"EXTRACTION OF OIL-SHALE"

By

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The world supply of petroleum is a natural resource that is rapidly being consumed. The fact that the supply is not inexhaustible, and the gravity of the situation that will result from the supply becoming so depleted as to be inadequate to meet demands have been generally appreciated only within the past few years. As a result there is now a widespread effort to conserve petroleum and its products, and to seek possible substitutes for it.

Even to-day, when the proven world sources of petroleum will last for several decades, many countries fearing that they will be cut off from the supply through war or other reason, are frantically searching for new fuels. For Great Britain especially, who imports all her oil, the question of possible substitutes for petroleum is of national importance.

As a source of substitute for petroleum oils, the reserves of oil shale in many countries throughout the world stand out as most important. Oil shale deposits in Scotland, France and Australia have been the source of products similar to those obtained by petroleum, and it is highly probable that the vast deposits of the United States and other countries will be extensively worked in the future.

Under present conditions the shale industry is unable to compete with the petroleum industry, largely because the only system employed is that of retorting. A retorting process for oil-shale cannot compete with petroleum, for though the investment cost of a retorting plant is much less than the average "well cost" of petroleum per barrel,
the cost of producing petroleum is much lower than that of producing an
equivalent quantity of shale-oil.

Difficulties involved in a retorting process are:

1. Maximum yield by distillation for average good grade oil-shale is
   40 gallons per ton of shale.
2. Retorts and equipment become rapidly corroded by reason of the high
temperatures involved in the process.
3. The high temperatures cause a certain amount of decomposition or
   cracking of the oil which affects adversely the products of the
   refining process.
4. The retorting process is not a continuous process.

If however, a continuous solvent extraction process could
be developed which would remove a larger fraction of the bituminous con-
stituent of the shale the cost of production could be reduced. High
temperatures would be unnecessary, corrosion avoided, extracted material
would not undergo decomposition, and the solvent recovered. The cost of
mining the shale which is 53% of the total cost in the retorting process
would be increased slightly for it would be necessary to secure fine
grinding for a solvent process.

Whether or not a new process for oil-shale could be made
a commercial success within the next few years, or whether it will have
to await further decreases in the world petroleum supply, the fact remains
that incalculable work needs to be done in the investigation of the
chemistry of shale-oil; that this field has been barely touched by workers
in the past, and that no time must be lost in pressing further investiga-
tions.
Soxhlet Extractors
SHALE INVESTIGATED

A representative high-grade Canadian oil-shale was chosen - Albert shale - obtained by the Department of Mines, Ottawa, from the vicinity of Rosevale, Albert County, New Brunswick. These particular samples, however, are not as good grade as most Albert shale.

Albert shale is dull black in colour when mined, but becomes brownish on exposure to the air, and in many ways corresponds to the Scottish shales.

The shale grinds and pulverizes easily with little dirt, and leaves no oil matter on the machinery.

TRIAL EXTRCTIONS

40-mesh shale was dried at 90 degrees, dessicated, and 35 gram samples used. Samples were extracted with acetone, benzene, propionic acid, and butyric acid, using Soxhlet extractors on hot plates. Each extraction was run for 200 hours, changing the solvent occasionally. Minimum heat was employed, using asbestos padding where necessary.

The solvents were distilled off under reduced pressure, and the extract residues dried in evaporating dishes on water-baths, for several hours. The brown-black asplalt products were dessicated and weighed.

Portions of the extracts were calcined to determine the percentage of inorganic material which was present. Qualitative analysis of the inorganic portion indicated the presence of Al, Fe, Zn, Ca, Mg.

1. For a fuller description see:
VACUUM DISTILLATION
The butyric extract was dissolved in benzene, filtered, solvent distilled, and extract dried on a water bath. Extract was weighed and calcined.

The following table was obtained:

<table>
<thead>
<tr>
<th>SOLVENT</th>
<th>TOTAL EXTRATION</th>
<th>TOTAL ORGANIC</th>
<th>TOTAL SOLUBLE IN BENZENE</th>
<th>ORGANIC SOLUBLE IN BENZENE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>2.4</td>
<td>2.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>3.0</td>
<td>3.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Propionic</td>
<td>23.4</td>
<td>18.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Butyric</td>
<td>20.7</td>
<td>16.5</td>
<td>14.7</td>
<td>11.8</td>
</tr>
</tbody>
</table>

(Figures are percentages of original shale).

**ANALYSIS OF THE SHALE**

A method for the determination of the organic matter, employed by Gaissen and Bader is tried. Finely powdered samples of the shale was fused with six times their weight of sodium hydroxide, with vigorous stirring over a low flame. The melt was poured into water, and filtered. The greyish-brown residue contained most of the silica in addition to the organic matter. The inorganic matter was leached out with dilute hydrochloric acid, and the residue was dried to constant weight at 100 degrees. This gave organic matter 36.92% which is high, probably.

CARIUS DETERMINATIONS.

COMBUSTION TRAIN
Samples of shale were dried in an oven, and then calcined in porcelain crucibles.

- Moisture = 0.85%
- Organic Matter = 29.15%
- Ash = 70.00%

Samples of the shale were heated in partially covered crucibles in a muffle furnace at 450°C, dessicated and weighed. Volatile material at that temperature was 19.6% of which 18.75 is organic (less moisture).

Carius determinations for sulphur and chlorine were made, following Gattermann's procedure.

Although micro analysis is considered simpler and more accurate for this type of work, there was available only apparatus for macro analysis. The Liebeg method was employed, using a quartz tube. The tube was heated at white heat for four hours, passing over oxygen instead of air. The average of four runs was taken, the values not checking well.

**TABLE OF ANALYSIS**

<table>
<thead>
<tr>
<th>S</th>
<th>CL</th>
<th>C</th>
<th>H</th>
<th>C/H</th>
<th>ORGANIC MATTER</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.004</td>
<td>0.355</td>
<td>9.87</td>
<td>1.68</td>
<td>5.86</td>
<td>29.15</td>
</tr>
</tbody>
</table>

EXTRACTION APPARATUS.
CONSTRUCTION OF EXTRACTION APPARATUS

Following the relatively successful extraction using the special solvents propionic and butyric acid, it was decided to attempt extraction on a larger scale. For this purpose three columns or stoves, 5 centimeters in diameter and 100 centimeters in length, were each wrapped with two parallel circuits of nichrome resistance wire and the outside heavily lagged with 1/8 inch asbestos paper.

The accompanying diagram shows how the stoves are placed on the frame work by means of adjustable copper bands, with glass delivery tubes leaving from the bottom of one stove to the top of the next. The stoves are staggered so that they are continually over half full of solvent.

Storage flasks with stop-cocks are provided at the top of the first stove and at the top of the heavily lagged 1000 centimeter distilling flask. The distilling flask is provided with peep-hole and back lighting and has a stop-cock in the bottom for the removal of the extract to vacuum distillation. The flask is heated on a sand-bath by a gas ring.

The distilled acid can be either removed from the system or sent back to the top by an air-lift. At the other end of the plant fresh acid is sent to the starting point from the supply, by air-lift.

The wiring diagram shows that the three stoves are connected in parallel but are provided with individual knife switches so that they can be heated independently. A variable resistance is included which can be cut out of the circuit when desired.

The stoves are provided with alumel-chromel thermocouples
and a direct reading pyrometer.

OPERATION OF THE EXTRACTION APPARATUS

After a trial run, followed by minor changes and adjustments in the apparatus, the main extraction was made.

Glass-wool was placed at the bottom of the stoves and a charge of 800 grams of shale added to each, with the following dimensions:

- Bottom layer: 10 mesh,
- Next layer: 20 - 40 mesh,
- Next layer: 40 - 60 mesh,
- Top layer: 20 mesh.

The charges half-filled the stoves and were entirely covered by solvent during the process.

The stoves could only be heated under supervision to prevent solvent boiling and escaping from the top; to regulate the flow of acid; to watch the distillation; and to return acid when necessary. The storage flask above the distillation flask was very important in the regulation of flow, for when gas in the stoves expanded quickly solution came over at a faster rate than the distillation could handle. It required nice adjustment to obtain regularity in the steps of the process.

Whereas the length of time of the extraction was 45 days or 1080 hours, the actual time of supervised heating with distillation was only 150 hours. Distillation of 350 c.c. batches could be run at approximately hour intervals. On the average 1800 cc. of acid were run through a day for the 30 working days, or a total of 54,000 c.c.
For the first few days the extract came over black, gradually lightening in colour through various stages of brown to a light red tinge. The temperature of the stoves was maintained as far as possible at 150°C., but the times when they did overheat the extract came out darker.

After every five batches of distillation, the heavy extract was run off and sent to vacuum distillation which was being operated simultaneously.

The extraction was continued until when for a week the weight of extract was reduced from 5 to 5 to 4 to 4 to 3 to 3 to 3 grams, for each 1800 cc. of acid put through.

551 grams of product were obtained which is a yield of 23.4%. This was a hard brown solid with a jet black brittle coating of very high lustre. On standing a few hours exposed brown surface changes to shiny black.

**TREATMENT OF THE EXTRACT**

The extract was tested for inorganic matter by calcining samples in platinum crucibles. It was found that 20.3% was inorganic, which means that the extraction removed 18.7% organic material from the shale.

10 gram samples of the extract were dissolved in carbon bisulphide, carbon tetrachloride, benzene, and petroleum ether. The solutions were filtered, washed with solvent until clear, the solvent distilled off, and the extracts dried on water baths.
In each case the extracted portion and the unextracted portion was tested for inorganic material by calcining in platinum crucibles.

Evidence of paraffin precipitating out could be seen on the flasks and funnels. In the case of the petroleum ether solution there was quite a heavy red precipitate remaining in the flask.

A 50 gram sample of extract was taken and extracted with petroleum ether, and this extract reduced to about 75 cc. in a tube inside a Dewar flask. The flask was cooled to minus 45°C. by solid carbon dioxide in methyl alcohol, and propane passed into solution to precipitate the high molecular weight hydrocarbons. A volume of liquid propane equal to the volume of extract solution was added, but no precipitate resulted.

The procedure was repeated, using a carbon bisulphide extract solution, but again no precipitate resulted.

The following table of results was obtained from experiments on the butyric acid extract:

<table>
<thead>
<tr>
<th></th>
<th>YIELD AS % OF BUTYRIC EXTRACT</th>
<th>YIELD AS % OF SHALE</th>
<th>% ORGANIC IN UNEXTRACTED PORTION</th>
<th>% ORGANIC IN EXTRACTED PORTION</th>
<th>YIELD OF ORGANIC MATERIAL SOLUBLE IN THE SOLVENT AS % OF SHALE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butyric Acid</td>
<td>100.0</td>
<td>23.4</td>
<td>79.7</td>
<td>18.7</td>
<td></td>
</tr>
<tr>
<td>Petrol Ether</td>
<td>20.6</td>
<td>4.84</td>
<td>86.5</td>
<td>4.17</td>
<td></td>
</tr>
<tr>
<td>Carbon Bisulphide</td>
<td>22.8</td>
<td>6.97</td>
<td>72.3</td>
<td>80.95</td>
<td>5.64</td>
</tr>
<tr>
<td>Carbon Tetrachloride</td>
<td>45.5</td>
<td>10.2</td>
<td>72.0</td>
<td>78.4</td>
<td>8.00</td>
</tr>
<tr>
<td>Benzene</td>
<td>45.6</td>
<td>10.6</td>
<td>71.6</td>
<td>80.85</td>
<td>8.55</td>
</tr>
</tbody>
</table>
A numerical example will serve to clarify the above. Suppose two 10 gram samples of butyric extract are taken. Carbon bisulphide will remove 2.98 grams and leave 7.02 grams; of that 2.98 grams, 2.39 grams are organic and 0.59 grams are inorganic; of the 7.02 grams, 5.05 grams are organic and 1.97 grams are inorganic. Benzene will remove 4.54 grams leaving 5.46 grams; of the 4.54 grams, 3.64 grams are organic and 0.90 grams are inorganic; of the 5.46 grams, 3.92 grams are organic and 1.54 grams are inorganic.

INTERPRETATION OF DATA OBTAINED

On the large scale extraction the total yield of product was 25.4%, or 18.7% organic yield, while on the small scale it was 20.7% total yield or 16.5% organic. Yet despite this on the large scale the yield soluble in benzene was 10.6% or 8.55% organic, and on the small scale was 14.7% or 11.8% organic. Why is it that in our trial extraction we got a smaller yield but a 25% increase in the amount soluble in benzene? It would appear that the large scale extraction was carried on for too long a period - 1080 hours against 150 hours in the Soxhlet extraction - and that the acid had too great an opportunity to act on the inorganic material in the shale. The formation of calcium and magnesium butyrates would account for the large percentage of organic matter and yet the relatively small part of this which is soluble in ordinary solvents. It is probable that the bituminous material was removed very early in the extraction, and that the remainder of the extraction merely succeeded in attacking other constituents.
The portion of the extract insoluble in the various solvents, which was over 70% organic, would be largely butyrates.

It is rather surprising that benzene should remove more organic material than carbon bisulphide. One might suspect that not all the heavier solvent was evaporated from the extract, but this is not the case. The extract was heated for several hours on the water-bath and continually pricked with a pin, until the extract was solid.

Benzene added to the substance insoluble in petrol ether removes 16.4% of the original extract, bringing the combined extraction to 37% yield.

The fact that liquid propane did not bring down a precipitate indicates the absence of high molecular weight hydrocarbon in the solvent extracts examined.

CONCLUSION

A yield of 8.56% of the shale organic matter soluble in benzene would only be 190 pounds per ton of shale, whereas a yield of 40 gallons of oil per ton, of average specific gravity .92 would be 88 pounds. On the face of it, then, the results of the extraction are not very satisfactory.

However it is probable that on extraction apparatus built on the plan of a large Soxhlet extractor, which would allow refluxing, would carry out the extraction in a relatively short time, would give the greater yield that is required, and would largely avoid the formation of the butyrates which appeared in the extraction.
To test out this theory, a large Soxhlet extractor will be constructed, and extraction tests made on Scottish oil-shale supplied by the Pumpherston Oil Company.

APPENDIX 1

EXTRACTION THEORY

INTRODUCTION:

Until recently no quantitative expression existed for extraction systems. Quantitative data on the rate of extraction of different materials, which might form the basis of calculations are practically non-existent, and in the various industries employing extraction processes the size of apparatus and time of contact are determined by empirical experience. In the past few years, however, several discussions have appeared in the Journals bearing on the subject of quantitative relationships.

CALCULATIONS BASED ON ATTAINMENT OF EQUILIBRIUM:

When certain assumptions are made regarding equilibrium in the extraction and washing apparatus, the calculations are: (1) The wash liquid is completely and uniformly mixed with the solution adhering to the surface of the solid; and (2) the solid exerts no selective absorbing action on the solute but is completely inert.

Hawley\(^2\) discusses such a case in the treatment of a definite quantity of solid with successive fresh batches of extracting liquid. If "a" is the solvent ratio, or the volume of the solvent drained off in one wash divided by the volume of the solvent retained by the solid, the fraction of the original amount of soluble material that remains unextracted is:

For 1 wash \( \frac{1}{a+1} \)

for 2 washes \( \frac{1}{(a+1)^2} \)

for 3 washes \( \frac{1}{(a+1)^3} \)

for \( n \) washes \( \frac{1}{(a+1)^n} \)

Utilizing these formulae a table can be constructed for the percent extracted with different solvent ratios and number of treatments. Such a table makes it very apparent that more washings with the same volume of solutions are more efficient than using the volume all at once.

If the washing is done in a countercurrent system the amount remaining unextracted after the washing is:

\[
\frac{1}{1 + a + a^2 + a^3 + \ldots + a^n}
\]

**RATE OF EXTRACTION:**

The general principles of extraction rate correspond closely to those of other diffusion processes. Consider a particle of solid containing some extractable material in contact with liquid which is being used for extracting. At any instant the solute in the extract is \(C\). At the same instant the concentration of the material at the interface may be represented by \(C_0\). This value of \(C_0\) may or may not be equal to the concentration of the material in the solid itself, depending upon the structure and nature of the solid. In any case the rate of diffusion from the interface into the liquid is proportional to \(C_0 - C\).

A general calculation of the rate of extraction would require a knowledge of the rate of diffusion through the solid itself, as well as the proportionality constant or film coefficient for the diffusion from the interface into the bulk of the extract. Certain cases can be distinguished.

First, consider a solid entirely impervious and inert to the action of the solvent, with a film of strong solution on its surface. For such a case the process would involve simply the equalization of concentrations in the bulk of the extract and in the adhering film. Such a process is rapid and any reasonable time of contact will bring about substantial equilibrium. This is especially true if there is agitation and if the system is warm so that viscosity is lowered and the diffusion
coefficient increased.

A second case is one where the soluble material is uniformly distributed through the interior of a permeable insoluble solid - for example, black ash or caliche. In this case the rate of diffusion of the solute to the interface may be the controlling factor in the rate of extraction. For such cases little help is obtained by decreasing the thickness of the liquid film, but the process is greatly hastened if the solid is finely subdivided.

A third important case is that in which the solid being leached is impermeable and contains the soluble portion distributed through it in very fine particles, plates, or needles. In such cases the actual surfaces of the particles of solute may be an extremely small portion of the total surface of the solid and the rate of extraction will be correspondingly small. In such cases the best method is to grind the solid to such a point that the individual particles of the soluble material are released.

Still another case is that typified by such substances as sugar beet chips and tanbark, where the soluble material is contained in cells and the process involves the diffusion of the solute through the cell walls, which act as semi-permeable membranes. Such a process involves the phenomenon of osmosis and the diffusion of crystalloids through colloids. In the case of such materials the soluble constituent is, in effect, very finely subdivided throughout the mass of inert solid. It would seem, therefore, that the logical procedure would be to grind the material very fine. This would necessitate grinding the material so fine that each individual cell would be ruptured. When it is recalled that
material ground to pass a 200 mesh screen represents almost the limit of fine grinding and that a particle that will pass a 200 mesh screen will contain hundreds of individual cells, it is seen that the suggestion is highly impractical. Further, in some cases, especially that of the extraction of beet sugar, the cell contains other substances than sugar in solution. If the material were so finely subdivided that all the cells were broken undesirable soluble impurities would pass into solution; whereas if extraction be carried out by direct diffusion, some of these impurities of high molecular weight are held back. For material of this sort the degree of subdivision should not be so great but the chips will form a mass which cannot be penetrated by the solute. At the same time the chips should have the largest possible surface to increase the area of contact between solvent and solid. The diffusion processes are accelerated by carrying out the operation at as high a temperature as possible, and any surface film resistance is decreased by making the velocity of the solvent high, with correspondingly great turbulence and decrease in the thickness of the stagnant film. If the velocity of the solvent past the chips is high, the necessary time of contact for producing high-concentration solutions can be made sufficiently great only by having the path of the solvent correspondingly long. This is accomplished in diffusion batteries by placing a considerable number of cells in series. The extraction of tanbark proceeds rather rapidly, the velocity of the solvent need not be so high, and 4 to 6 cells are usually sufficient. In the extraction of beet sugar the diffusional processes are slow, the velocity of the solvent is high, and from 10 to 19 cells must be placed in series to give sufficient time of contact.
T. W. Evans\textsuperscript{3} states that in the extraction of a solute by an invincible solute such that the partition law holds, the degree of solute removal is conditioned mainly by the relative volumes of the solvents. While use of several small portions is preferable to one combined portion, excessive subdivision is unjustified, since a limiting percentage removal exists for every ratio of solvent volumes. At least 94\% of this maximum removal of which a given volume of solvent is capable is achieved by division into five portions, so that in practice it is scarcely worth while to divide the extracting solvent into more than five portions.

In another article Evans\textsuperscript{4} has developed easily accessible graphical methods for the calculation of theoretical efficiencies in both multiple and counter-current extraction. The methods vary, depending on whether or not the solvents may be considered invincible.

Thiele\textsuperscript{5} claims that there is a close analogy between distillation and counter-current liquid extraction, and by suitable modification he has applied Ponchon's graphical method for the analysis of distillation columns, to this operation.

Recently Varteressian and Fenske\textsuperscript{6} have developed exact quantitative relations for liquid - liquid extraction.

The various methods of extraction are arranged as follows:


2. Cocurrent contact.
   (a) Multiple stage.
   (b) Infinite stage.

3. Counter-current contact.
   (a) Multiple stage.
   (b) Infinite stage.

"Cocurrent" means multiple contact using fresh solvent in each stage.

Although in extraction practice there are other methods or combination of methods, the mathematical treatment of the methods above bring out the essential principles applicable to all extraction processes. The use of reflux in counter-current extraction will reduce the number of stages necessary for a definite separation, yet will not introduce any new variables for its mathematical treatment.

Apart from operating data, phase equilibrium composition relations are the only data necessary for the mathematical treatment of extraction methods. The compositions of the phases at equilibrium at contact temperature and pressure are usually plotted graphically.

For their derivation of formulae, Varteressian and Fenske have taken the three component system chloroform - water - acetic acid at 18° C and 1 atmosphere. They had a given quantity of a mixture of chloroform and acetic acid of a definite composition, and desired to reduce the amount of acid in the chloroform to some other definite composition by extracting the acid with water. With each of the methods of extraction they had to find out the amount of water necessary for
extraction and the amount and composition of the two liquid layers pro-
duced.

The formulae are derived on the basis of equilibrium
relations and of material balances so that no assumptions are introduced
to limit their use only to cases where such assumptions will be justified.
Moreover, the number of given factors is kept at a minimum and all vari-
ables are expressed in terms of the amount of original charge and the
terminal compositions of the various stages.

The two layers, before the removal of the solvent are
distinguished by the names of "extract layer" and "affinate layer". The
extract layer contains a large proportion of solvent and a small pro-
portion of the liquid to be extracted, whereas the affinate layer will
contain a large proportion of the liquid to be extracted and a small
proportion of the solvent.

METHOD 1. SINGLE STAGE:

Let Ao, Co, and Bo represent the weight of chloroform,
acetic acid, and water, respectively, in the original mixture of weight
Ho; let xo, xo, and xo be the corresponding compositions in weight
fractions.

Let this mixture be treated with a weight, Sf of water in
order to reduce the acid concentration in the heavy layer to xf, the
corresponding composition of chloroform and water being Xf and Xf as
determined from the saturation plot. At this stage the concentrations
of the three components in the light layer will be Yf, yf, and Yf, for
chloroform, acetic acid and water, determined from a graph on which are
plotted the weight per cent of each of the three components in the light
layers vs. those in the heavy layers at equilibrium.

If \( H_f \) designates the weight of the resulting heavy layer,
and \( L_f \) that of the light layer formed, and material balances are made
on chloroform and acetic acid, we have the equation.

\[
H_f X_f + L_f Y_f = H_0 X_0
\]

\[
H_f X_f + L_f Y_f = H_0 Y_0
\]

which solved simultaneously for \( H_f \) and \( L_f \) give:

\[
H_f = H_0 \frac{X_0 Y_f - x_o X_f}{X_f Y_f - x_f Y_f}
\]

\[
L_f = H_0 \frac{X_f X_0 - x_o X_f}{X_f Y_f - x_f Y_f}
\]

From a total material balance:

\[
H_f + L_f = H_0 + S_f
\]

Substituting in equation (5), the values of \( H_f \) and \( L_f \) and
and solving for \( S_f \).

\[
S_f = H_0 \left[ \frac{X_0 (y_f - x_f) + x_0 (X_f - Y_f)}{X_f Y_f + x_f Y_f} - 1 \right]
\]

METHOD 2a: COCURRENT MULTIPLE STAGE:

With the two stage method it is possible to have any
desired concentration, \( x_1 \), of acetic acid in the first stage, provided
there results a concentration \( x_2 \), in the second stage equal to the final
concentration desired. In practice, \( x_1 \) could be fixed either by using
enough solvent in each stage so that the decrements of the acid concentra-
tions in the saffinate layer from one stage to the other are equal, or
by using equal amounts of solvent in each stage. In general, neither the
values of \( x_1 \), nor the amounts of solvent used, determined by the proced-
ures, will be the same.

By material balances around the first and second stages
employing a procedure similar to Method 1, values of \( H_p \), \( L_p \), and \( S_n \) are
obtained. By extending the formulations to cases of three, four or more
stages, the values of \( H \), \( L \), and \( S \), for any stage, \( n \), in a cocurrent
multiple stage system of \( N \) stages, are given by:-

\[
H_n = H_0 \prod_{i=1}^{n} \frac{x_{i-1} y_i - x_{i-1} Y_i}{x_i y_i - x_i Y_i}
\]  

(7)

\[
L_n = \frac{x_{n-1} x_n - x_{n-1} x_n}{x_n y_n - x_n Y_n} \prod_{i=1}^{n-1} \frac{x_{i-1} y_i - x_{i-1} Y_i}{x_i y_i - x_i Y_i}
\]

(8)

\[
S_n = \left[ \frac{x_{n-1} (y_n - x_n) + x_n (X_n - Y_n)}{x_n y_n - x_n Y_n} - 1 \right] \prod_{i=1}^{n-1} \frac{x_{i-1} y_i - x_{i-1} Y_i}{x_i y_i - x_i Y_i}
\]

(9)

For the case of equal \( x \) decrements:

\[
\Delta x_n = x - \frac{n(x_0 - x_n)}{N}
\]

And for the case of equal amount of solvent used:

\[
S_1 = S_n = S_N = \frac{S_N}{N}
\]
METHOD 2b: COCURRENT INDEFINITE STAGE:

In this method the extract layer would continually be removed from contact with the saffinate layer. At a given instant let \( H \) be the weight of saffinate layer, \( L \) that of the total extract layer formed, and \( S \) that of the total solvent used.

By material balances, using differential and actual quantities, for acetic acid, for chloroform, and for total materials:

\[
-\frac{dH}{dx} - \frac{dL}{dx} = \frac{dS}{dx} \tag{12}
\]

\[
-\frac{dH}{dx} - \frac{dL}{dx} = \frac{dS}{dx} \tag{13}
\]

\[
S = H + L = H_0 \tag{14}
\]

Combining (12) and (13) and integrating:

\[
\int_0^{H_0} \frac{H_0}{H_f} = \int_0^{X_f} \frac{dx}{y(X - \frac{x}{y})} - \int_0^{X_f} \frac{dx}{y'(X - \frac{x}{y'})} \tag{15}
\]

For the numerical calculation of \( H_f \) the right hand side of equation (15) may be evaluated by graphical integration plotting \( \frac{1}{y(X - \frac{x}{y})} \) vs. \( x \) for the first member and \( \frac{1}{y'(X - \frac{x}{y'})} \) for the second member. The relations \( \frac{X}{y} \) for \( x, y, X \) and \( X \) are obtained from the equilibrium diagrams.

The integration of (12) yields, for the amount of the extract layer,

\[
I_X = \int_{H_0}^{H_0X} \frac{1}{y} \, d(H_x) \tag{16}
\]

The numerical value of the integral may be obtained by graphical integration, plotting \( \frac{1}{y} \) vs. \( H_x \), the value of \( H \) for each \( x \) being obtained from (15).
Finally, $S_f$ may be obtained from (14) by substituting in it the given value of $H$, and the calculated value of $H_p$ and $L_f$.

**METHOD 3a. COUNTERCURRENT MULTIPLE STAGE:**

Consider a column of a total of $N$ theoretical plates numbered $1, 2, \ldots, n, \ldots N$ from top to bottom. A heavy feed $E_0$ is introduced at the top and withdrawn at the bottom as heavy product $E_N$, a light feed $L_{N+1}$ is introduced at the bottom and withdrawn at the top as light product $L_1$.

Making material balances around the entire column for acetic acid, for chloroform, and for total material,

$$H_0 x_0 + L_{N+1} y_{N+1} = H_N x_N + L_1 y_1 \quad (17)$$

$$E_0 y_0 + L_{N+1} y_{N+1} = H_N x_N + L_1 y_1 \quad (18)$$

$$E_0 + L_{N+1} = H_N + L_1 \quad (19)$$

Making similar material balances around any plate $n$,

$$H_{n-1} x_{n-1} + L_{n+1} y_{n+1} = H_n x_n + L_n y_n \quad (20)$$

$$X_{n-1} x_{n-1} + L_{n+1} y_{n+1} = H_n x_n + L_n y_n \quad (21)$$

$$H_{n-1} L_{n+1} = H_n + L_n \quad (22)$$

In addition $x_n, y_n$, and $y_n$ are functions of $x_n$ as plotted in the equilibrium diagrams.

Under the conditions of the problem, the unknown in equations (17), (18), and (19) are: $L_{N+1}, H_N, L_1, y_1$, and $y_1$. Assuming a reasonable $y_1$ equation (17) and (18) may be solved for $H_N$ and $L_1$, since $x_1$ will be determined by $y_1$ by means of the phase equilibrium plot.
Substituting the values of $H_n$ and $L_1$ in (19), the value of $L_{n+1}$ is obtained.

With the values of $L_1$ and $y_1$, and consequently of $Y_1$, $x_1$ and $X_1$ through the equilibrium diagram the equation for plate 1 may then be taken into consideration. Thus equations (20), (21), and (22) where $n = 1$ together with the saturation relation between $y_2$ and $Y_2$ will suffice to solve for the four unknowns $H_1$, $L_2$, $y_2$, and $Y_2$.

This process is continued until the equations for the last plate are taken into consideration, and so the test for the corrections of the assumed value for $y_1$. If the assumed value has been correct, the values of $H_n$ and $L_{n+1}$ originally calculated by equations (17) and (18) will check those calculated by material balances around the last plate.

**METHOD 3b: COUNTERCURRENT INFINITE STAGE:**

In an extraction tower of infinite height, the difference between the compositions of the saffinate layers, or of the extracted layers, from plate to plate become exceedingly small at that end where the material to be extracted is fed into the tower. This means that the outgoing extract layer may be considered in equilibrium with the incoming saffinate layer.

Using this concept and making material balances around the entire column:

\[
H_0X_0 + L_{n+1} \bar{Y}_{n+1} = H_{n+1}X_n + L_1Y_0 \tag{23}
\]

\[
H_0X_0 + L_{n+1} \bar{Y}_{n+1} = H_{n+1}X_n + L_1Y_0 \tag{24}
\]
\[ H_0 + L_{n+1} = H_n + L_1 \]  

(25)

From the given values of \( x_0 \) and \( x_n \), those of \( x_0, y_0, y_0, \) and \( y_n \) are read from the equilibrium graphs. Inserting these values as well as the given values of \( H_0, y_{n+1}, \) and \( y_{n+1} \) in equation (24), (24) and (25) values of \( H_n, L_1, \) and \( L_{n+1} \) are obtained, and three values of \( H_f, L_f, \) and \( S_f \).

**RELATIVE METHODS OF EXTRACTION METHODS:**

It is a mistake to evaluate extraction methods in themselves, without considering the particular problem to the solution of which they must be applied. The general belief that countercurrent extraction is in all circumstances superior to cocurrent extraction does not have a sound basis. It is a result of the failure to see that an increase in the concentration of a substance in one liquid phase is not always accompanied by an increase in the other; actually it is sometimes accompanied by a decrease.

In certain cases reflux may be used to great advantage in an extraction column. In this respect there are two practical points of interest.

1. Through the proper use of reflux it is possible, with a reasonable number of stages to make separations which would otherwise be impossible, even by the use of an infinite number of stages.

2. In order to separate a constituent from a mixture, the solvent used does not necessarily have to be selective towards that constituent, if the right type of reflux is used.
However these advantages may be obtained only at the expense of more solvent or energy per unit changing stock and less throughput of product.

APPENDIX II

SKETCH OF A CONTINUOUS COUNTER-CURRENT EXTRACTION PLANT FOR OIL-SHALE

In the accompanying diagram is a idea for a continuous extraction shale plant. Shale from the mine would run along on trucks and dumped into the crushers and rollers which would drop the required mesh through screens into a vertical helical screw conveyor. The ribbon spiral would take it along the heated acid-proof passage, all along meeting solvent coming in the opposite direction, so that the spent shale meets the freshest acid, and the acid which is nearly saturated with extract meets fresh shale.

Above the solvent entry line is a drainage portion so that the spent shale will not be too saturated. The spent shale is sent to a solvent recovery plant, where the acid would be removed with water or distilled.

After leaving the shale the solvent passes up a vertical tube to allow sediment to drop out, and be carried back by a conveyor. The solvent is then sent to the still where the extract is removed. The level of the solvent entry pipe would naturally have to be above the point where the solvent is removed at the other end.

The speed of the conveyor would be regulated for optimum
condition of as complete extraction as possible in a reasonable time.

The greatest problem would be an efficient separation of the butyric-water mixture from the spent shale.