BRANDSTOFNAVORSINGSINSTITUUT

VAN SUID-AFRIKA

FUEL RESEARCH INSTITUTE

OF SOUTH AFRICA

TEGNIESE
TECHNICAL MEMORANDUM   NO. 40 OF 1974

EXTRACTION BY MEANS OF GASES

OUTEUR :   J. JEZKO
AUTHOR :

EXTRACTION BY MEANS OF GASES

1. INTRODUCTION

The atmosphere of an inert compressed gas below its critical temperature
has little effect on the vapour pressure of liquids and solids that may
be associated with it, but on raising the temperature of the gas a re-
markable increase in the vapour pressure of the substrate occurs as soon
as the critical temperature of the gas is reached or exceeded*.
Under such circumstances the gas exerts a strong extraction effect on a
solid or liquid substrate.

Although the solvent power of compressed gases has been known for a
long time, it is surprising that more attempts have not been made to
apply this characteristic of pressurised systems to technological pro-
cesses.   Theoretically, the phenomenon, called gas extraction, has
certain distinct advantages over conventional liquid extraction and
molecular distillation.

The application of extraction capabilities of compressed gases near their
critical temperature to practical processes such as the removal of asphalt
from petroleum and separating pure substances from ozocerite and coal-
derived substances, has demonstrated the technological feasibility.
Suggestions have been made that the technique could be applied in the
manufacture of liquid fuels from coal.

There is strong evidence that this phenomenon plays an important role in
natural processes such as mineral deposition and the migration and
accumulation of petroleum in traps.

/A ....

----

*For instance, in the presence of ethylene at 285K (12°C) and 10 000 kPa
  (100 atm) the vapour pressure of naphthalene is increased by a factor of
  26 000 (1).

A brief summary of the theoretical basis of gas extraction and some practical applications are given in this report as an introduction to a comprehensive investigation that is to be initiated. The equipment required for the investigation is on order.

2. BASIC QUALITATIVE CONSIDERATIONS

The density-pressure diagram[1] (Fig. 1) shows that by compressing a gas to a certain pressure while the temperature is kept above the critical temperature, the density of the gas approaches that of the liquid. Also from the diagram it follows that the nearer the temperature is to the critical, the less compressed the gas must be to reach the same density. Gas of the same density as that of its liquid might be expected to have a solvent power similar to that of the liquid. Thus, at a given pressure the solvent power of a gas should be greater at lower temperatures (above critical), and at a given temperature the solvent power should be greater at higher pressures.

Control of the solvent power by simply changing the pressure can be of great advantage in extraction processes. For example, recovery of the solvent gas and of the extracted material is achieved merely by decompressing the solution.

Using the Phase Rule, a better description of the gas extraction system can be made than that given by single density-pressure relations.

For a two-component system the three-dimensional form of the phase diagram is needed. For this case the P-T-X (pressure-temperature-composition) diagram is the most suitable (2,3).

The general behaviour pattern of a liquid compressed-gas system can be seen from Figure 2,[1] which is a pressure-composition of a P-T-X diagram for constant temperature. The solvent gas is called component 1 and the solute component 2. Decompressing the system from point k to l

/yields ....

yields two phases at m and n.

In a gas-solid system the melting point of the solid is usually higher than the critical temperature of the gas.

Two cases may occur[2,3,4]: (a) the saturated vapour curve does not cut the critical points curve. (b) The saturated vapour curve cuts the critical points curve into two sections. P-T projections for these two cases are shown in Figures 3 and 4.

The type of behaviour given in case (b) occurs when the solubility of the solid is low. The critical curve is cut into two sections. The points between which there are no critical points are called, respectively, the lower and the higher critical endpoint. It is the region between those two points which is of the most interest here, because in this region the equilibrium is found only between two phases, i.e. solid and gaseous. The P-X sections of such a system for different temperatures are shown in Figure 5[1,2,3]. The dashed curve shows the ideal (Daltonian) behaviour.

3. QUANTITATIVE DESCRIPTION

With the help of statistical mechanics, a quantitative description of the system solid-gas can be made[1,2]. Liquid-gas systems are, however, much more complicated because the gas always dissolves in the liquid. To make the system amenable to theoretical treatment, it is assumed that solubility of the gas in the solid is negligible.

Only the final expression will be given here, the derivation of which can be found in the literature[1,2,15].

$$\ln \frac{X_2}{X_2{}^o} = \frac{P\,V_2{}^s}{RT} - \frac{2B_{12}}{V} - \frac{\frac{3}{2}\,C_{112}}{V^2} - \frac{\frac{4}{3}\,D_{1112}}{V^3} \quad \ldots\ldots\ldots\ldots\ldots \text{ (a)}$$

or in another form

$$\ln \frac{X_2}{X_2{}^o} = \frac{V_2{}^s - 2B_{12}}{V} + \frac{V_2{}^s\,B_{11} - \frac{3}{2}C_{112}}{V^2} + \frac{V_2{}^s\,C_{111} - \frac{4}{3}\,D_{1112}}{V^3} \quad \ldots\ldots\ldots \text{ (b)}$$

where X_2 is the molar fraction of component 2 in the solution,

$\quad\quad X_2{}^o$ is the molar fraction of component 2 in its pure saturated
vapour,

$\quad\quad P$ is the pressure,

$\quad\quad V_2{}^s$ is the molar volume of the solid,

$\quad\quad R$ is the gas constant,

$\quad\quad T$ is the temperature,

$\quad\quad B_{11}$, C_{111} are the second and third virial coefficients of
component 1,

$\quad\quad B_{12}$, C_{112}, D_{1112} are the cross virial coefficients.

For most practical purposes equation (b) can be terminated after the
second term on the right-hand side and for many purposes it can be
terminated after the first term.

The virial coefficients can, in principle, be computed in absolute terms
by statistical mechanics. This computation is so tedious that empirical
methods of estimating the cross-virial coefficients[2,4] were developed.
The second and a few third virial coefficients for pure gases can be
found in the literature[17,18].

Equation (a), terminated after the first term on the right-hand side,
is Poynting's wellknown equation. Figure 6 shows the composition of
solutions of carbon dioxide in compressed air in equilibrium with solid
carbon dioxide at -110°C. The full line is an experimental curve obtained
by Webster[16] and the dashed curves are for: (1) an ideal gas mixture,
(2) an ideal mixture with Poynting's correction for the effect of pressure
on the activity of the solid, (3) solubility calculated from equation (b).

/4. ....

4. GAS EXTRACTION COMPARED WITH LIQUID EXTRACTION AND DISTILLATION

Gas extraction can be considered as an alternative to extraction with liquid solvents and to distillation.

With gas extraction it is possible to achieve much higher gas-phase concentrations than with distillation, but it does not compare favourably with solute concentrations in liquid extractions. On the other hand, the advantage of gas extraction lies in the better separation of "solvent" from the extract and the residue. This advantage may even eliminate the need for a subsequent filtration stage. Gas extraction, like distillation, will yield a product which is free from solid contaminants such as mineral matter and insoluble material. In this connection it must be mentioned that the filtration of coal-liquid solvent extraction systems is a particularly difficult operation.

Another advantage gas extraction has over liquid extraction is in the matter of solvent loss. Most liquid solvents are expensive and in large-scale practice the loss of even small quantities of solvent may affect the economic viability of a process. This disadvantage is particularly important in the case of liquid extraction of coal where a small proportion of useful product is extracted from an inert solid contaminant. The losses involved in gas extraction are relatively small because the residue will only be gas contained at atmospheric pressure in the pores of the residue.

Gas extraction also has several advantages over distillation. Although the energy requirements of gas extraction are roughly equal to those of distillation, the cost of gas-pumping may be considerably reduced by the simple technique of feeding the gas into the system as a liquid and then raising the temperature to supercritical. The most attractive advantage of gas extraction over distillation is that substances of low volatility can be processed. In this respect gas extraction is an alternative to molecular distillation. Molecular distillation is carried out at low pressure and therefore at low gas-phase concentrations.

On the other hand, with gas extractions high gas-phase concentrations prevail so that a considerable increase in throughput should result.

5. PRACTICAL APPLICATIONS

The practical application of the principle of gas extraction involves the contacting of a substrate with a compressed gas, isolating the gas phase containing the dissolved material, and decompressing the isolated gas phase, which results in the destruction of the extraction capability of the gas, thereby precipitating the dissolved material.

The power of gas extraction has been amply demonstrated by using pure chemical systems[5,6,7]. These studies are of academic interest only and will not be discussed.

On the other hand, only a few investigations of a more practical nature, involving e.g. complex mixtures of hydrocarbons such as petroleum and coal tar, have been undertaken. Since the results of these investigations are of particular interest in the context of the present need to convert coal, they will be discussed in more detail.

The properties of gas extractants

The physical parameters rather than the chemical nature of an extractant are important. Therefore there is a wide range of commercially available compounds with different critical parameters to choose from.

In Table 1 some twenty compounds, covering the temperature range $191^{\circ}K$ ($-82^{\circ}C$) to $620^{\circ}K$ ($347^{\circ}C$) (taken from a compilation made by Kudchadker et al (13), are listed.

TABLE 1

CRITICAL DATA

Substance	Critical Temperature		Critical pressure MPa*	Critical density g cm^{-3}
	K	°C		
Ammonia	405	132	11,29	0,235
Carbon Dioxide	304	31	7,38	0,468
Methane	191	-82	4,88	0,162
Propane	370	97	4,24	0,217
n-Pentane	470	197	3,37	0,237
n-Octane	569	296	2,38	0,232
Ethylene	282	9	5,03	0,218
Propylene	365	92	4,62	0,233
Benzene	562	289	4,89	0,302
Toluene	592	319	4,11	0,292
Methanol	512	239	8,09	0,272
Acetone	508	235	4,70	0,278
Diethyl ether	467	194	3,64	0,265
Tetrahydrofuran	540	267	5,19	0,322
Chlorotrifluoromethane	302	29	3,92	0,579
Trichlorofluoromethane	471	198	4,41	0,554
Diethylamine	497	224	3,71	0,243
Pyridine	620	347	5,63	0,312
Sulphur hexafluoride	319	46	3,76	0,734
Nitromethane	588	315	6,31	0,352

* 10,133 atm = 1 MPa

Extraction of crude oil with compressed gases

Zhuze and Yushkevich published two papers dealing with gas extraction of crude oil[8,9]. The gases used were methane, ethylene, propane, propylene, carbon dioxide and mixtures of some hydrocarbons. The pressures varied from 5 to 80 MPa and the temperatures from 40 to 105°C. Their conclusions are:

1. In the pressure interval investigated, the solubility of crude oil in the gas increased with increasing temperature and pressure. Pressure increase has a more pronounced effect on solubility than temperature increase.

2. Increasing the volume ratio between gas and crude oil has the effect that the solubility of crude oil in the gas decreases, while with a decreasing ratio the solubility increases, reaching a constant maximum.

3. The solubility of the crude oil in the gas depends on the composition of the crude oil. The crudes rich in light fractions and poor in asphalt-resin components dissolve better than crudes rich in heavy fractions, under the same conditions. In the process of dissolution the gas phase dissolves the light components of the crude oil, while the residue contains the high-boiling components, including the asphalt-resin fraction.

4. The composition of gas extractant has a great effect on the solubility of crude oil.

5. Methane seems to be a poor solvent, while carbon dioxide is a very strong solvent for crude oil.

6. The solvent strength of hydrocarbon gases for crude oil increases in the series methane-ethane-ethylene-propane. Mixing these gases with methane increases the solvent power considerably. The

solubility of crude oil in mixtures of hydrocarbons which contain propane and propylene has strong extraction properties even at relatively low pressures.

7. The paraffinic and naphthenic hydrocarbons are dissolved at lower pressures than aromatic hydrocarbons with the same number of C atoms. Similarly, to dissolve bi- and polycyclic aromatics higher pressures are needed than for monocyclic aromatics.

De-asphalting of petroleum

Zhuze[11] describes the pilot-plant-scale de-asphalting of petroleum fractions, using compressed gas as an extractant. The plant can handle 150 kg of feedstock per day. The gas used is a mixture of propane propylene, containing from 6% to 27% propylene. The gas is compressed at $100^{O}C$ to 10 - 11 MPa and mixed in a ratio 2-3:1 by weight with the petroleum fraction to be de-asphalted. The solution of the hydrocarbon part of the stock in the compressed gas is decompressed to 4 - 5 MPa, at which pressure the gas loses its solvent capacity and the de-asphalted product precipitates. The gas is compressed again to initial pressure and returned to be mixed with the feedstock.
Advantages noted by Zhuze are as follows:

1. The gaseous solvent is easily regenerated, whereas with conventional methods (by means of liquid propane) multistage regeneration of propane is involved.

2. The ratio of the gas to the raw feedstock is small (2-3:1) compared with the conventional method (5:1).

3. The degree of compression of the circulating gas is only 2-2,5. (The energy consumption for compression is determined only by the degree of compression and not by the absolute value of the pressure.)

4. The constructional requirements of the plant for de-asphalting
   by compressed gases are much less than for plant using the conven-
   tional propane process.

Removal of ozocerite from ores

In the same paper[11] Zhuze describes the use of the compressed gas for
the extraction of ozocerite from ores.

The ore is charged into a column and heated to $100^{\circ}C$, and the compressed
(9 - 10 MPa) propane-propylene mixture is fed from the top. The
solution of ozocerite in the gas passes to the separator where the
pressure is reduced to 4 - 4,5 MPa and the ozocerite precipitated.
The regenerated gas is then recompressed to initial pressure and fed
back for further extraction. The product is periodically drawn off
into a heated collector at atmospheric pressure, where the residual
gas dissolved in the ozocerite is separated. The ratio of gas to
extracted product is 6-7:1 by mass.

The conventional method of extraction of ozocerite from ores is with
benzene. The characteristic features of this method are the incomplete
extraction, high losses of benzene in regeneration (1-1,2 tons per ton of
extracted ozocerite) and high resin content in extracted raw material.

For the purification of the extracted raw material, Zhuze proposed the
use of compressed gas as well. This eliminates the inconvenient conse-
quences of the use of concentrated sulphuric acid. The sulphuric acid
causes the oxidation and sulphonation of the most valuable branched
paraffins. The consumption of sulphuric acid is high and the yield of
commercial ceresin (wax) is low (70 - 75% of the ozocerite).
Furthermore, ceresin of only one melting point is produced.

By using a compressed gas as the extracting medium, the ceresin fractions
of different melting points can be produced by simply carrying out the
extraction in a number of increasing pressure stages (e.g. 6, 8, 10 MPa.

Coal-tar extraction

The Coal Research Establishment (England) has built equipment to study the extraction by compressed gases of coal-based systems[10]. The extraction of coal tar by ethylene at 25°C and 32 MPa was undertaken. Tar was brought into contact with ethylene, the gas phase removed for analysis, and the stripped tar again brought into contact with compressed gas. The process is analogous to differential distillation. It was shown that tar could be readily distilled in a compressed ethylene atmosphere to a hard pitch without the temperature being raised above 25°C.

Extraction of coal solution

A recent patent spesification[14] refers to the use of a gas extractant to recover, from a solution of coal in a liquid solvent, a fraction suitable as a feedstock for hydrocracking to gasoline.

Summary and proposed investigation

Gas extraction is a promising technique that can be utilized for the extraction and recovery of usable chemicals from complex substrates such as petroleum, coal, tar, and other carbonaceous materials. The technique has advantages that make it particularly attractive in cases where conventional separation techniques present difficulties in the recovery of solvents and extracted material.

The principles of gas extraction are well understood and, at least for simple systems, can be described by means of relatively simple mathematical expressions.

Since the chemical properties of the extractants do not play a significant role, gas extractions can be undertaken using a wide range of pressures and temperatures.

/A ....

A preliminary investigation is under way to evaluate the technique in
general, and the amenability to extraction of local coals in particular.
The equipment required for this work is on order.   Depending on the
results of these tests, further work may be undertaken to determine
the conditions for optimum extraction, to analyse the products and to
collect data for economic feasibility studies.

J. JEZKO
RESEARCH OFFICER

PRETORIA.
4/11/1974.
JJ/KW.

LITERATURE REFERENCES

1. Paul, P.F.M., Wise, W.S. "The Principles of Gas Extraction",
    M & B Monograph CE/5, Mills & Boon Limited, London, 1971.

2. Rowlinson, J.S., Richardson, M.J. Advan. Chem. Phys. $\underline{2}$, 85-118
    (1959)

3. Roozeboom, H.W.B. "Die Heterogenen Gleichgewichte" vol. 2,
    part 1. Braunschweig, 1904.

4. Prausnitz, J.M. A.I. Ch. E. Journal $\underline{5}$ (1), 3, 1959.

5. Diepen, G.A.M., Scheffer, F.E.C. J. Am. Chem. Soc. $\underline{70}$, 4085,
    (1948)

6. Diepen, G.A.M., Scheffer, F.E.C. J. Phys. Chem. $\underline{57}$, 575, (1953)

7. Tsekchanskaya In. V. Iomtev. B.B. Mushkina E.V., Zhur, Fiz.
    Khim. $\underline{38}$, 2166 (1964)

8. Zhuze, T.P., Yushkevich, G.N. Izvest. Akad. Nauk S.S.S.R., Otdel.
    Tekh. Nauk $\underline{11}$, 63-68 (1957)

9.   Idem, ibid. 12, 83 (1957)

10.   Wise, W.S. Chemistry and Industry, July 1970, p.950.

11.   Zhuze, T.P. Petroleum (London) 23, 298 (1960)

12.   Giddings, T.C. Science 162, 67 (1968)

13.   Kudchadker, A.P. Alani, G.H. Zwolinski, B.T. Chem. Rev. 68, 659 (1968)

14.   Hemminger, C.E., Stahl, S. Def. Publ. U.S. Pat. Off. 700485, (22 April 1969)

15.   Rowlinson, J.S. in S. Flüge, ed., Handbuch der Physik, Springer, Berlin, 1958, Vol. 12, Chap. 1, Sec. 6.

16.   Webster, T.J., Proc. Roy. Soc. (London), A214, 61 (1952)

17.   Guggenheim, E.A. Revs. Pure and Appl. Chem. (Australia) 3, 1 (1953)

18.   Pitzer, K.S., et al., J. Am. Chem. Soc., 77, 3427 (1955)
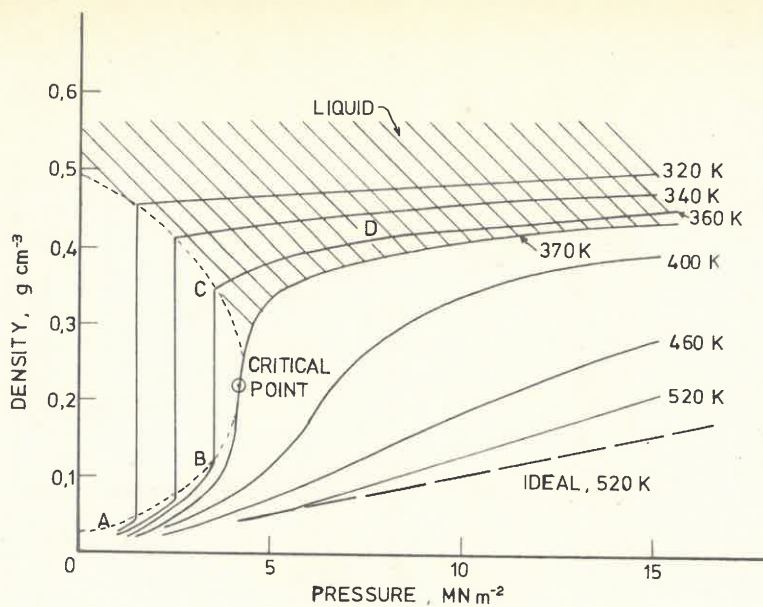

FIG. 1

THE DENSITY OF PROPANE AS A FUNCTION OF
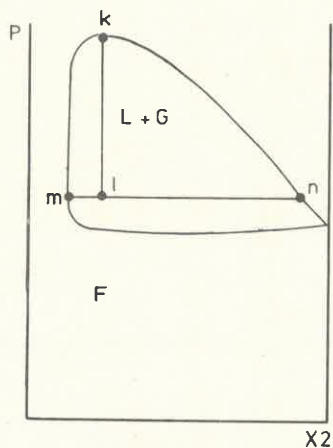PRESSURE AT DIFFERENT TEMPERATURES.

FIG. 2

THE P-X SECTION, AT CONSTANT TEMPERATURE, OF THE
P-T-X PHASE DIAGRAM FOR A TWO-COMPONENT SYSTEM
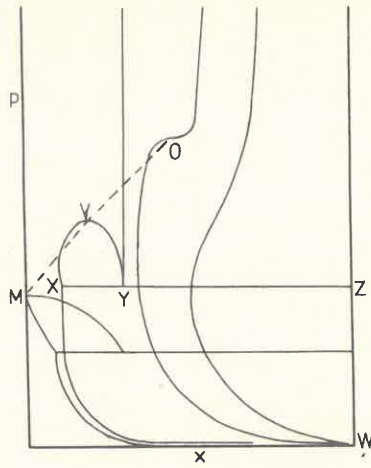ABOVE THE CRITICAL TEMPERATURE OF COMPONENT 1.

FIG. 5

SECTIONS AT CONSTANT TEMPERATURES LYING BETWEEN
THE CRITICAL POINT OF THE FIRST COMPONENT M, AND
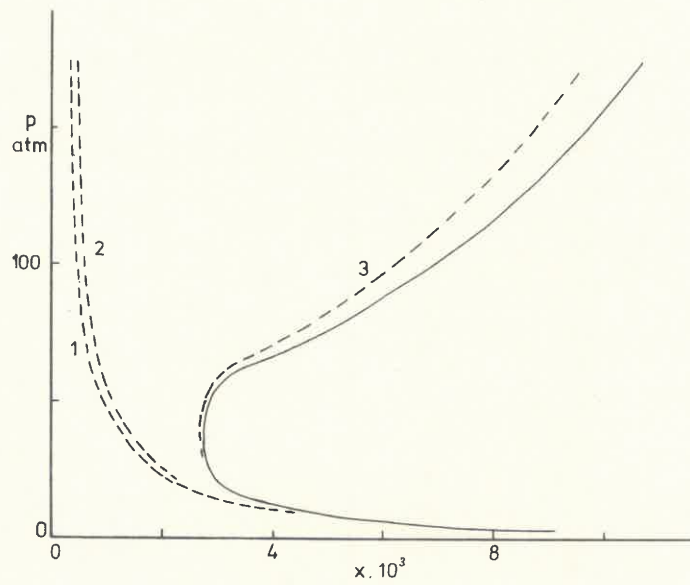THE LOWER CRITICAL END POINT, O.

FIG. 6

THE MOLE FRACTION OF CARBON DIOXIDE IN SATURATED
SOLUTIONS IN AIR AT −110 °C