Alcoholic Extraction of Oilseed with the Aid of Ultrasonics[1]

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Abstract

The ultrasonic extraction of cottonseed with ethyl alcohol is studied. Several treating systems are evaluated with the seed in different positions in regard to the ultrasonic field. A calorimetric method was used for measuring the ultrasonic power to the treating vessels. The ultrasonic field had a frequency of 26 Kc/sec, and there was a power range from 0 to 2 watts/cm^2. The temperature was varied between 25 and 75C for a set of runs, and a solvent flow rate of about 1 ml/sec was used for most runs. It appears that the temperature effect is the same for runs with and without ultrasonics. A capillary flow mechanism is discussed to explain the temperature effect. Only the extraction without ultrasonics could be predicted by the latter model at a given temperature level.

Considerable improvement in the extraction rate was obtained when the ultrasonic pressure gradient was used parallel to the main solid liquid interface. A generalized empirical equation is presented, relating the rate of extraction to the calorimetric power to the extraction vessel, the total area normal to the ultrasonic field, and the seed loading for a particular geometry. By using Fick's law of diffusion and a simplified physical model, the data are also presented as an equation of the diffusion coefficient as a function of the calorimetrically measured ultrasonic power, the total area in the path of the ultrasonic field, and the seed loading.

Introduction

ULTRASONIC ENERGY is used commercially in cleaning devices, homogenizers, fog arresters, and other applications, but no ultrasonically assisted, mass-transfer, industrial application is known.

As early as 1937 Marinesco (1) studied the effect of ultrasonics in the breaking of gels and other applications. Later an application of ultrasonics in fractionation was patented (2), and sometime ago some preliminary extractions of peanuts in an ultrasonic field were reported (3).

Numerous patents in the field deal with apparatus for the treatment of fluids, with apparatus for uniform exposure of the material, with concentrating mosaics of transducers, with sirens, whistles, etc.

The solution of the problem of visualization and measurement of ultrasonic fields has been approached by using compensated calorimeters, radiometers, dilatometers, microphones, and other equipment.

Ultrasonic energy produces two important phenomena: cavitation and microstreaming. Cavitation is the formation of tiny gas-vapor bubbles, which oscillate with the ultrasonic field and eventually collapse or coalesce into bigger bubbles that go to the surface of the liquid. There is a controversy about the origin of cavitation, but it is often mentioned that the presence of air nuclei and/or organic impurities and the physical properties of the liquid affect the cavitation thresholds. Microstreaming appears in the surroundings of a solid object, immersed in a liquid in which there is also an ultrasonic field. It is really turbulence distinct from the ultrasonic waves themselves. The effect of microstreaming on heat exchange, crystal growth, and sound absorption has been investigated by several authors (11).

The solvent extraction of vegetable oil from oil seeds may be thought of as consisting of the following steps: a) bulk flow of the lean miscella to the neighborhood of the seed particle; b) microscopic flow of the lean miscella to the interior of the seed; c) microscopic flow of the rich miscella to the outside of the seed; and d) macroscopic flow of the rich miscella from the neighborhood of the seed particle to the bulk of the miscella. The solubilization of the oil in the solvent takes place in all these steps. From the standpoint of morphology the oil is located inside cells, the walls of which are resistant to the traffic of the miscella.

It was postulated that the ultrasonic waves cause alternating pressure gradients that may accelerate the extraction by speeding up all or some of the steps in the mechanism. The objectives of this work were to evaluate the magnitude of the effect of the ultrasonic waves on the rate of extraction and to check the adaptability of models which have been proposed to explain the mechanism of vegetable oil extraction.

Experimental Section

Power Measurement

The literature presents the following methods of power measurement: inverted cone (4), microphonic techniques (5), radiometers (5), acceleration of the iodine starch reaction (6), and dilatometers (7). All of the methods were evaluated, but none was acceptable under the conditions of the experiments. However the last one gave support to the calorimetric method finally adopted. Calorimetry was suggested by Szilard (8).

The dilatometric and the calorimetric methods of the measurement of ultrasonics are essentially the same; the absorption of ultrasonic energy causes a temperature increase, the temperature elevation expands the volume, and either the temperature or the volume increases are measured.

The calorimetry was reliable according to several sets of runs (11). The effects of the depth of immersion of the temperature probe, the horizontal position of the probe, and the transducer's cooling water rate were not significant. Whether a thermometer (Hg) or a thermocouple was used as temperature probe did not affect the accuracy of the method. The frequency of the equipment was checked both by measuring the distance between power peaks in a standing wave field and by using an oscilloscope and a signal generator (11).

It is interesting to note that, with a fixed impedance, the power output is essentially linear with

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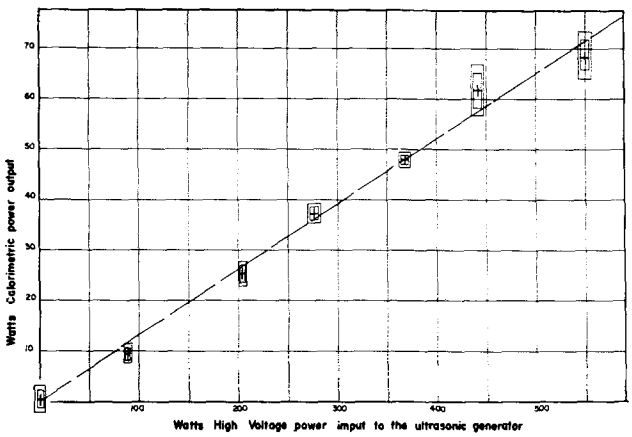

FIG. 1. Power input vs. calorimetric power output.

the input (Figure 1). From the slope of the line it is seen that the equipment efficiency is about 13%.

For batch operations the calorimetric method consisted of recording the temperature history of a known amount of seed-solvent mixture and determination of the heat input from the data. The continuous flow runs needed time for steady-state conditions to be reached. At steady state the temperature increase of the solvent stream because of the absorption of ultrasonic energy, multiplied by the flow rate and the heat capacity, yielded the heat input per unit time. The heat losses had to be accounted for, and these, added to the heat input calculated for a particular run, gave the actual ultrasonic energy input. A few dummy runs without ultrasonic energy did not suffice to evaluate the heat losses. Strong dependence of the heat losses on the temperature gradient for heat losses (average solvent temperature minus average room temperature) was found. Finally a set of corrections was developed in which the heat losses were expressed as a function of the seed loading. Once the heat losses were determined, it was simple to make a heat balance and calculate the exact ultrasonic power absorbed by the extracting system.

Apparatus

The ultrasonic generator was a DR400-A (Acoustica Associates) with an specified operating frequency of 25.9 Kc/sec. Variation of the power output was produced by inserting an autotransformer in the primary of the high voltage transformer. Two extra capacitors had to be added to filter out high frequency voltage peaks, which ruined the original insulation of the high power transformer. No change in the frequency of the generator was found when these capacitors were added.

The alcohol was recovered and reused; an Oldershaw vacuum rectifying column was used to concentrate the alcohol. A Mettler analytical balance was employed to determine the amount of oil extracted. Two sets of thermometers were used, one was graduated in half degrees, the other in tenths. The thermometers were cross-checked and found to be in agreement.

General

The 26 Kc/sec ultrasonic field cavitated with ease at the low power levels used. The ultrasonic power input to a treating vessel varied between 0 and 2 watts/cm^2 computed over the area normal to the pressure gradient of the acoustic field. The maximum power to a treating vessel was 72.5 watts. The longitudinal mode of vibration was characteristic of

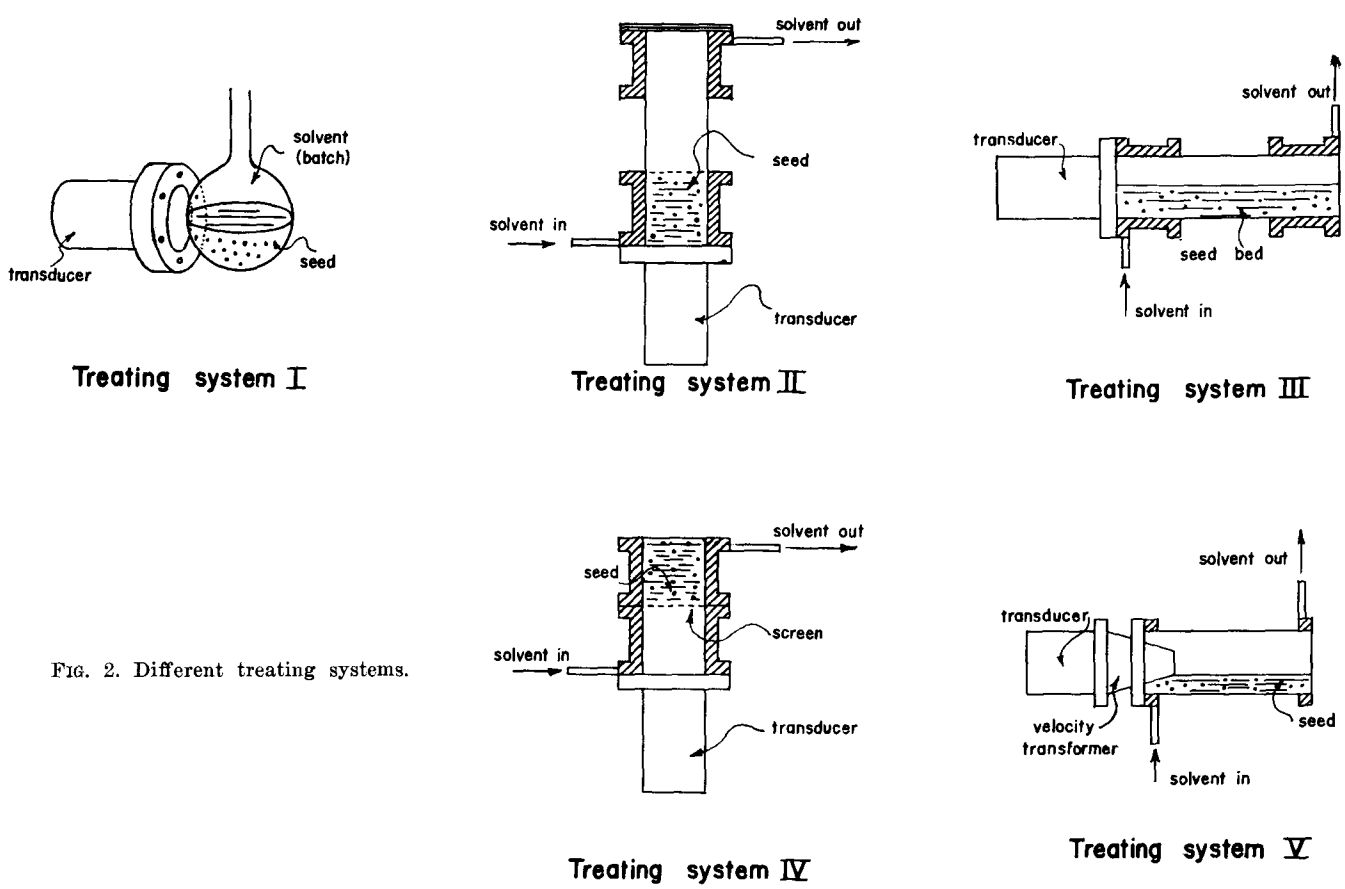

FIG. 2. Different treating systems.

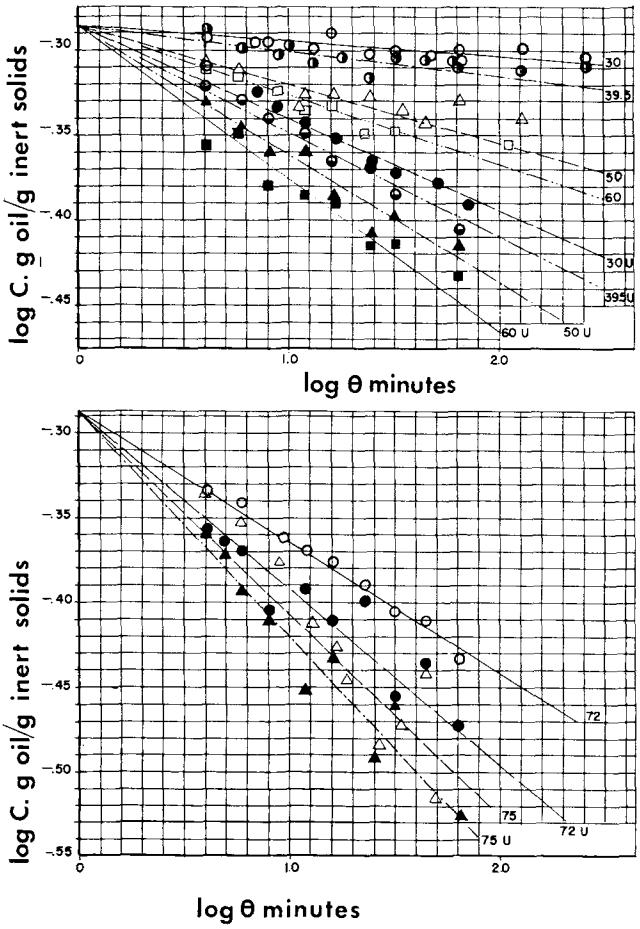

FIG. 3. Oil content vs. time. The numbers on the lines are temperatures. The "U" stands for runs with ultrasonics.

the field used. Standing waves were present when the acoustic pressure gradient was parallel to the main solid-liquid interface.

The solvent was 95% by volume ethanol, and the oil-bearing material extracted was cottonseed. On one set of runs the temperature was varied from 25 to 75C; all other runs were taken at 25–30C solvent inlet temperature to the extraction vessels. A solvent-to-seed ratio of 3 to 1 was used in the batch runs. In the continuous solvent flow runs, a solvent flow-rate of 1 ml/sec was used with seed beds of 60, 120, 180, 240, and 450 g.

The seed was flaked in a roll mill with .009 in. clearance and had the following screen analysis:

Mesh	% Retained
10	55–60
14	15–25
20	15–20
20 (pass)	5– 6

Different Treating Systems

The five treating systems used are shown in Figure 2. System I was a 300-ml, round-bottom flask immersed in a constant temperature bath and fitted with a condenser. In a typical run 60 g of seed were loaded in the flask, and, once temperature equilibrium with the bath was established, the solvent was added. At this moment the ultrasonic field was applied, and the starting time of the run was marked. At the end of the run a sample of miscella was taken, and the amount of oil in the sample was obtained by evaporating the solvent and weighing the residue. System I was abandoned because of unfavorable geometry and the limitations of batch operation.

System II consisted of a cylindrical upright vessel, for which the transducer's face served as bottom. The solvent flowed upward across the seed bed, which rested on the transducer's face. In a typical run the seed would be charged to the vessel and the solvent flow started. When the first miscella discharged, the ultrasonic field was applied and the start of the run marked. All the outflowing miscella was collected in tared flasks; 21 consecutive samples were taken at three-minute intervals. The solvent was evaporated, and the residual oil was determined by weighing. System II was abandoned because it was found that the weight of the seed bed hindered the vibration of the transducer's face.

System III was System II lying on its side. Depending on the loading, the seed bed occupied from one-fourth to one-half of the volume of the cylinder. The solvent was admitted near the transducer under the seed bed. The miscella discharged from the top of the cylinder at the opposite end from the transducer.

System IV consisted of an upright cylinder, divided in two parts by a Monel screen; the seed bed was placed in the upper compartment. The distance from the face of the transducer to the screen was one wavelength. The solvent flowed upward through the seed bed.

System V was similar to System III except for a velocity transformer which was intended to provide higher power densities. The transformer did not have the desired effect, and it was abandoned. The bulk of the work was carried out with System III.

Results and Discussion

Batch Experiments—Temperature Effect

For the exploratory experiments, System I (batch) was used. Data were taken at temperatures of 30, 39.5, 50, 60, 72, and 75C. The equations obtained by statistical analysis of the data give significant correlation coefficients. The data and the statistical fit lines may be seen in Figure 3. The general regressions obtained by further manipulation of the data are

for runs without ultrasonics

$$C = .518\ominus^{.00128t - .046}$$

for runs with ultrasonics

$$C = .518\ominus^{.00128t + .0008}$$

These equations have the same coefficients and the same exponential temperature term. Therefore it was concluded that the effect of the temperature on the extraction was independent of ultrasonics.

The rates of extraction for temperatures up to 65C may be written without serious error

for runs without ultrasonics

$$(dC/d\ominus)_t = (.00128t - .0460)\ .518\ \ominus^{-1}$$

for runs with ultrasonics

$$(dC/d\ominus)_t = (.00128t + .0008)\ .518\ \ominus^{-1}$$

The Capillary Flow Mechanism

The effect of the temperature on extraction has been discussed by Othmer and Agarwall (9), using a viscous flow in capillary passages physical model. These authors propose that the rate of extraction should be equal to a constant multipled by a function of the physical properties of the miscella. This function identified as *gamma* (Γ) is the product of the surface tension and the density, divided by the

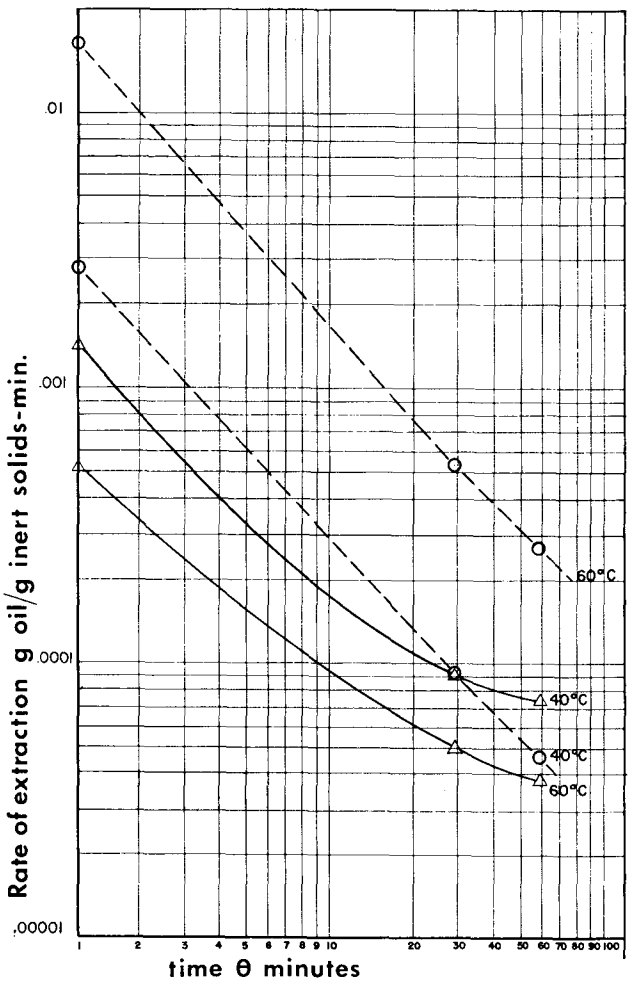

FIG. 4a. Rate of extraction from the viscous flow model and from the experimental empirical equation (runs without ultrasonics): ○, experimental data; △ viscous flow model.

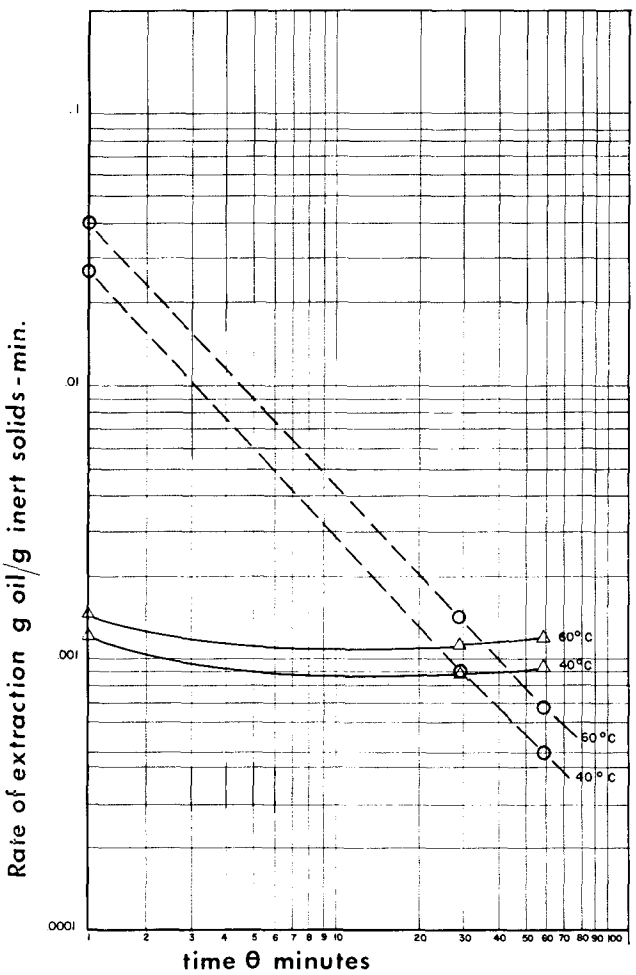

FIG. 4b. Rate of extraction from the viscous flow model and from the experimental empirical equation (runs with ultrasonics): ○, experimental data; △ viscous flow model.

viscosity. Although the concentration of the oil in the miscella in these runs was never above 5%, the combination of the physical properties of both 95% ethanol and cottonseed oil produce a *gamma* function that changes considerably with temperature. Since the surface tension, density, and viscosity are all temperature-dependent, this is to be expected.

In order to check whether this model explained the experimental data, the following relationships were investigated: *gamma* function versus oil concentration and temperature, oil in the miscella versus the temperature and the time of extraction, and combination of 1 and 2, yielding *gamma* as a function of temperature and time of extraction for runs with and without ultrasonics.

The first relationship was obtained by combining, for the binary, the physical properties of ethyl alcohol (95%) and cottonseed oil over the concentration and temperature ranges of the experiments (11).

According to the model the extraction rate may be written: $-(dC/d\ominus) = K\Gamma$

Therefore it is possible to compare the experimental and the theoretical results by using one experimental point to evaluate K. Figure 4 presents the lines obtained for the theoretical as well as the experimental results. The point used to evaluate K is the one common to both curves.

For runs without ultrasonics, the extraction rate may be predicted at any one temperature level by evaluating K from an experimental point. For runs with ultrasonics the model fails to predict the results obtained. This indicates the possibility that the ultrasonic waves travel deeper into the seed bed than what was thought possible.

Data with Other Systems

In regard to System I it was calculated that the coupling coefficients (efficiency of transmission of ultrasonic energy across interfaces of different materials) would account for a loss of more than 50% of the energy falling on a glass wall in a water-ethanol transmission path. The spherical geometry would lower the efficiency farther.

The data obtained have been considered under the discussion on temperature effect. The power to the treating vessel was 1.39 watts, and the amount of oil obtained in the extraction with ultrasonics in an hour was roughly 8.3 times more than the amount obtained without ultrasonics from the same weight of seed, or an improvement of about 830% on this basis.

The results with System II indicate that the power to the treating vessel was 3.67 watts and that the data could be fitted to a straight-line relationship between the time ($\ominus$) and the oil content at any time minus the oil content at time zero ($C-C_o$). Differentiation of the equation yielded the mean extraction rate at any time during the run. With a seed loading of 120 g the extraction rate was 10% higher with ultrasonics than without ultrasonics. Two runs with 450 g of seed did not yield any difference between data with and without ultrasonics.

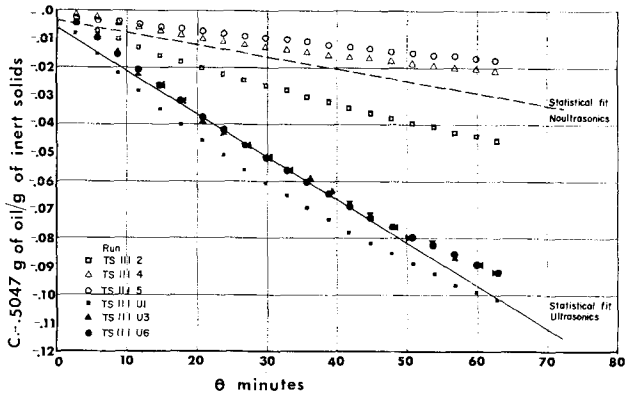

FIG. 5. Oil extracted vs. time-Treating System III with 120 g of seed.

The results obtained with System III are presented in Figure 5. The extraction rate with ultrasonics is 255% higher than without ultrasonics, it will be noted. The power to the treating vessel was about 18 watts for a seed loading of 120 g.

System IV was conceived with a positive solvent flow through the bed and with the seed weight removed from the transducer's face so that the latter would not be hindered in its vibration. The rate of extraction was 26% higher with than without ultrasonics. System V incorporated a velocity transformer aimed to an increase of the power per unit area. A 200% improvement in the extraction rate was realized, but no increase in the power density over that of System III was obtained.

Casual observation of the data with System II (11) led to the belief that the solubility of the oil was limiting the extraction with and without ultrasonics, but, in comparing the data for the runs with 120 g and 450 g, it was clear that the solubility was not limiting the extraction. Should solubility control the extraction, rates would be twice the ones obtained. Comparison of the data with Systems II and IV indicated similar extraction, as would be expected.

Systems III and IV have geometry favorable to the establishment of a standing wave field, that is, free transmission path and length of transmission which is a multiple of the wavelength, and, as expected, the calorimetric power gives higher values in these cases. Comparison of data for Systems II and IV with those of Systems III and V appears to indicate that the effect of ultrasonics is just agitation on a relatively stagnant main interface for Systems

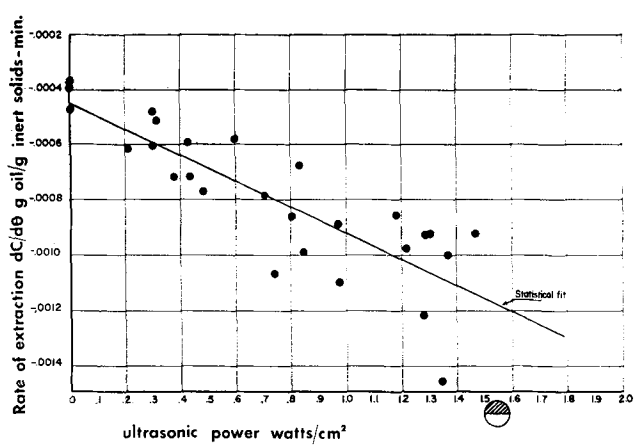

FIG. 6. Rate of extraction vs. ultrasonic power for runs with 120 g of seed.

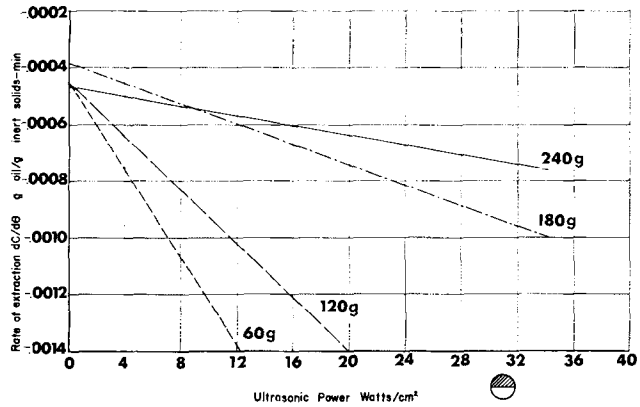

FIG. 7. Rate of extraction vs. ultrasonic power at different loadings for treating System III. The power per unit area is based on the solvent space only. The cross-section of the seed bed was subtracted from the total area.

III and V. To investigate this possibility the extraction per unit area of main interface was plotted against time for several seed loadings, but the results were poor. The correlation in terms of the weight of the seed bed gave better results, indicating that the extraction took place throughout the weight (volume) of the bed.

Variation at Different Seed Loadings

The extraction was evaluated with beds of 60, 120, 180, and 240 g. The power varied from zero to the maximum and was measured by the refined calorimetric technique (11). The data for 120 g showed some difference between individual seed-rolling batches coming from the same original master batch. However, when the particle size oil content and moisture analyses for the individual rolling batches were compared, no differences were found. Within the experimental error an extraction rate independent of time could be obtained by differentiating the data as oil content minus a constant versus time.

The power per gram of inert solids per cm² was based on two different areas, namely, the total and the free cross-sections normal to the acoustic pressure gradient. The over-all fit of the data for 120 g of seed was good, despite the scatter, owing to the considerable number of points (Figure 6). The statistical fit lines for the four seed loadings in Figure 7 indicate that lower seed loadings corresponded to higher extraction rates. This suggested plotting the data as rate of extraction versus power per unit weight of inert solids. The data are plotted in this fashion in

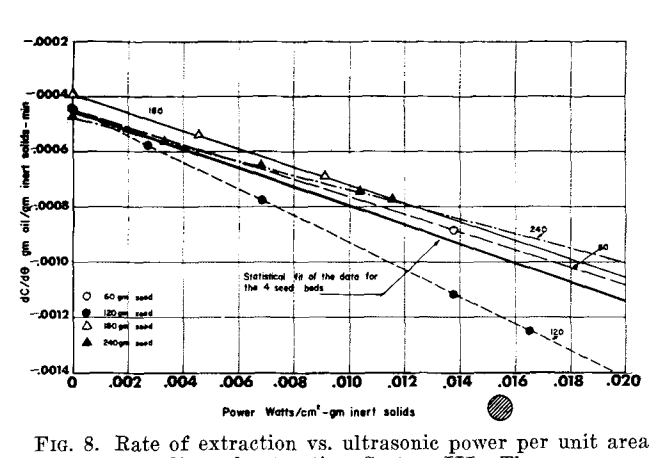

FIG. 8. Rate of extraction vs. ultrasonic power per unit area at different loadings for treating System III. The power per unit area is based on the total cross section.

Figure 8, based on the total cross-section of the vessel. There is still a difference in data for different loadings. This disorder of the curves may indicate experimental errors rather than inadequacy of the parameters chosen. The above is an empirical correlation.

An attempt was made to explain the results by the theoretical approach of Fan et al. (10). These authors used Fick's law of diffusion and a thin slab physical model in analogy with the heat conduction problem. The solution was the integration of the Fourier equation. The following conditions were imposed on the diffusion problem in order to obtain a simple mathematical solution: a) the diffusion coefficient D is a constant defined by the equation:

$$\delta C/\delta \ominus = D\ (\delta^2 C/\delta X^2)$$

b) the structure of the seed to be extracted is homogeneous in all directions, c) the distribution of oil in the seed is constant and uniform, d) the path for diffusion is small compared with the other dimensions of the flakes, and e) the thickness of all the seed particles being extracted at any time is the same.

Integration of the equation with appropriate boundary conditions gives an infinite series that, for practical applications, may be reduced to the first term. The simplified equation may be written:

$$\log_{10} C/C_o = -4.286\ [D/(2\,l)^2] \ominus -.0911$$

This is the equation of a straight line when $\log_{10}C/C_o$ is plotted against the time of extraction $\ominus$. The diffusion coefficient may be readily obtained from the slope. Figure 9 shows the general correlation developed for all seed loadings and

$$D = [71.74\ (P_o/A_2W) - .8240] \times 10^{-9}$$

It is believed that, in the range of the power levels investigated, the mechanisms of extraction with and without ultrasonics are the same, and both may be represented by the thin slab physical model and Fick's law of diffusion. The controlling factor of the diffusion process is the diffusion from the inner regions of the seed to the surface. The dependence of the diffusion coefficient on the ultrasonic power may be represented by a straight-line equation as a function of the power per unit area per unit weight of inert solids.

Conclusions

At 30C the improvement in extraction realized with ultrasonics by using System I may be represented by:

$$I = .522 \ominus^{-.0114} - .536 \ominus^{-.0655}$$

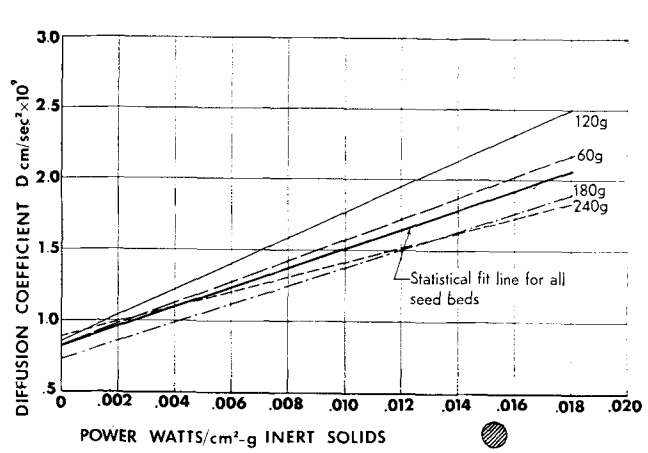

FIG. 9. Diffusion coefficient vs. ultrasonic power per gram inert solids. The power per unit area is based on the total cross section.

In the interval between 30 and 65C the data for System I may be represented by the equation:

$$I = .518\ [\ominus^{.00125t-.0135} - \ominus^{.00125t-.0085}]$$

The percentage improvement of the mean rate of extraction at 30C is 830%. The temperature effect on the extraction is the same with or without ultrasonics.

The viscous flow model predicts rates of extraction at a given temperature level from one data point for runs without ultrasonics but fails for runs with ultrasonics.

Systems III and V gave the higher ultrasonic power readings because of geometry favorable to standing wave fields. The positive solvent flow through the seed bed in Systems II and IV gave the highest rates of extraction. By percentage the highest improvements in extraction were obtained with Systems I, III, and V, that is, with the ultrasonic field axis parallel to the main solid-liquid interface. Placing the seed over the face of the transducer seems to hinder it, and above a certain seed loading no improvement in extraction is realized. The solubility of the oil in the alcohol does not limit the extraction.

The data for System III is correlated by the empirical equation:

$$dC/d\ominus = -.03478(P_o/A_2W) - .0003468$$

The use of Fick's law and a thin slab physical model yields the diffusion coefficient as a function of the ultrasonic power per unit area and the weight of seed:

$$D = [71.74\ (P_o/A_2W) - .8240] \times 10^{-9}$$

The extraction mechanism with or without ultrasonics is controlled by the counterdiffusion of oil and solvent within the seed. The ultrasonic action seems to improve the mixing of the miscella and oil within the seed. It appears that the ultrasonic energy travels deeper in the seed bed and in the individual seed particles than had been thought possible.

The ultrasonic power measurement by calorimetry is convenient and independent of temperature probe characteristics and position.

Nomenclature

A_2	Total cross-sectional area of the extracting vessel cm^2
C	Oil content of the seed g oil/g inerts at time $\ominus$
C_o	Oil content of the seed g oil/g inerts at time 0
D	Diffusion coefficient cm^2/sec
I	Improvement, difference between the oil content of runs with and without ultrasonics, g oil/g inerts
K	Proportionality constant
l	One-half thickness of the slab cm
P_o	Calorimetrically measured power in the treating vessel watts (output of the generator)
t	Temperature in °C
W	Weight of inert solids in the extracting vessel, g
X	Distance in the direction of diffusion from a central plane in a slab cm

Greek Letters

Γ	Gamma function of the physical properties; surface tension times the density, divided by the viscosity lbs-sec/$ft.^4$
$\ominus$	Time elapsed from the start of the extraction minutes

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