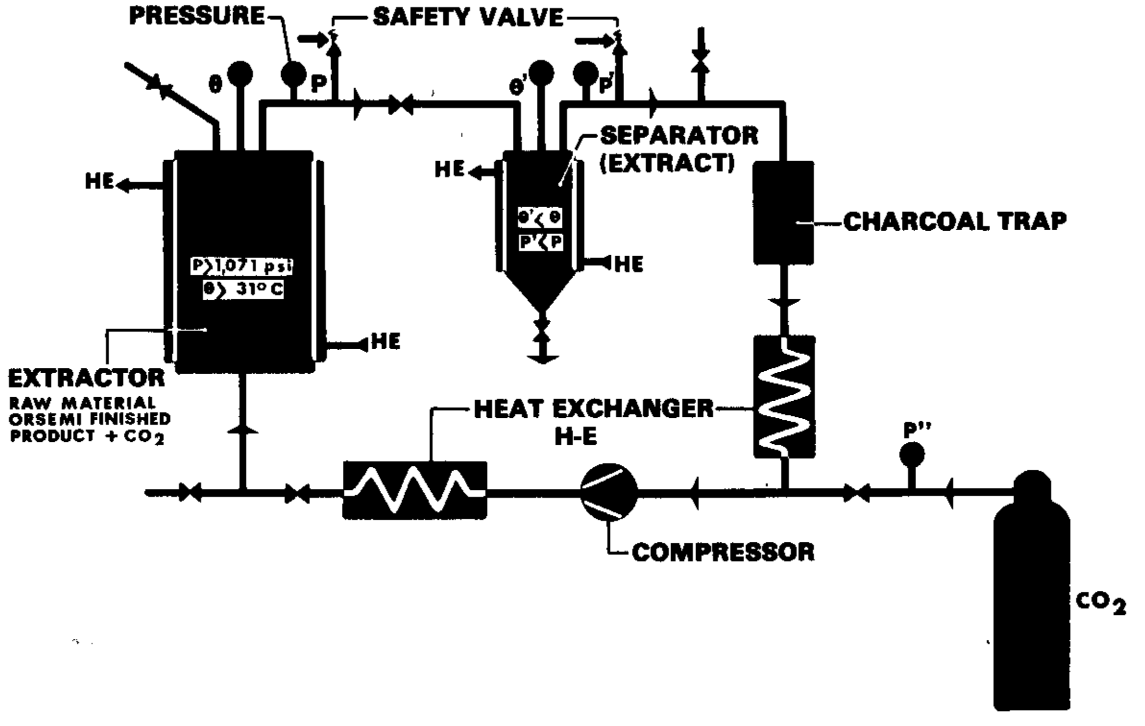
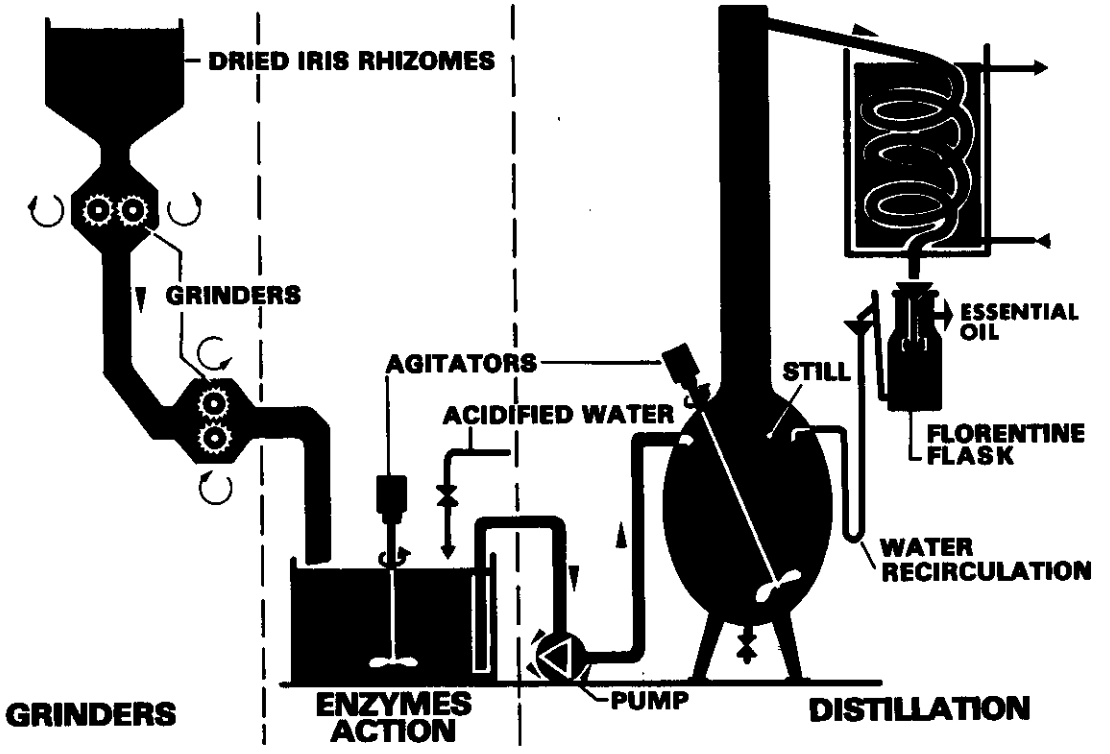


Figure 10. CO_2 extraction diagram

Figure 11. Oris rhizomes distillation



must mention jasmin, the king of the oils.

Jasmin

While produced in France, Italy, Egypt, Algeria, Morocco, Turkey, India, South Africa, the most delicate jasmin is the French and, to a lesser extent, the Italian one. But they only represent each 2.5% of the total production with France being stable and Italy decreasing. Egypt is by far the most important source of production with quite a regular quality. Morocco and India are second with Indian production picking up.

May I remind you that 10,000 flowers are needed for 1 kg of flowers and that a good worker spends two hours to harvest those 10,000 flowers. Each kg of concrete jasmin hexane needs 370 to 450 kg of flowers and 2 kg of that concrete give 1 kg of absolue jasmin hexane. When extracted with benzol only 250 to 300 kg of flowers are needed for 1 kg concrete jasmin benzol and only 1K°800 of that concrete jasmin benzol gives 1 kg of absolue jasmin benzol.

A 100% natural benzol note jasmin has been produced but without benzol and at a cheaper price. By a binary solvent we have obtained jasmin "CAMR." Thanks to a better yield the price is 40% below that of jasmin benzol.

Rose

Extracted by solvent (hexane), rose gives concrete and absolute, or by steam distillation it gives the essence. The Rose de Mai Pays produced in France is a special species called "centifolia." The other locations produce Rose "Dalmascena" or Dalmascena hibrid. 550 to 800 kg of concrete Rose Centifolia are produced in France. Among the average 3000 kg of concrete Rose Dalmascena produced per year, a major part (about 2000 kg) comes from Turkey. 450 to 500 kg of flowers are needed to obtain 1 kg of concrete and an average 1K°500 of concrete gives 1 kg of absolute. Of 1500 to 2000 kg of steam distilled rose produced, 50% comes from Turkey, the balance from Bulgaria and Morocco. Each kg of steam distilled rose oil needs four tons of flowers.

Iris

Figure 11 shows iris rhizome distillation. Though it is called iris concrete or iris butter, the product is obtained by steam distillation. The roots are used for extraction and not the flowers. It can also be extracted by benzene and then the product obtained is called Resinoid Iris.

400,000 kg of roots are produced every year in Italy, half of it is pealed at the time of the summer harvest. Roots have to be stored at room temperature for three years to have their irone percentage increased by enzymatic reaction. Two to three weeks before processing, roots are stored in a warm room (80°F), then put through a grinder. Acid water is added. In the distillation tank the solution is heated at boiling point and after passing through a refrigerator, iris concrete is separated from water in the Florentine flask. The yield is 1% with 15 to 20% natural irone content.

Bitter Orange

The bitter orange tree is quite special as nearly all the parts of it are used for producing an oil through different methods of production.

Orange Blossoms

Two alternatives of production are used. Hexane solvent extraction uses 400 to 500 kg of flowers giving 1 kg of concrete and 1K°800 of concrete is needed to obtain 1 kg absolute. Of an average yearly production of 1000 kg, 90% is produced in Tunisia and Morocco and the balance in France.

The orange blossoms can also be processed by steam distillation to obtain Neroli oil. Of the 600 to 1000 kg produced per year, Grasse only produces up to 50 kg and the balance comes from Tunisia and Morocco. 1000 to 1250 kg of orange flowers give 1 kg of Neroli oil plus 700 liters of "Eau de Fleurs d'Oranger." Extracted by alcohol, 3000 liters of Eau de Fleurs d'Oranger give 1 kg of Absolue Eau de Fleurs d'Oranger.

Tunisia and Morocco together produce 80 to 120 kg of Absolue Eau de Fleurs d'Oranger per year.

Leaves and Branches

These are steam-distilled to obtain petitgrain oil produced in Paraguay, Tunisia, Morocco, Egypt and Italy. 500 to 600 kg of leaves and end of branches give 1 kg of petitgrain oil plus 500 liters of Eau de Brouts ("brouts" means the end of branches). 3000 to 4000 liters of Eau de Brouts gives 1 kg of Absolue Eau de Brouts when extracted by alcohol. 150 to 300 kg of Absolue Eau de Brouts are produced per year. The bitter orange tree also produces fruit which is used in food and beverages.

Blackcurrant Buds

In order to strengthen the blackcurrant bushes produced in Burgundy, France, they are cut in September and the buds are pruned from the stem with a knife. Five hours are needed to obtain 1 kg of buds—35 to 45 kg of buds give 1 kg of concrete which in turn give 0.8 kg of absolute. Blackcurrant buds absolute is very thick; to make it easier to use and more homogeneous, it is often dissolved in DPG.

Marigold

Marigold absolute has been developed from a variety of "tagetes" which mainly grow in Egypt and South Africa. 450 to 500 kg of flowers are needed to obtain 1 kg of concrete which in turn gives 300 to 320 g of absolute.

In a perfume it gives a very floral note, green with a bitter, dry and woody touch. It is used in romantic perfumes and in bases like hyacinth, lilac, gardenia, réséda, jonquil, tuberose, narcissus, lily of the valley.

Mosses

Mosses are solvent extracted to obtain concrete and alcohol extracted to obtain resinoid. From the concrete or the absolute several qualities of colorless mosses have been developed using special processes including molecular distillation.

2000 to 3000 metric tons of tree moss are produced in France. Oak moss comes from Yugoslavia and, to a lesser extent, from Morocco. An average of 250 kg of moss is needed to obtain 1 kg of concrete which in turn gives 0.8 kg of absolute.

Galbanum

Galbanum gum is a secretion extracted from a tree in Iran with a yearly production of 120,000 kg. Steam distilled, the yield is 17% to 20%; alcohol extracted, the yield is 40% to 50% to obtain resinoid.

CONCLUSION

This discussion offers a brief overview of the different processes used to obtain natural essential oils. The trend of development in natural essential oils for the near future will be to:

—obtain products free of organic solvents
—improve the preparation of the plant matter in order to get better yields
—develop aromatic molecules through fermentation

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