1 Introduction to Extraction in Food Processing

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CONTENTS

1.1 WHAT THIS CHAPTER IS ABOUT

This chapter is strictly introductory. It aims to provide an overview of solvent extraction technology in general, so that the reader can place in context the detailed topics in subsequent chapters. It contains essentially no new information, so the reader will look in vain for detailed references to most of the issues discussed. Much can be found in standard chemical engineering texts. Texts such as Rydberg et al. (2004) or the earlier Lo et al. (1983) handbook provide much depth about the technology, but nothing about its application in food processing. Schügerl's (1994) monograph has some very relevant material, although its focus is definitely on biotechnology rather than food technology. A recent encyclopedic review of food technology (Campbell-Platt 2009) devotes a scant two pages to the topic of solvent extraction.

1.2 WHAT IS MEANT BY EXTRACTION

One of the oldest recorded methods of separation is solvent extraction, which dates back to the Palaeolithic age (Herrero et al. 2010). In food processing, extraction is defined as the transfer of one or more components of a biological feed from its source material into a fluid phase, followed by separation of the fluid phase and recovery of the component(s) from the fluid. The feed is usually of plant origin, but the principles of extraction remain the same if the material is animal or piscine in origin.

Extraction is a process that is growing in importance. It is generally more energy efficient than competitive processes such as expression—the pressing of biological feed materials to liberate fluids. For example, sugar is extracted from sugar beets with hot water, which yields a sucrose stream free of contaminants and of higher concentration (typically 15% sugar) than can be achieved by expression. Solvent extraction can be made selective for specific components of the feed. For instance, supercritical carbon dioxide (SC-CO_2) will selectively dissolve caffeine from coffee beans to yield decaffeinated coffee. The extracted caffeine can then be recovered for sale as a pharmaceutical. Extraction can recover thermally labile components that would be degraded by heating, such as gelatin from collagen. Table 1.1 gives some examples of typical extraction processes employed industrially.

The intent of this chapter is to give an overview of the broad principles underlying extraction, to provide a basis for understanding the rationale behind some of the technical advances described in later chapters.

TABLE 1.1
Some Examples of Industrial Extraction Processes

Solvent	Feed	Product	Component
Water	Apple pulp	Apple juice	–
	Malted barley	Brewing worts	Sugars, grain solutes
	Kelp	Carrageenan	–
	Manioc	Cassava	Cyanogenetic glycosides
	Citrus press residues	Citrus molasses	–
	Papaya latex	Papain	Papain
	Rosemary leaves	Rosemary essential oil	Rosemary essential oil
	Citrus peel	Citrus essential oils	Citrus essential oils
Acidic water	Collagen	Gelatin	Gelatin
	Citrus peel	Pectin	Pectin
	Hog stomach	Pepsin	Pepsin
Alkaline water	Defatted soy flour	Soya protein	–
Aqueous ethanol	Red beets	Betalains	Betalains
	Animal pancreas	Insulin	Insulin
	Spices	Spice extracts	–
	Vanilla beans	Vanilla essence	–
Methylene chloride	Green coffee beans	Decaffeinated coffee	Caffeine
Supercritical CO_2	Green coffee beans	Decaffeinated coffee	Caffeine
	Hops	Hops extract (resin)	Hops essential oils (myrcene, humulene, caryophyllene, and farnesene), alpha and beta acids
	Ginger rhizomes	Ginger extract	Gingerols
	Pomegranate seeds	Pomegranate seed oil	Pomegranate seed oil
	Vanilla beans	Vanilla essence	
	Spices (turmeric, nutmeg, mace, cardamom, etc.)	Spice extracts	
	Egg yolk	Decholesterolized egg yolks	Cholesterol
	Wheat germ	Wheat germ oils rich in tocopherols	–
Hexane	Soybeans	Soybean oil	–
Methyl ethyl ketone	Spices	Spice oleoresins	–
Tributyl phosphate	Phosphoric acid	Food-grade phosphoric acid	–

Source: Schwarztberg, H.G., in *Handbook of Separation Process Technology (Chapter 10)*, R.W. Rousseau (Ed.), New York: Wiley-Interscience. ISBN: 0471 89558X, 1987.

1.3 PHYSICAL PRINCIPLES OF EXTRACTION

1.3.1 Nomenclature of Extraction

A component that it is desired to be removed from the feed through extraction is called the "solute." The phase that is mixed with the feed to remove the solute is the "solvent." After the solvent has been mixed with the feed and the solute has transferred from the feed phase into the solvent phase, the solvent phase is called the "extract" and the feed phase is now called the "raffinate." It must be stressed that, in food processing, the feed is usually solid, semisolid, or gel-like, whereas much of the science of extraction is based on liquid feeds. However, there are very close parallels provided allowance is made for the impact of the nature of the feed on mass transfer properties, as further discussed in Section 1.3.3. Indeed, much of the rest of this text is concerned with means of improving the rate of mass transfer so that the science derived from liquid feeds may be better applied to the processing of food products.

1.3.2 Solubility

When a feed containing a solute is contacted with a solvent in which the solute is reasonably soluble, then the solute will distribute itself between the feed and the solvent until there is equilibrium between the feed and the solvent phases. When this occurs, the chemical potential of the solute in each phase is the same. The chemical potential is made up of two terms—the concentration of the solute and its activity in the phase concerned. However, in processing foods, it is rarely possible to measure the activity of the solute in the feed; thus, the primary concern is with the solubility of the solute in the solvent. Figure 1.1, for instance, shows the solubility of caffeine in SC-CO_2 and in SC-CO_2–ethanol mixtures. The solubility increases with pressure and with the addition of ethanol to the solvent, but decreases with temperature.

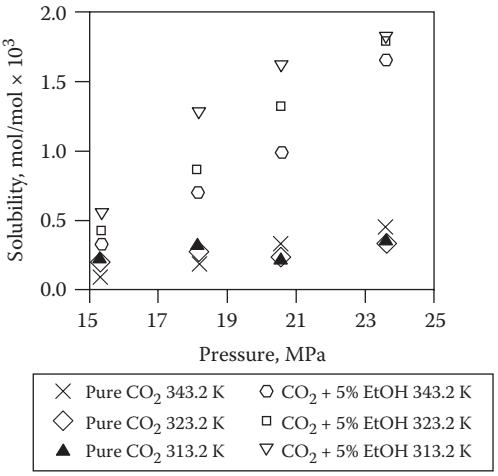

FIGURE 1.1 Solubility of caffeine in SC-CO_2 and CO_2–ethanol. (From Kopcak, U. and Mohamed, R.S., *J Supercrit Fluids* 34, 209, 2005. With permission.)

Determination of solubility is covered in many standard texts. Today, there are powerful packages for estimating chemical properties, which have a wide range of experimental data and strong theoretical bases to permit almost any solubility to be estimated. A recent paper (Kumhom et al. 2010) gives an introduction to these methods, for biochemical solids dissolved in mixtures such as the SC-CO_2–ethanol mixtures illustrated in Figure 1.1. A typical software package is Aspen Properties, part of the AspenTech suite (AspenTech 2010), while the U.S. Environmental Protection Agency's SPARC suite is a free resource (U.S. EPA 2010). Because these methods now find widespread use, there is little purpose in an extended discussion of solubility in a text such as this.

It is, however, useful to understand how solubility can be represented graphically. Figure 1.2 shows the triangular coordinates used to represent solubility. This is an equilateral triangle, with the concentrations of each component along each side as shown.

The composition at point *M* is then 50% solute, 20% solvent, and 30% feed. A useful feature of such diagrams is that mixtures can be represented by straight lines, and the result of mixing two streams of different composition is determined by simple geometry. Consider two streams of masses *D* and *E* and with compositions given by points *D* and *E*. Then the result of mixing these two streams will give a composition that lies on the straight line *DE* and has a composition given by point *F* such that *E*/*D* = *DF*/*FE*. This feature will be used in much of the discussion that follows.

The equilibrium between the various phases can readily be shown on triangular coordinates. Figure 1.3 illustrates this.

The line *WXY* represents the boundary between a single-phase and a two-phase region. Above the curve, the presence of the solute allows the feed and solvent phases to dissolve in each other, which is of course undesirable from the point of view of separation. The difference between the single-phase and the two-phase region is critically important in extraction because it is the existence of a second phase that

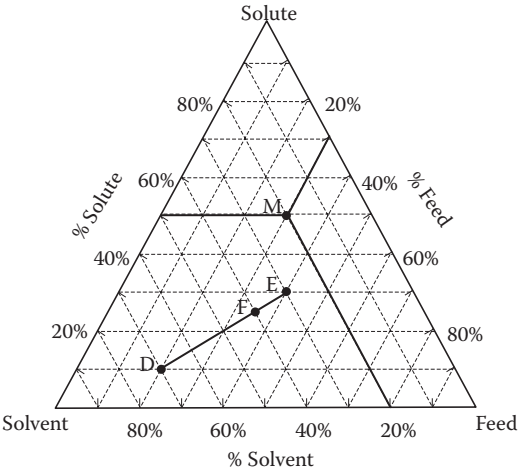

FIGURE 1.2 Use of triangular coordinates.

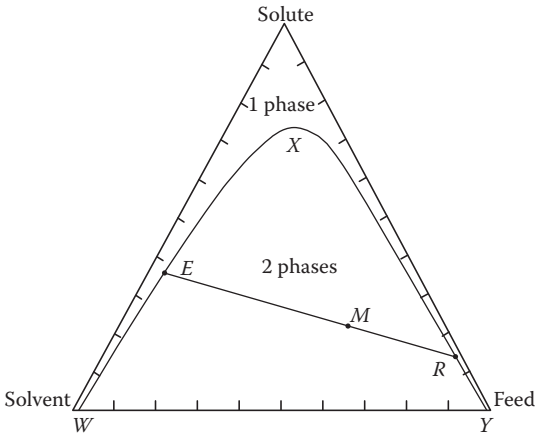

FIGURE 1.3 Solubility representation in a ternary diagram.

permits extraction to take place. The challenge in selecting a solvent is often to find one that will give as large a two-phase region as possible. Ideally, the feed and solvent will be essentially immiscible, and the presence of the solute will not change this immiscibility. However, in many biological systems, it is difficult to reach this ideal state. It then becomes necessary to allow for the effect of a single-phase region and operate so that its influence is minimized.

Because the side of the triangle between the solvent and feed corners represents the line of zero solute, then point *W* represents the solubility of the feed in the solvent and point *Y* represents the solubility of the solvent in the feed. Line *WXY* represents the boundary of the two-phase region.

Consider mixing some solvent with a feed, such that the average composition of the mixture is given by point *M* in the diagram. Then, provided *M* is within the two-phase region, the mixture will split and give two phases whose compositions will be given by points *E* and *R* on line *WXY*. These represent the concentrations in the extract and raffinate, respectively. Line *ER* is called a "tie line," and it joins the composition of two phases at equilibrium. There is a whole series of such tie lines, depending on the starting conditions. *EMR* is a straight line, as indicated previously, and the mass ratio of solvent to feed is given by the ratio of the lengths *EM*/*MR*.

These diagrams refer to conditions at a constant temperature, and the equilibrium line *WXY* is often referred to as an "isotherm" for this reason.

1.3.3 Mass Transfer

During the process of extraction, one or more compounds ("solutes") transfer from the biological feed material into the solvent. The physical process underlying the transfer is that the concentration* of the solute in the solvent is less than its

* Strictly speaking, concentration is an approximation to the "chemical potential" of the solute in the feed or solvent.

concentration in the feed, so that the solute diffuses from the feed into the solvent. However, the diffusion process is hindered by a number of phenomena.

First, there will be some interface between the feed and the solvent. The feed may also be liquid, but the interface between two liquids will slow the diffusion. Consider two liquid phases fully mixed in the bulk of the phases. Thus, the concentration in the bulk of each phase will be the same everywhere in that phase, except close to the interface where diffusion is occurring. This is illustrated in Figure 1.4.

On the feed side, there is a concentration difference between the bulk concentration and the concentration at the feed side of the interface, and it is in this non–fully mixed zone where diffusion takes place. The width of the diffusion zone may be less than a millimeter. Similarly, on the solvent side, there is a concentration difference between the bulk concentration and the concentration at the solvent side of the interface, and diffusion occurs across this narrow layer. At the interface itself, there is a drop in concentration that reflects the difference in chemical potential on either side of the interface.

Thus, three physical layers resist the transfer of mass from the feed to the solvent:

- The diffusion layer on the feed side
- The resistance to transfer of the interface itself
- The diffusion layer on the solvent side

In the case of food processing, the last of these is of little significance. The solvent is generally a liquid of relatively low viscosity, which means that it can relatively simply be fully mixed and the thickness of the boundary diffusion layer can be reduced to a minimum. The challenge in applying extraction to food processing is to minimize the first two of the resistances—that in the feed phase and that at the interface.

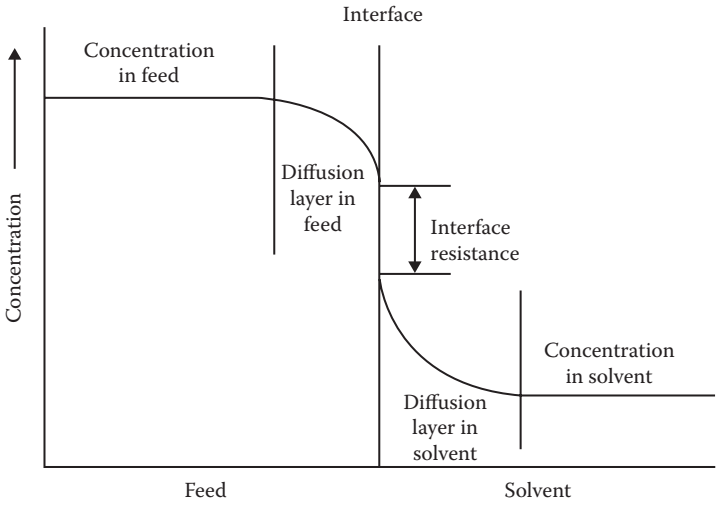

FIGURE 1.4 Transfer of solute between two liquid phases.

In food processing, the feed phase is generally not a low-viscosity fluid. It may be semifluid or gel-like. It may be semifluid contained within cellular structures. It may be quite solid. Whatever its state, it will resist mass transfer to a far greater extent than a low-viscosity fluid. Much of the rest of this book is devoted to ways and means of increasing the rate of mass transfer from real-life feeds, and doing so in such a way as not to change the properties of the desired solute and not to enhance the extraction of additional solutes that might detract from the properties of the desired solute.

Similarly, in food processing, the interface is generally not the simple interface between two low-viscosity fluids. It may, as we have seen above, be the interface between a solvent and a semisolid or even a solid. It may be attractive to surface-active substances present in the feed, which thicken the interface and thus increase its resistance. It may be a cell wall designed by nature specifically to resist the release of the desired solute. It may even be a solid and even, in some cases, a crystalline solid. Methods for coping with all these forms of resistance to mass transfer are described in later chapters.

The reason for being concerned about mass transfer is that the slower the rate of mass transfer, the longer the feed and solvent must be in contact. This means, other things being equal, that the longer the two are in contact, the larger must be the equipment in which the contact takes place—and larger equipment is inherently more expensive than smaller equipment. Also, the longer the two are in contact, the greater the chance of the solvent dissolving other solutes from the feed, or for the desired solute to be degraded by temperature or exposure to the atmosphere—or even by reaction with the solvent.

1.3.4 Diffusion

The rate of diffusion of a single species in a single fluid can be described by Fick's law

$$J_A = -cD_{AB}\frac{dx_A}{dz} \tag{1.1}$$

where J_A is the rate of diffusion (mol m^{-2} s^{-1}), c is the concentration (mol m^{-3}), D_{AB} is the diffusion coefficient of solute A in solvent B (m^2 s^{-1}), x_A is the mole fraction of A in B, and z is the direction of diffusion.

What this makes clear is that the greater the area over which diffusion can take place, then the greater will be the rate of mass transfer. Thus, when extracting from a liquid feed, the solvent and the feed are agitated together to increase the surface area between the two to maximize the rate of transfer. Similarly, when extracting solute from a solid feed, the solid should be reduced in size as far as possible to maximize the area through which mass transfer can take place (Pronyk and Mazza 2009).

There are, of course, some constraints on this maximization of surface area to enhance the rate of extraction. With two liquids, for instance, it is possible to mix them so intimately that one emulsifies in the other, so that separation of the solvent

after extraction becomes difficult. With a solid feed, the very process of size reduction may be so energy intensive that labile substances are altered. While as large an area as possible can enhance the rate of extraction of a desired solute, it may also make the rate of extraction of a less-desired solute sufficiently high that the desired solute is unacceptably contaminated. Nevertheless, the general rule holds good—a large surface area will speed the rate of extraction.

1.3.5 Choice of Solvent

The solvent should, naturally, be capable of dissolving the desired solute. It is useful if the solubility of the solute in the solvent is high because this will reduce the quantity of solvent needed to extract a given quantity of solute. However, this is not an essential requirement. Other factors guide the choice of solvent. For instance, in many cases, it is desirable to ensure maximum selectivity—that is, that the solvent dissolves the desired solute preferentially to other potentially soluble materials present in the feed. Water is generally nonselective, but in some cases, as Table 1.1 illustrates, even it can be sufficiently selective given the right feed and solute.

An important requirement is that the solvent should be reasonably stable and that it should not react chemically with the solute in such a way as to adversely affect the properties of the solute. There are classes of solvents that are inherently acidic or basic, and they can be used to extract anionic or cationic solutes, respectively. Contact with an acidic or basic solution will then recover the solute and regenerate an acidic or basic solvent. In these cases, there is a chemical reaction between the solvent and the solute, but it is employed beneficially and does not adversely affect the properties of the solute.

A further requirement is that the solute should be reasonably readily recovered from the extract (i.e., the solution after the extraction process) in those cases where the desired product is the solute. As Figure 1.1 indicates, merely reducing the pressure suffices to lower the solubility of caffeine in SC-CO_2. If the extract is saturated at high pressure, then the pressure can be reduced, caffeine will crystallize from the solution, and the depleted solvent can then be repressurized for reuse. In some cases the solute is not thermally labile, and the solvent can be recovered and separated from the solute by distillation. A further possibility is that the recovery of the solvent can take place through extractive distillation. For example, in the recovery of acetic acid from dilute aqueous solutions with methyl *tert*-butyl ether (MTBE), the extract contains both water and acetic acid; however, when the solvent is distilled, an azeotrope of water and MTBE is formed and the solute (acetic acid) is recovered as anhydrous glacial acetic acid (de Klerk 2008). The azeotrope is then cooled, when it separates into an aqueous and an MTBE layer, and MTBE can be recycled directly.

A further consideration in the choice of solvent is that it should readily be separated from the raffinate (i.e., the feed material following extraction). Generally density differences suffice to bring about a high degree of separation, although in some cases the difference is so small that centrifuges must be employed. Centrifuges are also employed when the raffinate is a pulp that tends to entrain the extract. It may be necessary to wash such pulps with fresh solvent to recover trapped extract, particularly if a high yield of the solute is required.

The solvent will dissolve to some extent in the raffinate. One seeks to minimize the quantity lost in this way because it represents an economic loss, but possibly more importantly because it may contaminate the raffinate. The choice of a solvent with a very low solubility in the raffinate will naturally assist, but other considerations may force the choice of a solvent that has a significant solubility over one with a very low solubility. Removal of dissolved solvent from the raffinate may rely on the vapor pressure of the solvent being sufficiently lower than that of the raffinate that vapor scrubbing or distillation can remove it. Alternatively, if the raffinate is reasonably liquid, residual solvent may be stripped by adsorption on a solid such as activated carbon or clay. In extreme cases, it may be necessary to employ a second solvent that has a very low solubility in the raffinate to remove the solvent that was first used to remove the solute.

1.4 ENGINEERING CONSIDERATIONS

1.4.1 Batch Operations

In the simplest extraction step, a feed is mixed with a solvent for a period sufficient for the solute to reach equilibrium between the two phases. The two phases are then separated, and the solute is recovered from the solvent. The question is how much of the solute will be extracted.

A simple mass balance with feed F, solvent S, extract E, and raffinate R, and c_i being the concentration of the solute in the ith stream, gives

$$F + S = E + R = M \tag{1.2}$$

$$Fc_f + Sc_s = Ec_e^* + Rc_r^* \tag{1.3}$$

where c^* represents the concentration at equilibrium. This is illustrated in Figure 1.5.

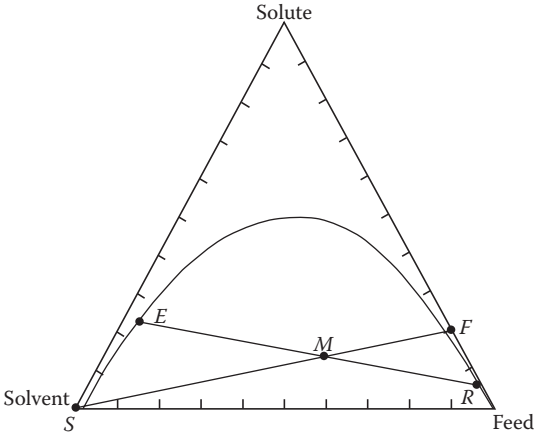

FIGURE 1.5 Extraction in a single stage.

The position of M on line SMF is found from the relationship

$$\frac{F}{S} = \frac{\overline{MS}}{\overline{FM}} \tag{1.4}$$

where overstrike indicates the length of the section of the line. The equilibrium relationship, shown as the tie line EMR in Figure 1.5, links c_e^* and c_r^* such that

$$c_e^*/c_r^* = D_T \tag{1.5}$$

at any one temperature T. For many systems, the distribution coefficient, D_T, is close to constant at low concentrations, but will vary with temperature.

If the solvent is recycled free of solute ($c_s = 0$), the quantity of solute extracted will be given by Ec_e^* and the fraction extracted by Ec_e^*/Fc_f. Because the solvent is usually chosen to be reasonably insoluble in the feed, the volume of extract will be close to the volume of solvent fed (i.e., $E \approx S$), so that the fraction extracted will depend strongly on the volume ratio of feed to solvent, S/F. However, increasing the volume ratio will reduce the concentration of the solute in the extract, which will in turn increase the cost of removing the solute from the solvent. Therefore, there is an economic balance to be struck that sets a limit on the maximum quantity of solvent that can be employed and the maximum achievable recovery of the solute.

1.4.2 Differential Batch Operations

It is possible to maximize the recovery of a solute by repeated extraction with fresh solvent. A practical way of achieving this is shown in Figure 1.6.

The feed and solvent are mixed together, then overflow to a settler and allowed to separate. The raffinate is returned to the mixer and the extract passes to a solvent recovery stage where the product is removed and the recovered solvent is recycled

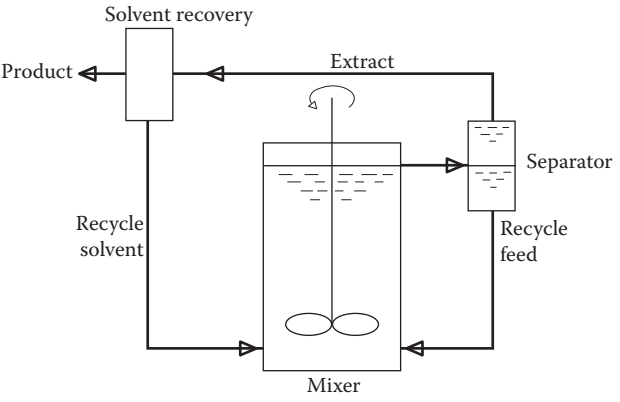

FIGURE 1.6 Differential extraction circuit.

to the mixer. This type of process is employed where a highly valued solute is at low concentration in the feed. It is widely used in the essential oils industry for extracting trace aromas or flavorants from plant material. Particular care must be taken to avoid trace contaminants in the fresh solvent, as there is a risk that these will also be concentrated in the product and in turn contaminate it unacceptably.

1.4.3 Countercurrent Operations

1.4.3.1 Batch Countercurrent

In the process shown in Figure 1.6, the quantity of solvent that must be separated from an increasingly dilute extract becomes very large. An alternative, which has the advantage of reducing the quantity of solvent for a given duty, is to operate in such a way that the fresh feed is extracted with solvent containing nearly the maximum quantity of solute. The raffinate from that stage is then extracted with solvent containing even less solute, and the extract from that stage then forms the feed to the first stage. This can be done batch-wise, as illustrated in Figure 1.7.

In Figure 1.7, there are four tanks, the first of which is empty in the first stage of operations. Solvent enters the fourth tank, overflows to the third tank, which

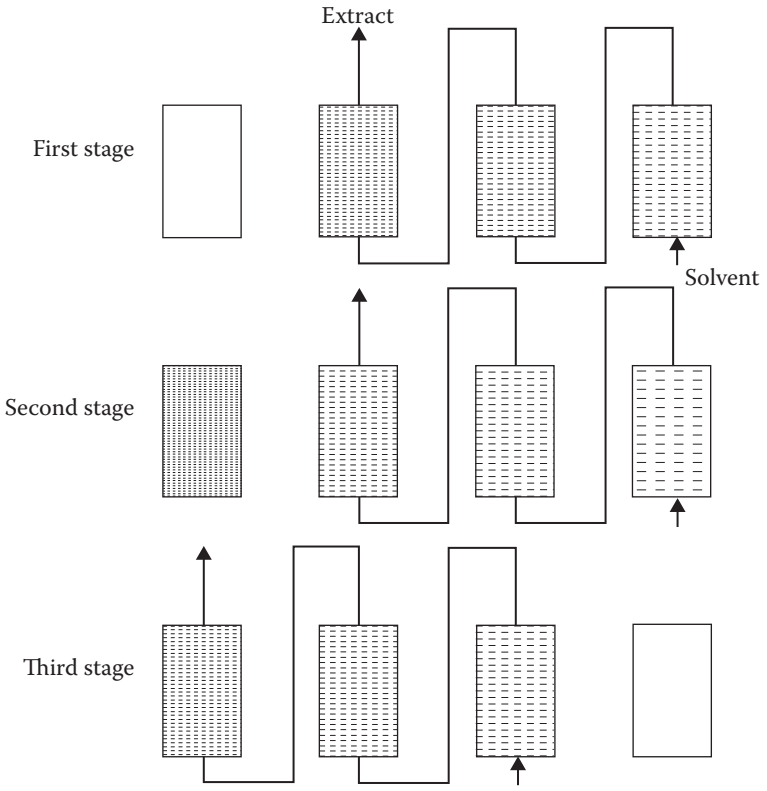

FIGURE 1.7 Batch countercurrent operation.

overflows in turn through the second. The extract comprises the solution leaving the second tank. The feed material is stripped of solute progressively from the second to the fourth tank.

In the second stage, the first tank is filled with fresh feed, while the material in the other tanks is progressively depleted. Eventually the material in the fourth tank loses all its solute, and the operation enters its third stage.

In the third stage of operations, the solvent enters the third tank and the extract leaves the first tank, while the raffinate is emptied from the fourth. The system is then effectively back at its starting condition, and the process continues.

The type of batch operation is frequently used where the feed material does not flow readily. It is somewhat expensive, partly because of the need to operate a large number of valves in a strict sequence, which involves control and maintenance challenges, and partly because the emptying of solids from the tank once the extraction is complete is not necessarily straightforward. Nevertheless, this type of extraction is quite widely applied in the industry.

1.4.3.2 Mixer–Settlers

Where the feed is reasonably fluid, then continuous countercurrent extraction is preferable to batch operation. In one variant, the feed and solvent are physically mixed, and then allowed to settle, usually under gravity. The settled extract phase then passes to the next mixer upstream while the settled raffinate passes to next mixer downstream. Figure 1.8 illustrates this for three stages of mixer–settler.

The two flows are separated at the end of the settler by a simple weir arrangement. Figure 1.9 shows this.

The lighter extract phase overflows a weir at the end of the settler and is withdrawn. The heavier raffinate phase flows out at the bottom of the settler into a chamber, from the top of which it overflows. The height of the raffinate weir determines the depth of each phase in the settler, because a simple pressure balance in the settler and the raffinate chamber gives:

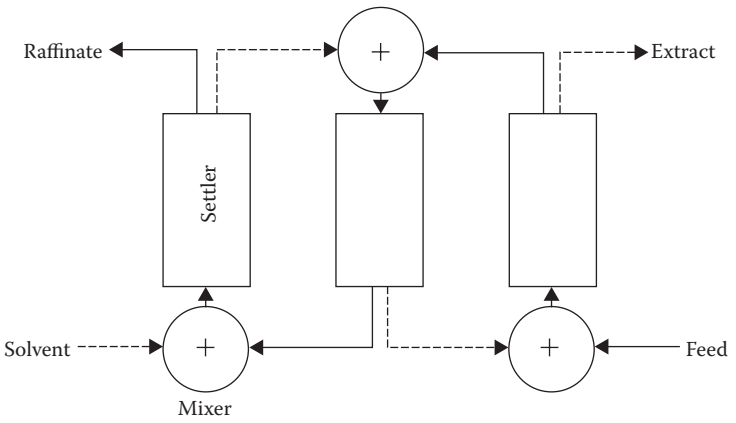

FIGURE 1.8 Continuous countercurrent mixer–settler.

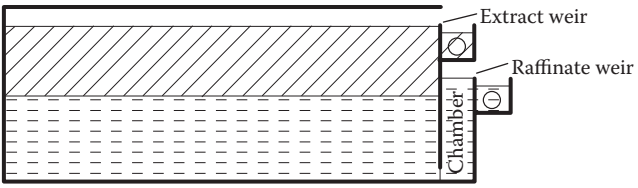

FIGURE 1.9 Elevation view of a settler, showing weir arrangement to separate phases.

$$h_{rs}\rho_r + h_{es}\rho_e = \text{pressure at base of settler} = h_{rc}\rho_r = \text{pressure at base of chamber}$$

where h is the height, ρ is the density of the phase, subscript r refers to raffinate, subscript e refers to extract, subscript s refers to settler, and subscript c refers to the chamber.

It is often found that any solids in the feed tend to collect at the interface between the extract and the raffinate in the settler, where they may interfere with the efficiency of separation. For this reason many settlers also have an arrangement by which material can be withdrawn from the region of the interface and treated separately for the recovery of the extract or raffinate.

The phases move from one mixer–settler unit to the next either by pumping or by gravity. Some designs incorporate a pump function in the mixer, which minimizes the number of pumps required. Each unit may be placed on a different level, so that one phase may gravitate while the other is pumped between stages.

Mixers require careful design. They have to disperse one phase in the other, and to do so without creating such fine droplets that the phases will not separate readily in the settler. Care must be taken to keep surface-active agents out of the system, as they will lower the interfacial tension between the phases and thus cause a fine dispersion that will not settle. Many biological systems contain natural surfactants; thus, it is often necessary in developing extraction systems to pilot them carefully to ensure that substances that affect the interfacial tension are not present—or, if they are present, to design the mixer to minimize the influence of the surfactant.

It is possible to employ centrifugal forces to hasten settling, and centrifuges are occasionally used instead of gravity settlers. There are designs of centrifugal mixer–settlers where several stages are packed within a single centrifugal unit. However, these tend to foul if there are any solids in the feed, and thus have not found widespread use in food processing.

1.4.3.3 Columns

It is possible to contact two liquid phases countercurrently in a column, as Figure 1.10 shows.

In the simplest design, one phase may be dispersed in the other by spraying through nozzles. The droplets rise or fall (as the case may be) through a counterflowing stream of the other phase. In Figure 1.10, the solvent phase is continuous, and droplets of the feed fall through a rising stream of solvent before forming a pool at the bottom of the column, from where the raffinate is removed. At the top of the column, the extract merely overflows.

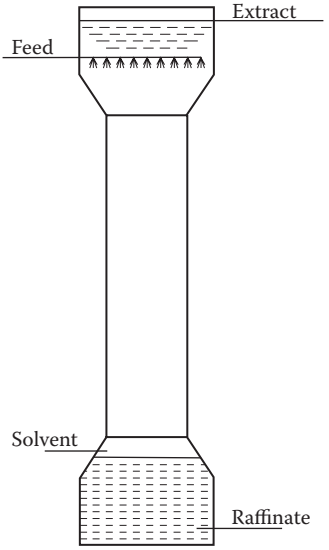

FIGURE 1.10 Extraction column operated with the solvent phase continuous.

This simple arrangement is not very efficient for a variety of reasons. One is that the surface area of the droplets is not very large. Another is that the falling droplets drag solvent molecules with them, and this means that solvent containing a lot of solute is mixed with lean solvent lower in the column. This reduces the concentration difference on which mass transfer depends, and thus reduces the efficiency.

For these reasons most columns contain a packing, the function of which is to increase the surface area of the phase that preferentially wets the packing. Because there is a larger area, the velocity of the dispersed phase is reduced and consequently there is less backmixing. There is a wide range of proprietary packing that may be employed. Some have less tendency than others to collect suspended solids, and are therefore preferred in food processing applications.

1.4.3.4 Extent of Extraction

It is obviously necessary to be able to estimate how many stages of countercurrent extraction are necessary to achieve a desired degree of extraction. It may be necessary to remove essentially all of a particular solute from the feed. Alternatively, there may be little point in recovering the last traces of a solute if the value of those last traces is too low to justify the expense of building additional extraction stages and operating them. Whichever the case, methods for estimating the number of stages required to perform a given extraction are essential.

With the equilibrium information available, it is obviously possible to solve the various mass balance equations numerically. However, for more than two or three stages, solving the resultant set of equations becomes tedious even in environments such as MATLAB®, and, if anything, it is self-defeating, because it is not possible to achieve 100% efficiency. Thus, a simple estimate suffices in the majority of cases.

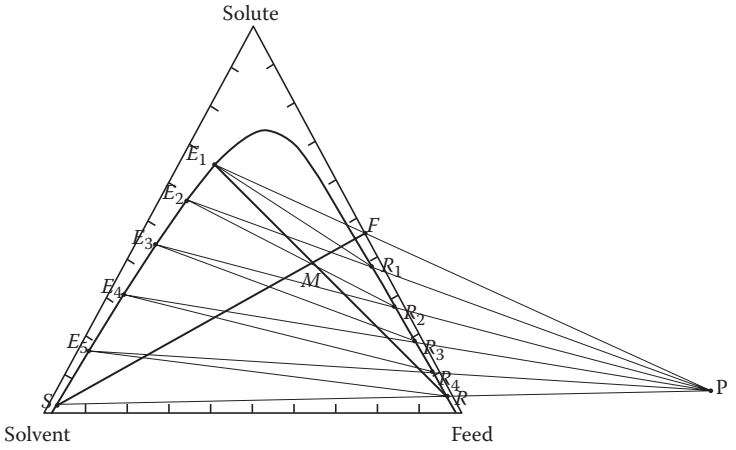

FIGURE 1.11 Graphical estimation of number of countercurrent stages.

For this reason graphical methods still find use. Figure 1.11 gives an example.

The feed concentration F and the solvent composition S should be known. Then assume a raffinate concentration R and an extract composition E_1. The extent of extraction obviously follows from $1 - (R/F)$. Construct SR and E_1F and extend until they meet at P, the "operating point," because

$$F + S = E_1 + R,\ F - E_1 = R - S = P \tag{1.6}$$

Then there is a tie line from E_1 to R_1, the raffinate concentration in equilibrium with E_1. A mass balance over the first and second stages gives

$$F + E_2 = E_1 + R,\ F - E_1 = R - E_2 = P \tag{1.7}$$

Therefore, a construction from P through R_1 will give E_2, which in turn will give a tie line to R_2, and a construction from P through R_2 will give E_3. Continuing in this way, eventually the graphical R_n will be at or below R. In the example given in Figure 1.10, $R_6 \approx R$; thus, six stages are needed to reduce the concentration of the solute from F to R. The ratio of solvent to feed is given as was the case in Equation 1.4 by the position of M.

There is a special case when there is no mutual solubility between the extract and the raffinate. In this case, the equilibrium shown in Figure 1.5 is much simplified and can be shown on rectilinear coordinates with, typically, the raffinate concentration of the solute on the ordinate and the extract concentration of the solute on the abscissa. This is illustrated in Figure 1.12.

As before, the feed concentration F and the solvent composition S should be known, and a raffinate concentration R and an extract composition E_1 is assumed. Then, with reference to Figure 1.12, the equilibrium between the two phases is given by the curve shown. Construct an operating line AB where point A has the coordinates $[F, E_1]$ and point B the coordinates $[R,S]$. Mass balance considerations show

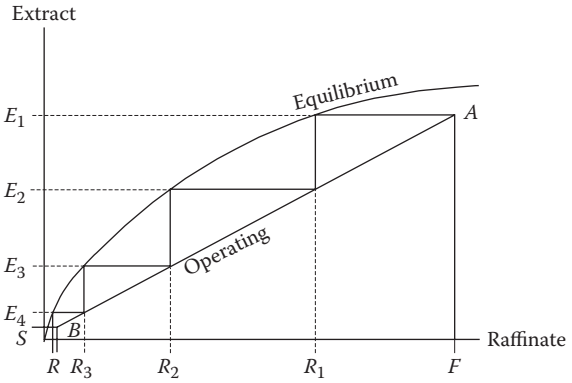

FIGURE 1.12 Graphical estimation of number of countercurrent stages where extract and raffinate are mutually insoluble (McCabe–Thiele diagram).

that the slope of this line is the same as the phase ratio (i.e., the ratio of volumetric flow of extract to the volumetric flow of raffinate). This is readily shown from mass balance considerations and, of course, only holds true provided the raffinate and extract are mutually insoluble.

Then if equilibrium is attained in each stage, the feed at concentration F will be in equilibrium with the final extract at a concentration E_1; thus, the raffinate concentration will fall from F to R_1. In the next stage R_1 will be extracted to equilibrium with E_2, and the raffinate concentration will fall further to R_2. Continuing in steps in this way, there will come a point where the raffinate concentration is below the desired final concentration R. In the example given in Figure 1.12, four stages suffice to reduce the concentration to the desired level. The graphical representation of countercurrent extraction in this manner is known as the McCabe–Thiele diagram after the chemical engineers who originally derived it.

Note that if the flow of feed is reduced—that is, the phase ratio is increased—then the slope of the operating line will be increased. It is not possible to reduce the feed flow indefinitely—at some point the operating line will cross the equilibrium line, and point A will lie above the equilibrium. It is no longer possible to construct the diagram, and E_1 must be reduced until point A is again below the equilibrium line at the new phase ratio.

1.5 TREATMENT OF THE EXTRACT AND RAFFINATE

1.5.1 Extract

The extract will need to be treated to recover both the solvent and the solute. A range of separation technologies is available for this purpose. If the solute is not thermally labile, then separation may be effected by distillation, with recovery of the solvent in a condenser. Vacuum distillation can often be employed if the solute is thermally labile, although this may give rise to considerable cost because of the need to run the condenser at low temperatures to recover the solvent. It may also be possible to recover

the solute by reducing the temperature of the extract and thus crystallizing the solute and settling, filtering, or centrifuging to remove the solvent from the solute crystals.

Chemical methods may also be employed. For instance, soy protein is extracted by alkaline water at approximately pH 9. Acidifying the water to about pH 4 precipitates the protein as a curd, which is centrifuged to remove the remaining water.

The solute can also be back-extracted from the extract. For instance, quinine is extracted from the bark of the cinchona tree into warm mineral oil and the solute is stripped from the extract using sulfuric acid–acidified water. The acidic water containing the quinine solute is filtered to remove insoluble material, and the quinine is recovered by adding alkali when the sulfate salt precipitates.

Similar principles can be applied to many extracts. The methods to be employed in any particular case will require testing before application, but in the majority of cases a simple and cost-effective method can be found for recovering solute and solvent separately. It is noteworthy that complete removal of the solute from the extract is not essential. The solvent may contain some of the solute and still be recycled to extract more material.

1.5.2 Raffinate

The principal task in raffinate treatment is usually the complete removal of the last traces of solvent. In food processing, the raffinate often contains significant quantities of solids, which adds complications. However, considerable separation may be possible by agitating the pulp with water, when the solvent will coalesce above the aqueous layer and can be removed that way. Oily solvents can be removed by washing with a much lighter, volatile hydrocarbon such as hexane, from which the residual solvent can be recovered by distillation, while any hexane left in the raffinate is removed by heating.

A wider range of separation processes is available if the raffinate is liquid and contains minimal solids. In that case residual solvent may be removed by adsorption on activated carbon or even clay. Centrifuging will take advantage of the density difference to remove droplets that are too fine to settle under gravity. In some cases, fine air bubbles have been used to scavenge traces of solvent. The surface of the bubbles is hydrophobic, which therefore attracts the solvent, and can be removed from the surface as a scum.

1.6 NEW TECHNOLOGIES

1.6.1 General

Increasing energy costs and the global imperative to reduce the carbon footprint has sparked the development of a number of new separation techniques for the chemical, pharmaceutical, and food industries (Bousbia et al. 2009a). Currently, many extraction processes in the food industry involve the use of organic solvents. However, these solvents not only present as atmospheric pollutants but also remain in the raffinate, as well as in the extracts, detracting from their purity (Reverchon 2003; Temelli 2009). While water, not organic solvents, is most often used in the extraction

of essential oils (Berka-Zougali et al. 2010), water is also becoming a scarce commodity, sufficient to engender an interest in processes that conserve this precious solvent. Hence, to satisfy the growing demand for product purity, nonpolluting and energy-efficient processes, with the added advantage of using less solvent, alternative processes to the aforementioned solvent extraction methods are being sought (Reverchon 2003; Bousbia et al. 2009a). At present, supercritical fluid extraction (SFE) is the most extensively used alternative to solvent extraction with many commercially produced SFE compounds already available (Reverchon 2003; Brunner 2005; Bousbia et al. 2009a). More recent extraction techniques developed in the quest to create commercially viable, efficient, energy-saving, safe, compact, and sustainable extraction processes include extraction assisted by pulsed electric field (Loginova et al. 2011), solvent-free microwave extraction (SFME) (Bayramoglu et al. 2008), instant controlled pressure drop technology (DIC; from the French, *Détente Instantanée Contrôlée*) (Berka-Zougali et al. 2010), microwave hydrodiffusion and gravity (MHG) (Bousbia et al. 2009a), ultrasound assisted extraction, subcritical water extraction (Bousbia et al. 2009a), high pressure–assisted extraction (Jun 2009), aqueous two-phase extraction (Chethana et al. 2007), and enzyme-assisted aqueous extraction (Niranjan and Hanmoungjai 2004). Some examples and features of these processes will be discussed in the following sections.

1.6.1.1 Supercritical Fluid Extraction

Owing to its low cost and ready availability at high purity, the mostly commonly used supercritical fluid solvent in food applications is carbon dioxide (CO_2). CO_2 is not flammable, with a moderate critical temperature (31°C) and pressure (7.4 MPa), ensuring its safety in handling, while its easy removal from the extract to sound physiological levels brokered its "generally regarded as safe" status—that is, it can be used in food processing without declaration. Moreover, when recycled during the process—for example, after recovery by reducing the pressure during caffeine extraction as mentioned in an earlier section—it does not contribute to the carbon footprint. Some examples of everyday products where SC-CO_2 extraction is used are decaffeinated coffee and tea, flavor-enhanced orange juice, dealcoholized wine and beer, defatted meat and French fries, beer brewed with CO_2 hop extracts, rice parboiled using CO_2, spice extracts, and vitamin E– and β-carotene–enriched natural products (Davarnejad et al. 2008; Sahena et al. 2009; Temelli 2009; Herrero et al. 2010). Until recently, SFE was considered too costly for producing low-value, high-volume commodity oils, and only viable if applied to high-value, low-volume specialty oils (Brunner 2005). However, increasingly stringent environmental regulations, particularly regarding the use of hexane, has led to significant progress in optimization of design and operation of large-scale supercritical oil extraction plants, such that their cost structure is now comparable with that of conventional plants (Pronyk and Mazza 2009; Temelli 2009). However, to realize the full potential of SFE in terms of oil extraction, it should be extended to include oil refining, as well as further extraction of valuable biomass components (e.g., proteins and carbohydrates). Hence, SC-CO_2 extraction, combined with subcritical and supercritical water extraction, may result in biorefineries that are "green" in the true sense of the word (Temelli 2009).

1.6.1.2 Pulsed Electric Field-Assisted Extraction

Pulsed electric field (PEF)-assisted extraction has been shown to enhance solid–liquid extraction processes in the food industry. PEF had been successfully employed to extract anthocyanins and phenolics in red wine must (Puértolas et al. 2010); sucrose, proteins, and inulin from chicory (Loginova et al. 2010); betanine from beetroot (López et al. 2009), sugar beet, apple, and carrot juice; and maize germ and olive oils (Toepfl et al. 2006). The high extract yield, lower operating temperatures (preventing thermal degradation), high product quality and purity, high process efficiency, shorter extraction times, and lower energy cost of PEF extraction methods are key advantages of this technique, heralding its potential for energy-efficient and environmentally friendly food processing.

1.6.1.3 Microwave-Assisted Extraction

Essential oils, the single most widely extracted commodity, are extracted from herbs and spices and other botanicals for flavors, fragrances, and antimicrobial applications (Anon 2004; Bakkali et al. 2008; Shrinivas 2008). Conventional extraction techniques, namely steam distillation, hydrodistillation, and extraction with lipophilic solvents, have been successfully replaced by SC-CO_2 (Bakkali et al. 2008; Bayramoglu et al. 2008), with the attendant cost savings in terms of energy (lower process time and temperature), as well as superior product quality (Atti-Santos et al. 2005). The most recent developments in this field are the use of microwave-assisted hydrodistillation (MAHD) (Wang et al. 2010), SFME (Bayramoglu et al. 2008), DIC, and MHG. Compared with hydrodistillation, MAHD, SFME, and MHG not only produce superior quality essential oils but also result in higher yields and significant savings in process time (Luchessi et al. 2007; Bayramoglu et al. 2008; Bousbia et al. 2009a, 2009b; Wang et al. 2010); in addition, energy savings and lower water consumption are achieved (Bousbia et al. 2009a). The savings in energy and solvent is due to the absence of distillation or solvent extraction, those being the unit operations responsible for high energy and solvent consumption (Bousbia et al. 2009a). MHG, in particular, shows great promise for industrial-scale operations. With both energy consumption and carbon emission being 6% that of hydrodistillation, as well as its very short process time, nonrequirement for water or other solvent nor for postprocess waste water treatment, and higher-purity final product, this process ticks all the boxes for a green, effective alternative to conventional solvent extraction techniques (Bousbia et al. 2009a).

1.6.1.4 Ultrasound-Assisted Extraction

Ultrasound-assisted extraction (UAE) is another emerging technology with industrial-scale processing equipment designs available. Applications to food processes include extraction of vanillin, almond oils, herbal extracts, soy protein (with enhanced removal of flatulence-causing soluble sugars), polyphenols, and caffeine from green tea. UAE also offers a process that reduces the dependence on solvents such as hexane, with improved economics and environmental benefits (mainly due to an increased yield of extracted components), increased extraction rate, reduced extraction time, and higher process throughput (Vilkhu et al. 2008; Jadhav et al. 2009; Karki et al. 2010). A more recent modification of UAE, namely ultrasound-assisted

dynamic extraction, was used to extract chickpea oil. This process entails circulation of the solvent while the sample and solvent are subjected to ultrasound, and results in further reductions in solvent consumption and extraction time and, therefore, environmental impact (Lou et al. 2010).

1.6.1.5 Subcritical Water Extraction

Subcritical water, also known as pressurized low-polarity water, or pressurized hot water extraction (PHWE) (Chapter 8), utilizes hot water (100–374°C) under pressure (1000–6000 kPa) to replace organic solvents (Herrero et al. 2006). PHWE delivers higher extraction yields from solid samples than conventional solvents. This technique was used effectively to extract peppermint oil, carotenoids from microalgae, carnosic acid and aroma compounds from rosemary, quercetin from onion skins, and rice bran oil through simultaneous lipase inactivation, to name a few. Compared with conventional extraction methods (i.e., solid–liquid extraction, hydrodistillation, and organic solvents), PHWE offers several advantages, namely shorter extraction times, higher-quality extracts, a less costly extracting solvent, and an environmentally friendly process (Herrero et al. 2006; Pourali et al. 2009; Pronyk and Mazza 2009; Ko et al. 2011).

1.6.1.6 High Pressure–Assisted Extraction

High pressure–assisted extraction has also gained ground as an environmentally friendly alternative to solvent extraction. Advantages include shorter extraction times, higher yields, extract purity, and lower energy consumption (Jun 2009). A variation on this, known as DIC, uses high-pressure steam to extract essential oils, followed by rapid transfer and cooling to a vacuum chamber. The rapid condensation in the vacuum tank produces a microemulsion of water and essential oils (Berka-Zougali et al. 2010). Further information on this process is given in Chapter 9.

1.6.1.7 Aqueous Two-Phase Extraction

Aqueous two-phase extraction was successfully employed for purification and concentration of betalains (a natural colorant from beetroot), resulting in a simpler and therefore more environmentally friendly process (Chethana et al. 2007).

1.6.1.8 Enzyme-Assisted Aqueous Extraction

This process has been applied to extract oils from various oil seeds and some fruits. The advantages of the method reside in the fact that processing occurs at relatively low temperatures and use water as a solvent, ensuring superior product quality and making the method safe and environmentally friendly. The presence of food-grade enzymes improves the oil yield (Niranjan and Hanmoungjai 2004).

1.6.2 Impact of Refining

Another aspect of vegetable oil processing is that the steps after solvent extraction, namely solvent recovery and refining, also have high-energy demands, consume large quantities of water and other chemical reagents, and produce significant quantities of effluent. The above concerns had been addressed by employing membrane

technology, particularly ultrafiltration and nanofiltration. The technology has been applied successfully at the pilot scale for solvent recovery from soybean and cotton seed oil and shows great promise with regard to deacidification and degumming, obviating the use of sodium hydroxide. It had been estimated that using membrane technology for solvent recovery rather than heating could effect a savings of 2.1×10^{12} kJ year^{-1} in the United States alone, while having considerably less noxious effect on the environment (Coutinho et al. 2009).

1.6.3 Combined Methods and Sample Extraction

As will be seen in later chapters, combinations of the above processes have also been researched (Chapter 6), while many of the techniques are also used as alternatives to solvent extraction as applied to food analytical techniques—for example, microwave-assisted extraction (Chapter 3).

1.7 CONCLUSION

In this short introduction, it had not been possible to do more than outline some of the principles underlying solvent extraction technology. However, the reader should now be equipped to appreciate the many advances reported in the remaining chapters of this book. We need advances, because extraction can make a significant contribution to the safe and environmentally friendly processing of food. Extraction has not realized its full potential partly because of the difficulty of ensuring efficient transfer of the solutes from the food to the solvent, and perhaps also because the equipment available to deploy the developing technologies has not yet reached the market.

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