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Problems Associated with the Development of Gas Extraction and Similar Processes

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ABSTRACT

The potential scope and possible areas of application of gas extraction as a separation technique are outlined. Some problems to be overcome are discussed and the need for accurate physical data determinations and also operating experience at pilot plant level are stressed. Some work directed towards fulfilling these needs is described. Reliable economic appraisal is essential before large scale design can be contemplated but is probably not practicable with sufficient accuracy until the above needs have been met.

1. INTRODUCTION

The use of gases near the critical point for selective extraction has been examined experimentally for some time, although in recent years the technique has been more intensively studied. The interest has been centered largely in two industries: the fuel industry and specialised food processing.

There are a number of attractive features which the supercritical process offers; these include

1. high-boiling and/or heat sensitive components may be taken into the extracting phase at relatively low temperatures. This is an advantage shared with liquid extraction.

2. recovery of the solute is generally a straightforward matter from the supercritical or near critical solution since relatively small changes in the conditions can result in considerable changes in solubility. This feature presents a distinct advantage over liquid extraction, where considerable energy may sometimes be expended in evaporating off the solvent.

3. the range of solvents which can be used is greater than in the case of normal liquid extraction. For example, a cheap non-flammable, non-toxic solvent such as carbon dioxide may be employed. The solvent power of an appropriate gas may be improved, if required, by the addition of a third component often called an entrainer, thus extending further the range of solvent characteristics available.

4. the fact that supercritical compressed gases have a comparatively low viscosity for a given density imparts to the supercritical fluid excellent powers of penetration into a solid structure which in turn confers improved opportunities for extraction from solids.

Because of the above features some separations can be achieved which would be very difficult by more usual methods such as distillation and, with rising energy costs, interest is also being shown in the possibilities offered for energy economies in separations presently carried out in other ways. The possibility of utilising good non-toxic solvents (such as carbon dioxide) in supercritical and near-critical extraction operations is an advantage particularly in the food industry.

2. THE SCOPE FOR EXTRACTIONS CARRIED OUT NEAR CRITICAL CONDITIONS

A number of processes based on supercritical gas extraction may be envisaged; in some instances research work has been initiated and extended, in others the process is little more than an idea to be examined when the technology has developed further. The latter group includes the recovery of waste materials, waste water treatment and desalination, and single cell protein manufacture.

An indication of the widespread interest which exists in the potentialities of gas extraction as a separation technique is provided by the large number of patents which have been issued in recent years, particularly for potential applications in the food industry and the oil and coal industries. Some of these patents are listed in Tables 1, 2 and 3.

TABLE 1

Some Patents for Specific Extraction Processes

Process material	Patent		
Flavours and spices	German	2127611.9	1971
	French	2140096	1973
	Canadian	989662	1976
Oil seeds	German	2127596	1972
	German	2363418	1972
	Austrian	331374	1972
	Dutch	7207441	1972
Cocoa butter	USA	3923847	1975
Tobacco	German	2043537	1970
	German	2142205	1973
Coffee	German	2005293.1	1970
	German	2357590	1975
Hops	British	1388581	1972
	Canadian	987250	1972
	French	2140097	1973
	German	2127618.6	1973
Deodorisation processes	Austrian	347551	1972
	German	2332038	1974
	German	2441152	1975
	USA	3969382	1977

TABLE 2

Proposed Applications of Near-Critical Fluid Extraction in the Food Industry

Patent	Application	Ref
Dutch 7 315 634 (1973)	Defatting using various gases and gas mixtures	
US 3 966 981 (1976)	Solvent removal using liquid CO_2	
British 1057 911 (1967)	Extraction of rich milk, vegetable oil with supercritical C_2H_4	
German 2 347 590 (1978)	Decaffeination of coffee using CO_2 at 28-30°C	
	Separation of mono-glycerides of oleic acid from a glyceride mixture using compressed CO_2 in countercurrent columns	1,2
	Extraction of fruit juices, concentrated essence with CO_2	3
	Extraction of volatiles from delicious apple essence using CO_2 or isopentane	4
	Selective aroma extraction using liquid CO_2 at room temperature and 918 psig	5
US 4 104 409 (1978)	Extraction of air-dried hops with supercritical CO_2	
German 2 106 133 (1972) German 2 212 281 (1973) German 2 357 590 (1975)	Decaffeination of coffee using supercritical CO_2	6
Dutch 7 300 796 (1973)	Deoderization of fat with compressed near-critical CO_2	
Dutch 2 707 533 (1972)	Recovery of cocoa butter with supercritical CO_2 or (after careful solvent purification) with supercritical N_2O, SF_6, CF_3Cl, $CHF_2Cl, CF_2CH_2, C_3F_8, CHF_3, C_2H_6, CH_4$	

TABLE 3

Proposed Applications of Near-Critical Fluid Extraction in the Oil and Coal Industry

Patent	Application	Extracting Fluid	Ref
	Extraction of lignite	Supercritical toluene	7
	Extraction of coal products and oil from oil shale	Supercritical toluene	8
	Supercritical gas extraction of coal	Supercritical toluene	9
	Coal extraction	Supercritical toluene	10
	Residuum oil supercritical extraction process (ROSE)	Supercritical pentane	11
US 3 474 863	Shale oil extraction process	Supercritical toluene or benzene	
	Reduction of the vanadium and nickel content of petroleum by supercritical extraction	Supercritical propane	12
	Extraction of liquid fuels and chemical feedstock from coal by supercritical gas extraction	Petroleum naphtha	13
	Extraction of coal tar	Supercritical ethylene	14,15
US 1978 4 108 760	Extraction of oil shales and tar sands using aromatic extractants under supercritical conditions. These extractants should consist of a benzene ring and preferably not more than four carbon atoms in substituent groups	Benzene, toluene, ethylbenzene, trimethylbenzene, or tetramethylbenzene	

A few of the entries in these tables are for applications which have been proposed in the open literature but most are patents.

A typical example of such a patent is provided by the last one on the list in Table 3. This patent describes a process for the extraction of oil shales and tar sands using suitable aromatic hydrocarbons in a supercritical condition. Recommended pressures and temperatures are in the range 70 to 200 bar and 370 to 450°C respectively. If shale is to be extracted, this should preferably be crushed to a size smaller than 1.5 mm. Suitable solvents are stated to include aromatic hydrocarbons having a single benzene ring and preferably not more than 4 carbon atoms in substituent groups, e.g., benzene, toluene, xylene, ethylbenzene, isopropylbenzene, trimethylbenzene and tetramethylbenzene. Virtually the whole of the bitumen in tar sands can be extracted with benzene at or above 290°C or with toluene above 320°C. A very high proportion of the kerogen in shales such as the Colorado shale (which release all their kerogen on heating sufficiently strongly) can be extracted with aromatics containing 2 to 4 carbon atoms in substituent groups at about 440°C.

Other work (16) on the extraction of tar sands and of peat with supercritical pentane has involved simultaneous separation in fixed bed adsorbers; not only is extraction achieved in the process but a rough separation of the products is also possible.

3. TECHNICAL PROBLEMS ARISING IN THE DEVELOPMENT OF PRACTICAL GAS EXTRACTION UNITS

At first sight, the basic information required for the design of a large-scale supercritical or near-critical extraction unit would be anticipated to be rather similar to that required for the design of other forms of separation equipment namely:

1. a knowledge of the phase equilibrium and enthalpy data for the system.

2. a knowledge of the extent to which equilibrium is actually approached at each point in the actual column.

In this belief, work was initiated by Professor Ellis at Birmingham with S.R.C. support to obtain equilibrium data and carry out column tests on promising systems. The separation equipment used is shown in Fig. 1 and the equipment used for the equilibrium determinations is shown in Fig. 8. The following discussion is in part based on this work.

3.1 Prediction and Extension of Equilibrium Data

Feasibility calculations on separation processes are considerably speeded up if it is possible to predict and extend equilibrium data and also to predict the mass transfer rate parameters. One of the first problems that would be encountered in a design, therefore, would be prediction or extension and collation of the equilibrium data, if at all possible.

The systems of interest in gas extraction studies tend to be composed of a comparatively high molecular weight solute (or mixture of solutes) contacted with a comparatively low molecular weight gas. Prediction of equilibrium data for this type of system is difficult, particularly if the molecules of the solute can form hydrogen bonds with each other. The problem of prediction becomes yet more complex when a natural product, such as tobacco, is considered. As an example of this: in the search for safer cigarettes, attempts have been made to extract nicotine and other harmful constituents from tobacco using organic solvents and also using supercritical carbon dioxide at a pressure of about 300 bar. The work with supercritical carbon dioxide and tobacco is described by Hubert and Vitzthum (17). These workers find that the presence of water is essential to the extraction of nicotine. There is naturally some water present in tobacco (10 to 13% by weight), but to extract nicotine in a single stage process satisfactorily, they found that it was necessary to increase this up to at least 25%. (The presence of water may also

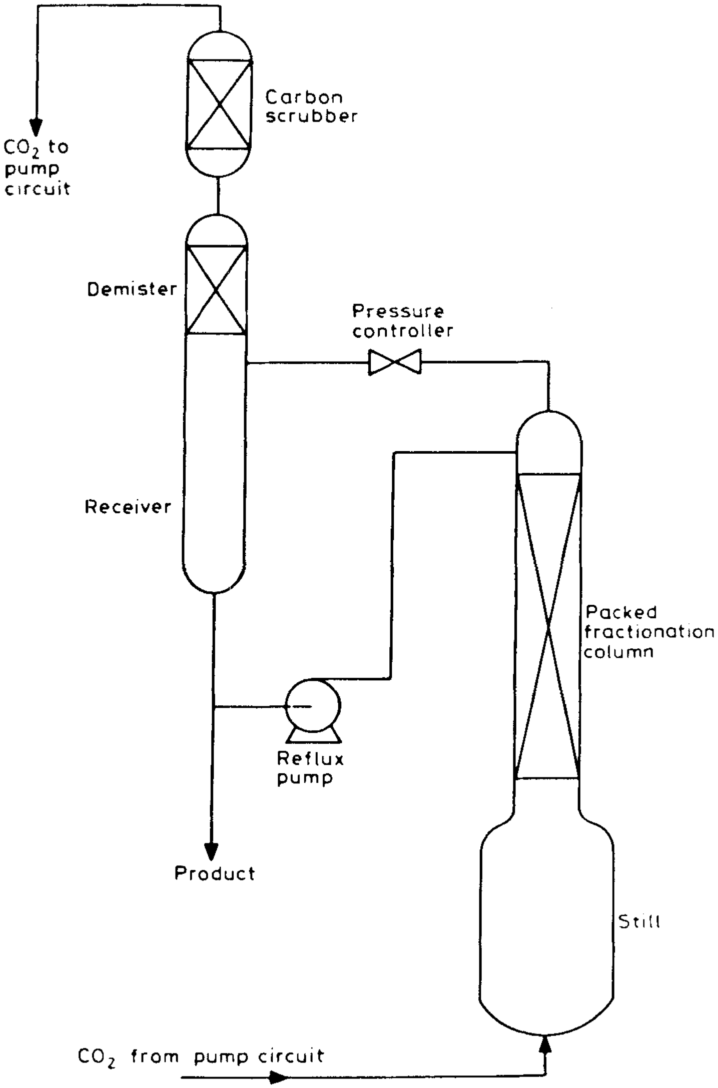

FIGURE 1. Simplified diagram of equipment used for column test.

be important in other extractions of natural products with carbon dioxide. For example, Zosel (18) states that coffee beans should be soaked with water prior to decaffeination with supercritical carbon dioxide). Hubert and Vitzthum also find that tobaccos of different origins behave very differently. In further illustration of these findings we carried out some tests using Burley Air cured tobacco with a moisture content of about 10% using carbon dioxide at 35.0°C and 122 bar. Very little nicotine was present in the extract, but instead it was found that neophytadiene ($C_{20}H_{38}$) had been extracted, together with a smaller amount of methyl palmitate. (See Fig. 2). Neophytadiene has the structure 3-methylene-7,11,15-trimethyl-1-hexadecene. When similar tests were carried out with Virginian and Oriental tobaccos, no neophytadiene was found.

Clearly, prediction of equilibrium data for tobacco leaves would be a formidable problem. However, in simpler situations some progress can be made. Broadly speaking, there are two approaches which have been applied to the problem of estimating equilibrium data in clearly defined systems of the type encountered in gas extraction calculations:

1. the use of solubility parameters
2. the use of equations of state.

The equation of state may either be applied to the gas phase only, in which case one of the standard activity coefficient correlation methods is applied to the liquid phase, or it may be applied to both the gas and liquid phases. The first of these approaches suffers from the drawback that, because different equations are used to represent the two phases, the convergence of the behaviour of these phases at the critical point is difficult to represent. Frequently, as a result, erroneous phases and phase behaviour are predicted in the critical region (19). This is particularly unfortunate in supercritical gas extraction work since best operating conditions are often to be found around this region. In the examples given below, the same equation of state has been applied to both phases. Using standard thermodynamic relationships,

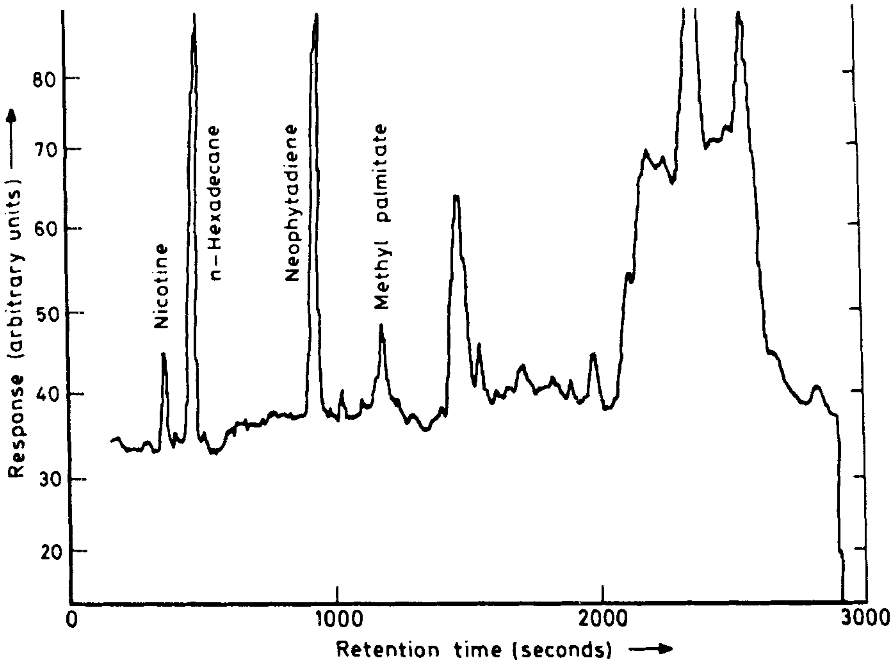

FIGURE 2. Gas chromatographic trace of the extract obtained from Burley air-cured tobacco (moisture content about 10%) using carbon dioxide at 35.0°C and 122 bar.

<u>Notes</u>

(1) The nicotine content of the extract is low since the leaves were comparatively dry. It is necessary to increase the water content of the leaves to at least 25% to obtain substantial extraction of the nicotine.

(2) The n-hexadecane was added artificially and will probably have had an "entraining" action on the neophytadiene. An interesting aspect of gas extraction is that it is possible to obtain enhanced vapour loadings by using suitable <u>entrainers</u>.

(3) The unresolved peaks of high molecular weight are waxy materials.

(4) The chromatographic conditions were as follows:

<u>Column</u>: 1.83 m x 0.32 cm I.D. (6 ft x 1/8 inch I.D.) packed with 5% SP-2250 (a phenylmethyl silicone, 50% phenyl) on Chromosorb W.

<u>Flow rate</u>: 30 cm^3/min of helium.

<u>Temperature program</u>: 150°C for first five minutes, then rising at 4°C/min to 250°C.

the fugacity of every component was calculated in each phase from the volumetric behaviour predicted by the equation of state, and the conditions for which the fugacity of every component was the same in the gas phase and in the liquid phase was established by trial and error. The solubility parameter approach (37) as presently developed is only intended to provide a qualitative indication of the types of substances which will dissolve in a given gas under given conditions. If this approach could be shown to be reliable, it might be very helpful, but more work appears to be required on it.

The well known Redlich-Kwong equation (20) is the equation of state most frequently used for phase equilibrium calculations, though in adapted forms in which the parameters a_m and/or b_m are allowed to be temperature dependent.

$$P = \frac{RT}{V-b_m} - \frac{a_m}{T^{1/2}V(V+b_m)} \qquad (1)$$

The composition dependence of the parameters a_m and b_m is usually expressed by the mixing rules

$$a_m = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j (a_i a_j)^{0.5}(1-l_{ij}) \qquad (2)$$

$$\text{and} \quad b_m = \sum_{i=1}^{n} x_i b_i \qquad (3)$$

(x_i is the mole fraction of component i in the fluid phase considered and l_{ij} is the interaction parameter: $l_{11} = l_{22} = \ldots l_{nn} = 0$). Many other equations of state provide a better representation of experimental data for the volumetric behaviour of fluid mixtures than does the Redlich-Kwong equation. However no equation of state has conclusively been shown to be any better for the purpose of phase equilibrium calculations of the type considered here in non polar systems. The reason for this is not altogether clear but may be connected with the fact that the calculation of liquid phase fugacities required in these calculations implies an integration of the partial molar volume along an isotherm which passes from the gas phase to the liquid phase through metastable and unstable regions. In these regions no experimental data are available for comparison and it may well be in the representation of these regions that the Redlich-Kwong equation is superior.

The pure component parameters a_{11}, a_{22}, ... a_{nn} and b_{11}, b_{22}, ... b_{nn} required in Equations (2) and (3) may be calculated from the liquid molar volume and vapour pressure of each component at the temperature of interest using a method proposed by Zudkevitch and his co-workers (21). A difficulty in applying their method to systems encountered in gas extraction calculations is that many of the components to be extracted are of very low volatility and vapour pressure data are not available for them. As part of the present work a convenient thermodynamic method has been developed for extrapolating vapour pressure data to lower temperatures using heat capacity data (22,23) and this method was applied to hexadecane in one of the examples below.

At the critical temperature of a component, a and b may be calculated from the expressions

$$a = 0.42748\left(\frac{R^2 T_c^{2.5}}{P_c}\right) \tag{4}$$

and

$$b = 0.08664\left(\frac{RT_c}{P_c}\right) \tag{5}$$

These so-called "universal values" are normally used at temperatures at or above the critical temperature of a given component. Correlations giving a and/or b as functions of temperature exist and are useful under conditions where Zudkevitch's method cannot be used. Soave's correlation (24) is typical and is used in one of the examples below. In this correlation, b is the universal value given by Eq. (5). The parameter a is given as a function of reduced temperature and acentric factor by the expressions

$$a = 0.42748\ T^{1/2}\alpha\left(\frac{R^2T_c^{\ 2}}{P_c}\right) \qquad (6)$$

$$\text{where} \quad \alpha = \left[1 + m(1-T_r^{\ 1/2})\right]^2 \qquad (7)$$

$$\text{and } m = 0.480 + 1.574w - 0.176w^2. \qquad (8)$$

T_r is the reduced temperature and w the acentric factor. Soave's correlation does not extend to substances with acentric factors higher than that of decane and it cannot be used for substances whose critical constants are not known. Under these circumstances correlations of Hederer, Peter and Wenzel (25) and of Brunner (26, 27) are useful.

In view of its simplicity the Redlich-Kwong equation does work surprisingly well with complex systems, though whether it is quite good enough with the very complex systems encountered in gas extraction work is perhaps debatable. The accuracy of fit (and of prediction) which can be obtained with moderately complex systems (when the necessary parameters can be evaluated) is illustrated in the following examples.

Fig. 3 (28) shows the fit obtained to data for the system ethylene/toluene at 73.5°C with $l_{12} = 0$ and values of a and b obtained from pure component data (universal values in the case of carbon dioxide and values calculated from vapour pressure and liquid

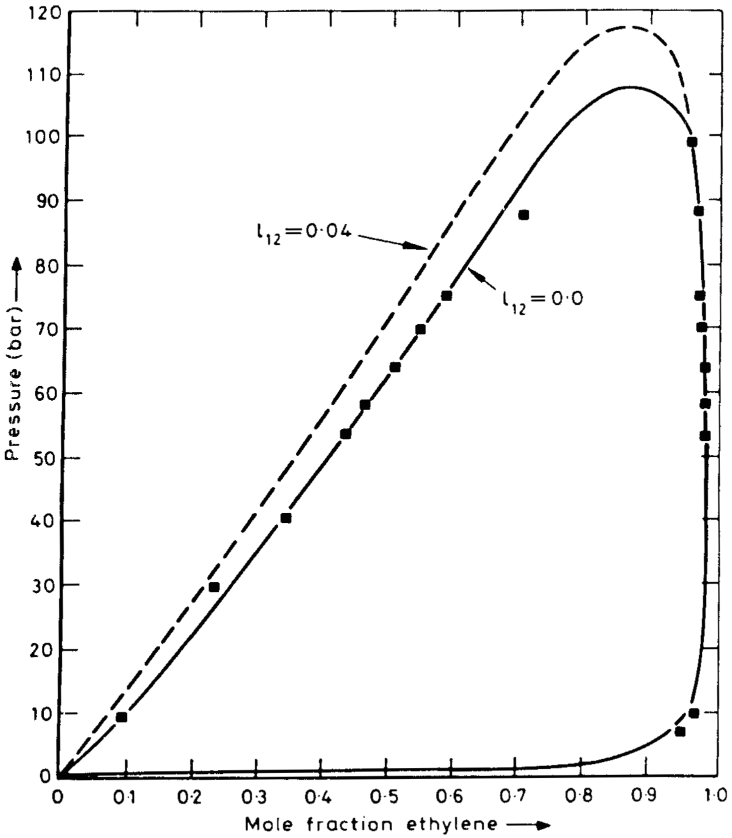

FIGURE 3. Pressure-composition diagram for the system ethylene/toluene at 73.5°C.

The full and broken curves have been predicted using the Redlich-Kwong equation with L_{12} = 0.0 and 0.04 respectively (according to this equation

$$P = \frac{RT}{V-b} - \frac{a}{T^{\frac{1}{2}}V(V+b)}$$

where $a = x_1^2 a_1 + x_2^2 a_2 + 2x_1x_2(a_1a_2)^{\frac{1}{2}}(1 - L_{12})$

and $b = x_1b_1 + x_2b_2$).

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volume at 73.5°C in the case of toluene). The fit could hardly be bettered. Fig. 4 (29) shows the fit obtained for the system carbon dioxide/n-hexadecane at 60°C, using a and b values obtained as in the previous example; l_{12} is here 0.08. In this case the fit obtained using the method developed by Lee and Kesler (30) and by Joffe (31) (incorporating the generalised mixing rule of Plocker, Knapp and Prausnitz (32)) is also shown. This method is based on the Benedict, Webb and Ruben equation of state (33). It is clear that the Redlich-Kwong equation fits the data better. A similarly close fit can be obtained for the system carbon dioxide/diphenylmethane at 60°C, with l_{12} = 0.07. Having established l_{12} for two of the constituent binary systems, an attempt may be made to predict the "relative volatility" of diphenylmethane to n-hexadecane in the ternary system carbon dioxide/n-hexadecane/diphenylmethane. (The relative volatility of diphenylmethane is here defined as

$$(y^1_{DPM}/x^1_{DPM}) \;/\; (y^1_{HD}/x^1_{HD}) \qquad (9)$$

where y^1_{DPM} = mole fraction of diphenylmethane on a CO_2 - free basis in vapour phase
y^1_{HD} = mole fraction of hexadecane on a CO_2 - free basis in vapour phase
x^1_{DPM} = mole fraction of diphenylmethane on a CO_2 - free basis in liquid phase
x^1_{DPM} = mole fraction of hexadecane on a CO_2 - free basis in the liquid phase)

It is seen from Fig. 5 that the experimental and predicted relative volatilities are in reasonable agreement, though an arbitrary value of 0.03 had to be ascribed to the interaction parameter in the n-hexadecane/diphenylmethane system.

It is also possible to predict and collate data for the solubility of solids in gases by applying the Redlich-Kwong equation to the gas phase. It is seen from Fig. 6 that the data for the system

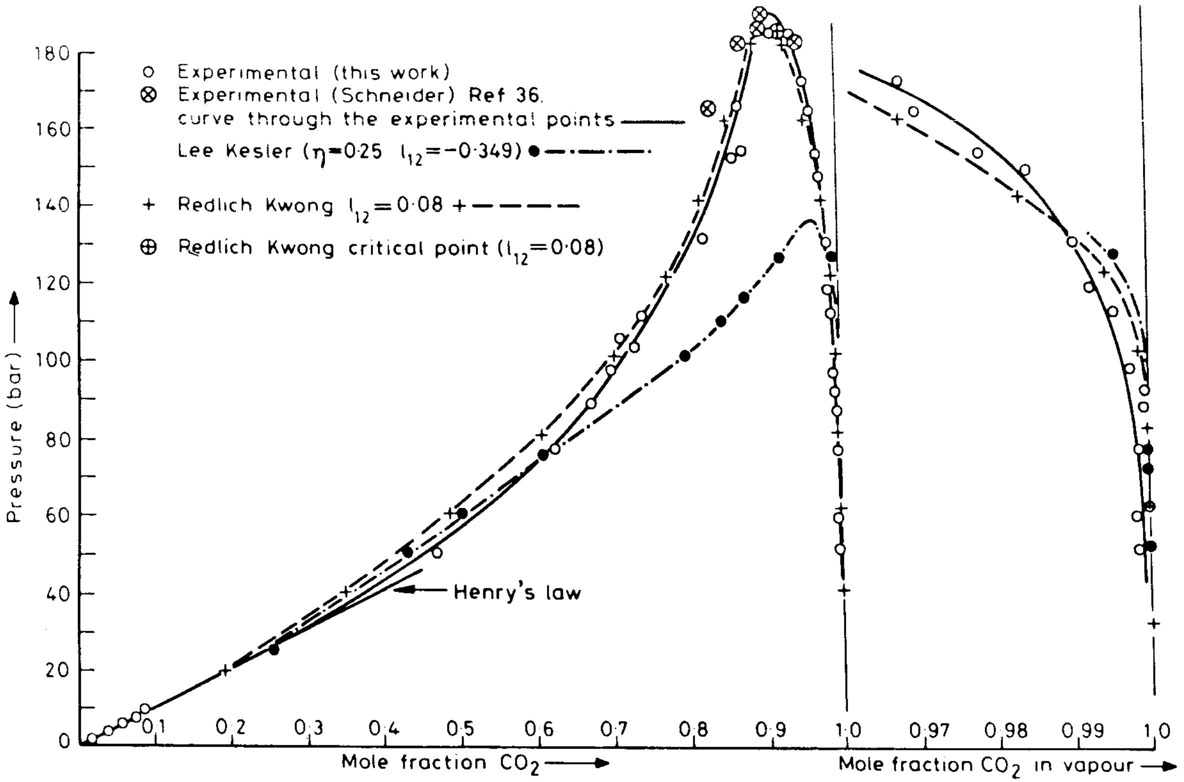

FIGURE 4. The carbon dioxide/hexadecane system at 60°C showing experimental data and the predictions obtained using the Lee-Kesler correlation and the Redlich-Kwong equation of state. The work on which this figure is based is to be described in a subsequent publication.

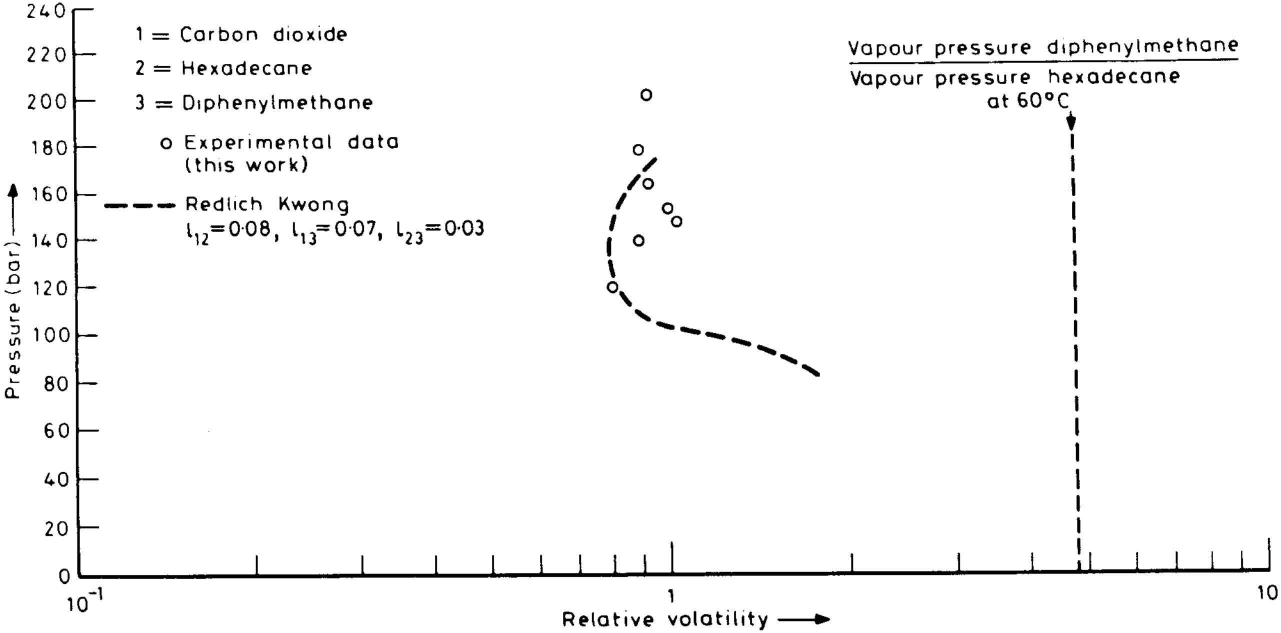

FIGURE 5. Relative volatility of diphenylmethane to hexadecane in carbon dioxide at $60^{o}C$ when the gas free liquid composition is 50 mole % hexadecane, 50 mole % diphenylmethane showing experimental data and the prediction obtained using the Redlich-Kwong equation. The work on which this figure is based is to be described in a subsequent publication.

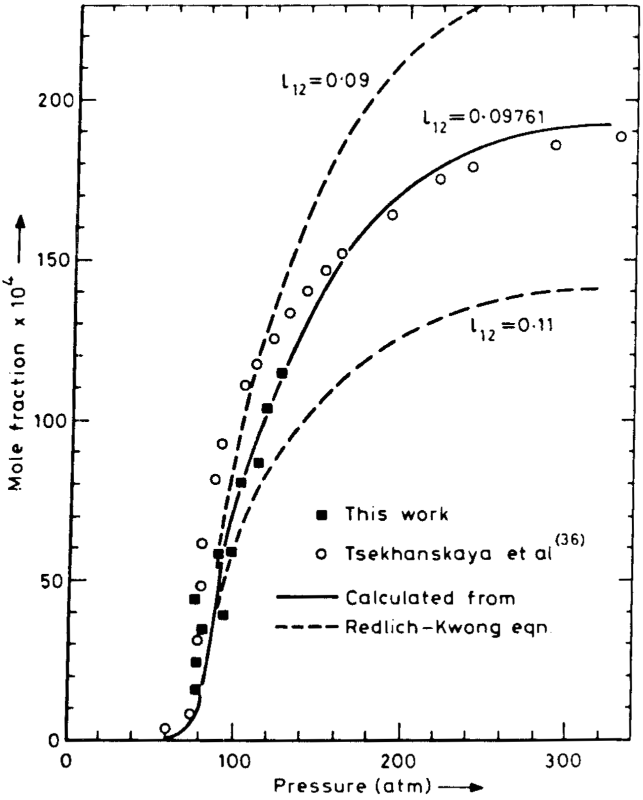

FIGURE 6. The solubility of naphthalene in compressed carbon dioxide at 35°C compared with values predicted by the Redlich-Kwong equation with a and b given by Soave's correlation. The work on which this figure is based is described in an accompanying paper (38).

carbon dioxide/naphthalene at 35.0°C can be collated quite well with l_{12} = 0.0976 (34).

3.2 Other Problems in the Design and Construction of an Extraction Unit

So far only one aspect of the design has been considered; there are other problems to be overcome. Those of a commercial nature are considered in Section 4, but there are others, some of which are listed below:

(1) Handling of solids. In the earlier section it was stated that one of the important characteristics of compressed supercritical gases was their good powers of penetration into solids. It is in the extraction of solids, therefore, that one potential application of the process lies. Unfortunately, it is very difficult to introduce solid material into a high pressure region and then to remove it without incurring a substantial loss of the high pressure gas. (The usual approach which is followed, for instance in the pressure gasification of coal, involves the use of lock-hoppers.

When comparatively high-boiling solvents (such as toluene) are used, the most favourable approach is probably to form a slurry between the solvent and the solid at a subcritical temperature and normal pressure and to inject this slurry into the high pressure region. The stream of pressurised slurry is then heated to the extraction temperature. This technique is employed by the National Coal Board (35).

(2) Development of an extract-recovery system which does not incur substantial energy loss. One method of recovery is to lower the pressure: the energy loss on raising the pressure of the recycled gas can then be recovered to some extent by carrying out the initial expansion through a turbine. Problems could result from this arrangement, however, since the deposit of solute and the possible presence of liquid droplets could produce severe erosion. Alternative techniques which have been tried are (a) adsorption in a fixed bed, (b) washing the gas with a subcritical liquid solvent, and (c) precipitating the solute by a change in temperature. These three alternatives do not involve extensive pressure changes.

(3) Pump design. Problems associated with the pumping of gases near critical conditions are well known to engineers who are required to work with these conditions. The combined effects of relatively high pressure and pressure gradients within the pump

system can lead to early pump component failure. These difficulties may be attributed to the substantial changes in the physical properties accompanying pressure changes near the critical point.

(4) Materials of construction. In certain processes, the necessary choice of solvent requires a relatively high temperature. This is the situation, for example, when using a complex solvent to extract coal substance. Earlier, trimethylbenzene and tetramethylbenzene were cited as suitable solvents for tar sands and oil shale at around 450°C and between 70 and 200 bar. Such conditions demand a high quality material of construction; even so, the vessel wall thickness required to withstand the severe conditions could be extremely large. Special fabrication and careful examination techniques would be required and these vessels would be expensive.

(5) Safety problems. The design of equipment to operate at elevated pressures requires care. Applications of gas extraction in the food industry should present less difficulty than in the coal industry since the extraction temperature is low. However, at the higher temperatures required in the extraction of coal and similar substances, the strengths of materials drop considerably and gland materials for valves will present difficulties. It should be pointed out that there is always a risk in operating with gases at high pressures or with liquids at pressures only slightly below the critical pressure since, in the event of failure, each element of fluid is capable of a very considerable degree of expansion.

(6) Contamination problems. As in other extraction processes there is a danger that the materials used to extract the product may contaminate the product. Contamination by an extracting gas, such as carbon dioxide or by impurities in it, is unlikely in gas extraction and the process is superior to normal liquid extraction in this regard. However, the use of entrainers could produce problems.

7) Control problems. The need for correct pressure and temperature programming of extraction processes cannot be over stressed.

(8) Possible difficulties in gaining acceptance for a process involving elevated pressures in industries not accustomed to high pressure processes. In some industries, e.g., the ammonia manfacturing process or coal gasification under pressure, high pressure technology is well understood and presents little difficulty in operation although adequate safety precautions are imperative. In other industries, such as food processing, the use of high pressure is quite alien and could lead to operating and safety problems. It is recognised, however, that even in the food industry, the use of high pressure steam for sterilising purposes is quite common.

4. COMMERCIAL PROBLEMS ASSOCIATED WITH THE PROCESS

4.1 Patent Problems

In many unique and difficult processes there is a tendency to use Patent Laws as a protection against competition. Often applications for patents are made on the very minimum of evidence in order to reserve a commercial position. Tables 1 to 3, which give only a relatively small number of patents, are sufficient evidence to indicate the difficulty with which a potential user of the process is faced. The morass of patents in the field makes it extremely difficult to determine if infringement is likely in a particular application. The situation, unfortunately, is likely to restrict the development of commercial processes.

Licensing of processes through patent protection may involve additional, and sometimes high, costs.

4.2 Capital Costs

High pressure process plants are not cheap. The additional requirements of the supercritical gas extraction process already described make the process very highly capital intensive. The technical problems, unless extensive research has been carried out, make capital investment a high risk.

4.3 Operating Costs

The need in some instances, as in the coal industry, for the use of high temperatures coupled with the other operating difficulties suggests that plant maintenance costs will be high. The use of high pressure may also result in excessive operating costs unless energy recovery can be effectively practised.

4.4 Scale Up Problems

The problems already noted in connection with design are emphasised in scale up operations. Empirical data obtained on a small scale are extremely difficult to translate into full scale operation. The reason for this difficulty is the lack of understanding of the mechanisms governing the rate processes in the extraction process.

The uncertainty of being able to "scale up" from laboratory type experiments makes it almost certain that pilot plant data would be required to reduce the risk associated with the high capital cost mentioned in Section 4.2. The use of pilot equipment represents further extensive costs and an inevitable delay in the commissioning of the commercial process.

5. EXPERIMENTAL APPARATUS

For the reasons outlined at the beginning of Section 3, we have, at Birmingham, carried out both phase equilibrium determinations and column tests.

The essential details of the column which we use and its flow diagram are shown in Fig. 1. It was designed and built to operate at a pressure of up to 110 bar (1600 psig) and about 150°C maximum. The volume of the still (autoclave) was 4.5 litres and the known charge for experimental work was of the order of 500-600 mL (relatively small samples were used to reduce the possibility of physical entrainment).

The control part of the equipment consists of a supercritical packed separation column (stainless steel Knitmesh, 2.54 cm I.D.). The top product from this passes through a pressure reducing valve to the receiver. Components deposited in this receiver are partly removed as product and partly refluxed. The carbon dioxide from the top of the receiver passes to the liquefaction, storage and pumping unit from which it returns (after vapourisation in a heated stainless steel coil) to the base of the still. The pressure is generated by two diaphragm pump heads which pump liquid carbon dioxide. These heads are placed in a deep freeze unit and are hydraulically actuated by a heavy mechanism outside the freezing cabinet. Some of the components in the liquid charge to the still (during the enriching mode of operation) or in the charge pumped into the head of the column with subsequent trickling down the packing counter-currently (during the stripping mode of operation) are selectively dissolved in the carbon dioxide stream rising up the column. The loaded carbon dioxide is partly cooled down during its passage through the pressure reducing valve, where the pressure is reduced to one-half or one-third. The pressure controller and the line downstream are electrically heated to prevent their freezing and blocking during the expansion of carbon dioxide. The low pressure carbon dioxide then enters the receiver (a pressure sight-glass, or later a stainless steel pipe) where the separation of the dissolved components should be completed (separation begins in the column head and continues in the top line before entering the receiver). The top product is withdrawn as it accumulates in the receiver or is partly returned as a reflux to the column head by means of a reflux pump. Carbon dioxide, containing droplets and traces of dissolved components, is then led to the demister (a tube packed with KnitMesh) and a carbon scrubber for purification before it enters the liquefaction coil and the reservoir of the liquid carbon dioxide in the deep freeze unit. Balancing the feed-rate of the fresh carbon dioxide and the withdrawal rate of the scrubbed carbon dioxide for liquefaction is a delicate operation which determines the actual flowrate of carbon dioxide through the column. This flowrate varied from about 10 to 100 mL of liquid carbon dioxide per minute. Difficulties of control can arise due to the malfunctioning of the carbon dioxide pump which is operating under adverse conditions.

Sampling points were provided at the centre and at the top of the column for direct micro-sampling. The microsamples were allowed to flow out through ports in the equipment and dissolved in a suitable organic solvent. Analysis was either by TLC or GLC techniques in another laboratory. Direct spotting of a thin layer chromatographic plate (as suggested by Stahl) has also been attempted. After some initial difficulties these tests were found to be valuable since they indicated the components (and unknowns) in a given sample.

In some of our work we have investigated the possibility of removing the product from the gas stream using adsorption columns. The equipment used in this work is shown in Fig. 7.

The apparatus was designed to operate at up to 100°C and 140 bar (2000 psig) max. The extraction unit consisted of a pressure feed vessel holding 7 litres of liquid, a preheater, a hot-air bath containing a temperature equilibrating coil with the extractor (and carbon columns, if used), a cooler, a split-flow double valve, a sampling arrangement (made of glass) and the LC detector for monitoring of the concentration of the extract.

Two types of extraction vessel were used in the experiments. The larger vessel (approximately 1.5 litres), an autoclave, was originally used for the extraction of liquids and later modified to reduce its volume so that smaller samples introduced/contained in some form of cylindrical cartridge could be extracted; the cup cartridge (with 8 cups, each approximately 1.5 mL, on a central stem) was used for soft solids and liquids; a static bed extractor of 76 mL capacity was used for high-melting solids. A small tubular

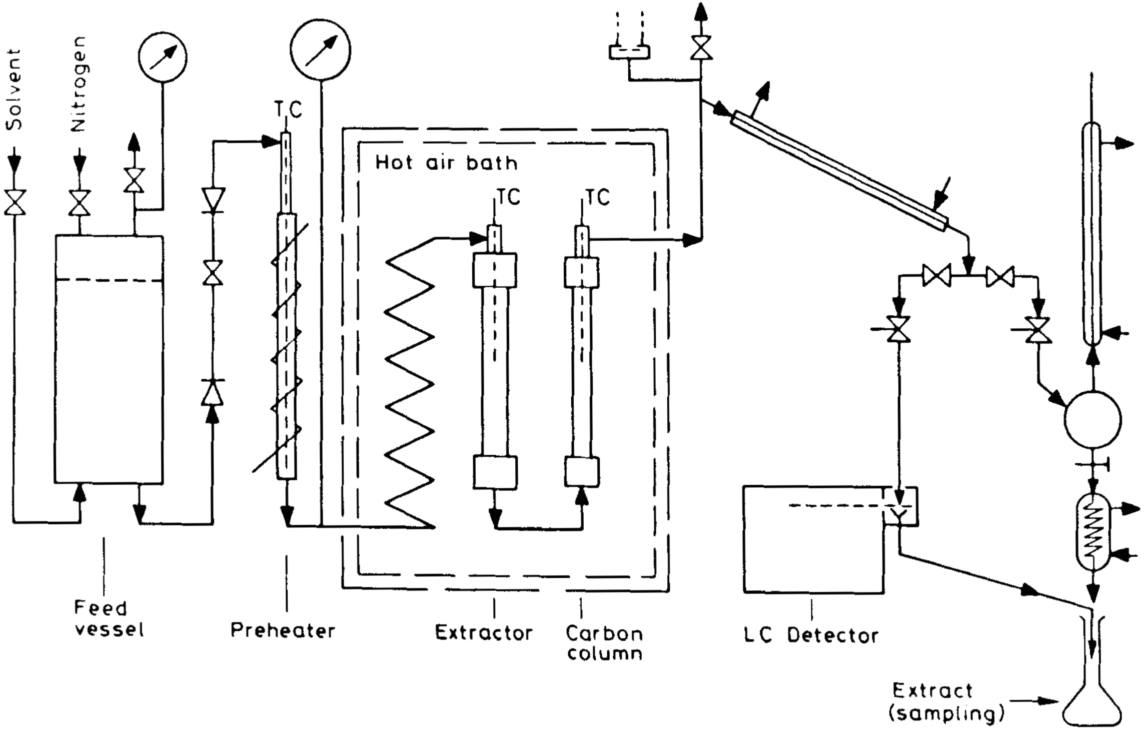

FIGURE 7. Sub- and super-critical extraction with separation by adsorption.

extractor made from a 20 mm I.D. stainless steel tube 23 cm long was used in later test runs, its extraction volume being 18 mL.

The two carbon adsorption columns were of 15 mm I.D. pipe 25 cm and 12 cm long respectively. The purpose of the columns (which were packed with commercially available activated carbon) was to effect a partial separation of the extract. The adsorbed material was separately analysed.

Continuous sampling and monitoring of the extract concentration was achieved using a liquid chromatograph detector (PYE System 2 with a FID detector).

A sensor indicating the actual physical state of the fluid during the extraction in the critical region was developed in the form of a heat and pressure-resistant Cerl-Planer strain gauge, based on a micro air-capacitor. The strain gauge was attached to a 2.54 cm (1 inch) OD plug to fit in the 2.54 cm (1 inch) port of the large extractor. Its normal capacitance was 1 pF (measured to 10^{-3} pF by the Wayne-Kerr Universal Bridge and recorded).

6. EQUILIBRIUM DETERMINATIONS

The equipment which is at present used for fluid systems is shown in Fig. 8. Some of our earlier work (including that on the ethylene/toluene system shown in Fig. 3) was carried out using a static cell with internal stirrer. In this equipment, which is to be described in detail in another publication, pressure was maintained constant during sampling by mercury injection.

In the equipment shown in Fig. 8, the vapour phase is recirculated through the liquid phase contained in the autoclave until equilibrium has been achieved under controlled conditions of temperature and pressure. Samples of the vapour and liquid phases are then valved off in sample bombs and the contents are analysed. During the analysis process the contents of the sample bombs are

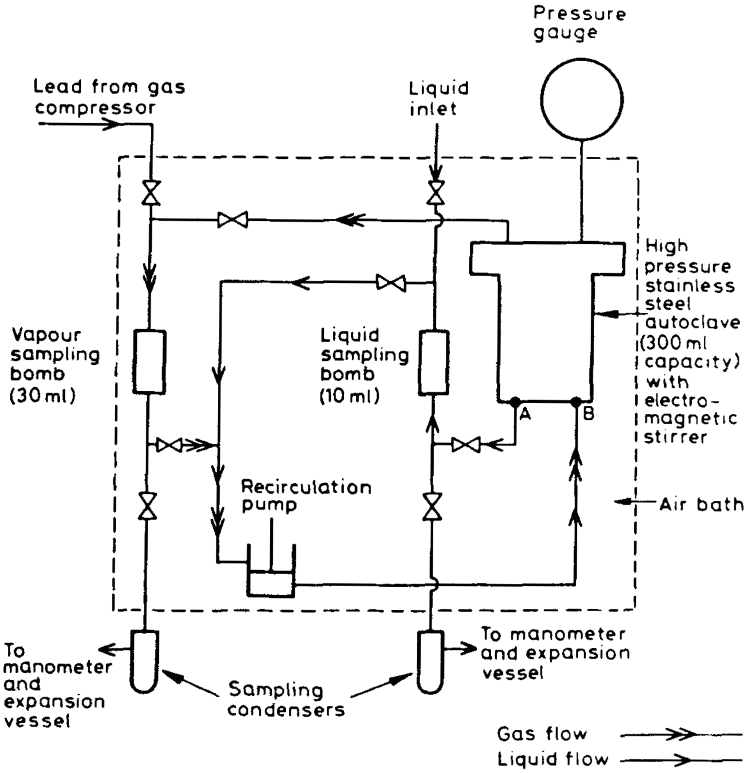

FIGURE 8. Equipment used for equilibrium determinations in fluid systems.

allowed to expand gently into previously evacuated glass sampling vessels, which are placed immediately beneath the bombs, and thence into evacuated metal expansion vessels of known volume (34.34 dm^3 in the case of the vapour sample bomb and 6.46 dm^3 in the case of the liquid sample bomb). If the extracted material has appreciable volatility, the sampling vessels are cooled by immersion in a suitable freezing mixture. The number of moles (and hence, the weight) of the lightest component, i.e., of the extracting gas, present in each sample bomb is calculated from the pressure rise in the expansion system during the expansion process. During this process the material which was intitially in solution in the compressed gas is deposited at and around the valves immediately below the sample bombs and also more generally within the sampling bomb and connecting piping. Some of this "heavy" material is carried down in the gas stream and collects directly in the glass sampling vessels. The remainder is transferred to these vessels by methods appropriate to the system under study. If the heavy material is comparatively volatile and mobile it has been found that a gentle slow nitrogen stream introduced immediately above the sampling bomb and vented via the sampling vessels (which in this situation are cooled with a freezing mixture) is effective for this purpose. If the "heavy" material is comparatively involatile, it is washed down into the receiving vessels using a suitable volatile liquid solvent, which is subsequently evaporated off. For example, the solvent used for the carbon dioxide/n-hexadecane/diphenylmethane system (Figs. 4 and 5) was acetone. (To be suitable, the solvent should be (1) capable of dissolving the extract readily and (2) its relative volatility with respect to the extract should be so large that losses of extract during the evaporation of the solvent are negligible. A blank test is carried out for each solute/solvent combination employed in which a known amount of extract is dissolved in the solvent. The solvent is then evaporated off and it is verified that no appreciable loss of extract has occurred). Having transferred the heavy extract to the sampling vessels and evaporated off the solvent, the weight of heavy material initially in the sample bomb is determined by weighing these vessels. In the case of a binary system, such as carbon dioxide/n-hexadecane (Fig. 4), this completes the analysis process, though spot checks on the purity of the extract are often made. In the case of a ternary system, samples of the extract are removed for further analysis. For example the mixtures of n-hexadecane and diphenylmethane which collected in the receivers in the work on the carbon dioxide/diphenylmethane system were analysed by gas chromatography (silicone gum type SE-30 was used as stationary phase in 1.52 m x 0.64 cm O.D.

(5 ft x ¼" O.D.) stainless steel columns which were operated with a flame ionisation detector at 200°C with nitrogen as carrier gas).

The equilibrium equipment which we use for studying extractions of solids and of components embedded in a solid matrix is very similar to the apparatus used for vapour liquid studies except for the omission of the liquid sampling bomb. This equipment was used for the studies on the extraction of naphthalene (Fig. 6) and tobacco leaves (Fig. 2), the wash solvents used being diethyl ether and acetone.

Most of the examples given earlier in the paper involve data obtained with the above pieces of equipment. A more detailed account of the equilibrium studies is in preparation.

7. CONCLUDING REMARKS

The problems associated with the introduction of supercritical gas extraction as a commercial process are formidable. The major difficulties are associated with the basic understanding of the thermodynamics of the process and the mechanisms of the rate processes involved. In addition, the design of commercial scale plant from laboratory results can present "scale-up" difficulties. Finally the engineering problems associated with high pressure accompanied by high temperature, in some instances, need acceptable solutions.

The protection of processes by patents and the costs associated with the technical problems represent commercial difficulties which also need solution before widespread use of the technology is possible.

Despite the difficulties, however, it is certain because of the inherent advantages of supercritical gas extraction that the process has a commercial future. The initial applications will be for high value products but as the technology develops its use in other extraction applications is more than possible.

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