A PULSED LABORATORY DISTILLATION COLUMN

By

GILBERT VINCENT MC GURL

Bachelor of Science

Carnegie Institute of Technology

Pittsburgh, Pennsylvania

1961

Submitted to the faculty of the Graduate School of the
Oklahoma State University of Agriculture and
Applied Science in partial fulfillment
of the requirements for the degree
of MASTER OF SCIENCE
May, 1962

A PULSED LABORATORY DISTILLATION COLUMN

Thesis Approved:

R. N. Maddox
Thesis Adviser

W. C. Edmister

Dean of the Graduate School

PREFACE

Since World War II there has been a great deal of interest in pulsed extraction. Pulsation increases the efficiency of an extraction column and makes possible separations by extraction that were uneconomical with normal extraction. This leads to the study of pulsation in a distillation column.

This thesis presents the results of a preliminary study into pulsed distillation. It presents a qualitative discussion of the factors affecting efficiency in a pulsed distillation column on a laboratory scale.

I would like to express my profound thanks to Dr. R. N. Maddox, without whose advice and counsel I would never have finished this study.

I would also like to express my gratitude to Mr. E. E. McCroskey whose help with equipment was invaluable.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER I

INTRODUCTION

During the past few years there has been a great amount of work done in the field of pulsed extraction columns. The original patent on the pulsed extraction column was that of Van Dijck in 1935 (18). The first large scale application of this principle was made during the second World War when pulsed extraction was used to recover fissionable materials (9). Much of the pulsed extraction work that has been done has not been published because it is in classified reports (5). One of the most popular ways of operating a pulsed extraction column is to pulse the continuous or heavy phase.

The reasons that pulsed extraction increases the efficiency of extraction are that the total contact area is much greater and that the turbulence in the two phases is increased. This increase in turbulence causes a decrease in the thickness of the boundary layer which controls the resistance to mass transfer.

The success of the pulsed extraction column prompted this study into the pulsed distillation column. The first reason for the success of the pulsed extraction column is possibly not valid in the case of a similar distillation column, since there is always turbulent mixing on the plates in a distillation column. However it did seem possible that the resistance to mass transfer could be decreased without a corresponding decrease in the residence time in the column. This would lead to an increased efficiency on the individual trays in the distillation column.

Qualitatively, the behavior of a distillation column may be described in the following way. The approach to 100 per cent efficiency of a distillation column is a function of the residence time of the gas in the liquid and the resistance to mass transfer. The residence time is almost inversely proportional to the throughput of the column. The larger the residence time the closer each individual plate will come to equilibrium and thus the more efficient the column will become. Also, the greater the mass transfer coefficient the closer a stage may approach equilibrium for a given residence time. By pulsation it should be possible to increase the effective mass transfer coefficient by decreasing the laminar boundary layer which controls mass transfer without materially affecting the residence time.

This study was initiated with the following goals in mind.

(1) To first find out if there could be obtained in distillation an effect similar to the one obtained in pulsed extraction.

(2) Once this effect had been noticed, to measure it quantitatively and discover the effect of different variables on it.

(3) The variables chosen were pulse amplitude and pulse frequency. The liquid and gas flow rates in the column were also included because the efficiency of the non-pulsed column is dependent on these variables.

(4) To propose a possible mechanism for the phenomena observed on the basis of the results.

An extensive search of the literature has failed to uncover any previous attempts to pulse a distillation column artifically. There are, however, some reports of natural pulsations being observed in distillation columns (13). These natural pulsations were observed at high gas and liquid flow rates and had the effect of raising the efficiency of the column. The reason that the efficiency was raised was said to be a decrease in the amount of backmixing on the trays. Backmixing can be defined as the turbulent transport of mass against the direction of bulk flow. In a small scale distillation column such as was used in this study there is almost complete mixing on individual trays and no phenomenon similar to backmixing would be expected.

CHAPTER II

EXPERIMENTAL EQUIPMENT

The distillation column used for this study is a batch type distillation column. It is the type designed and first described by Oldershaw (15). It is a perforated plate column of 32 mm in diameter. Each plate contains 82 perforations 0.85 mm in diameter. The weir height is 1 mm. The weir is placed in the center of the plate and is constructed of a 10 mm tube. The outlet of the downcomer is on the side of the tray below. The downcomer is constructed of 3½ mm tubing and there is a ½ mm glass ball in the outlet. The weir is surrounded by a baffle 10 mm in height and the weir opening is on the side opposite the downcomer outlet. The tray is shown schematically in Figure 1. The tray spacing in the column is 30 mm. The column is surrounded by a silvered vacuum jacket to insure adiabaticity to the operation. The silver jacket is provided with a slit to allow for visual observation of column operation. Each section of the vacuum jacket is equipped with a bellows type expansion section to allow for the thermal expansion of the glass.

The column is equipped with a condenser with a manual takeoff device for the collection of samples. After condensing, the reflux is slightly subcooled in a cooler and it is then

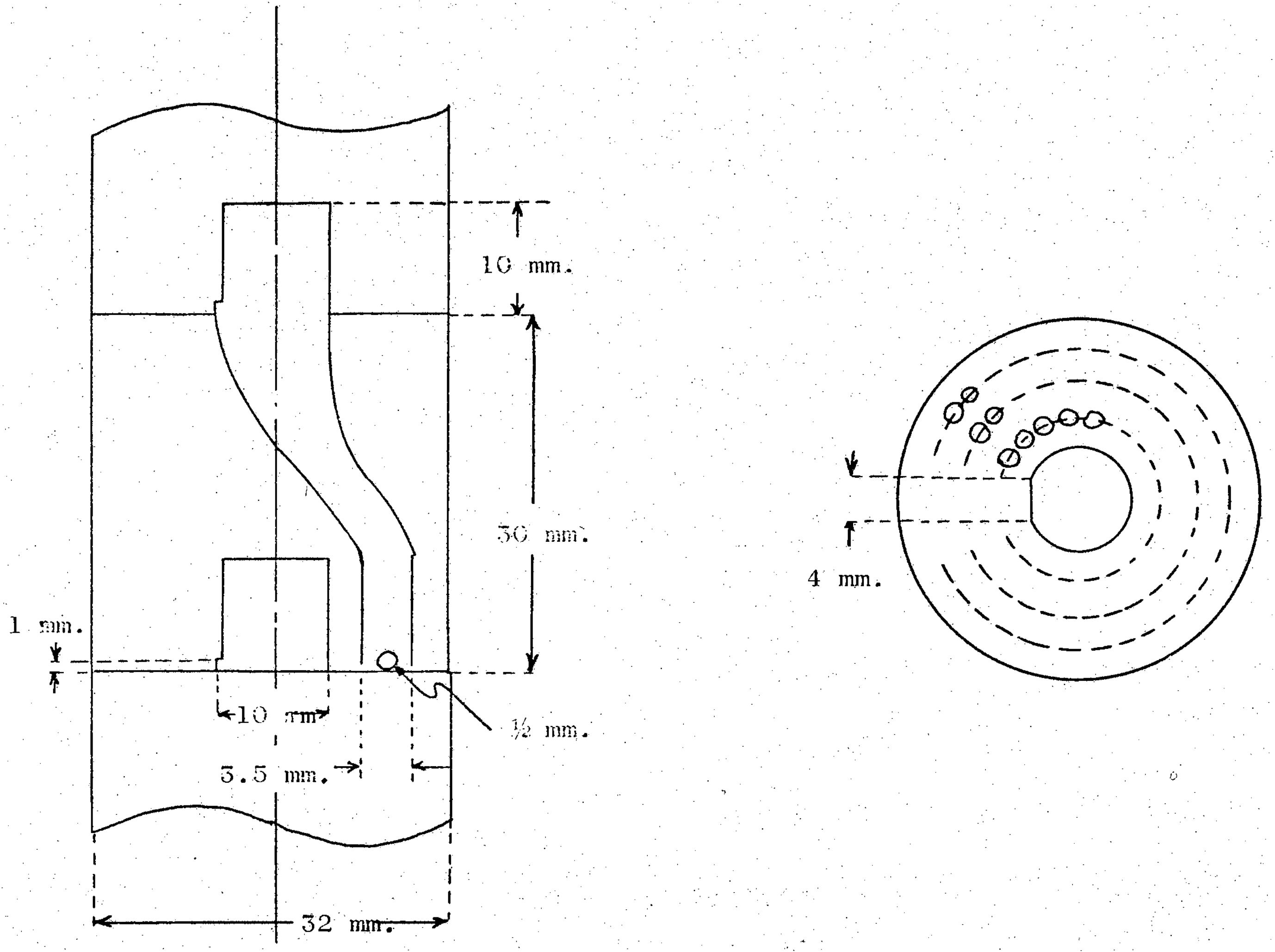


Figure 1. Column Construction

either returned to the column as reflux or it is drawn off through a capillary tube as a sample. In order not to disturb the composition at the top of the column the lead from the line carrying the condensate to the stopcock of the sampling line is as short as possible. The stopcock is placed less than one centimeter from the reflux return line and is connected with 1 mm bore tubing. The construction of this arrangement is shown in Figure 2.

A reflux rate and holdup apparatus similar to that described by Oldershaw (15) was used to determine the reflux rate in the column. This device is essentially an annulus in which vapor flows up the inner tube. This inner tube is covered with a dome which prevents the returning reflux from running down the tube. The reflux runs down the outer tube. This tube is closed at the bottom except for one line which leads to a three way stopcock. The stopcock may be turned to allow the reflux to go directly into the reboiler, or it may be turned to allow the returning reflux to be removed for analysis. The third position of the stopcock will allow the ascending vapor to be removed. It is also possible to close the stopcock completely by using an intermediate position. When the stopcock is in a closed position the returning reflux collects in the outer tube of the annulus. This outer tube has a calibration mark exactly 50 ml above the stopcock. This allows the reflux rate to be measured by closing the stopcock and determining how long it takes for 50 ml of reflux to collect. This apparatus is shown in Figure 3.

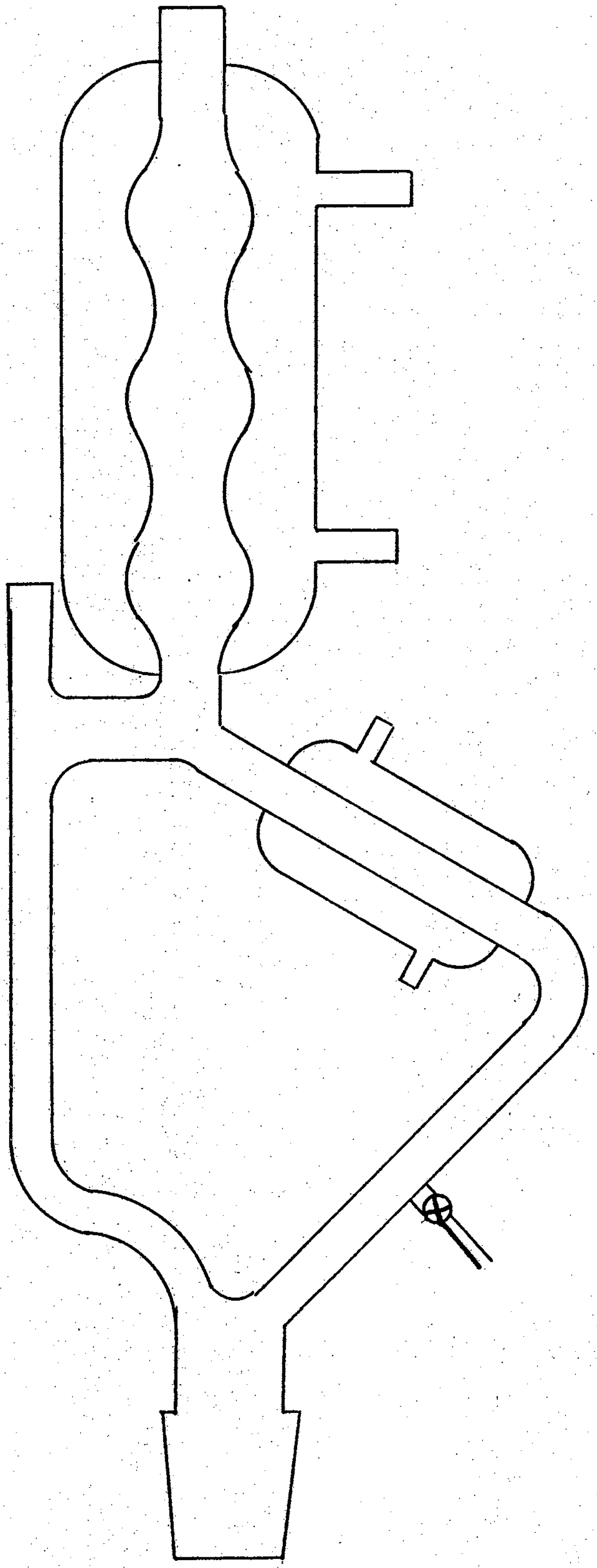


Figure 2. Reflux Condenser

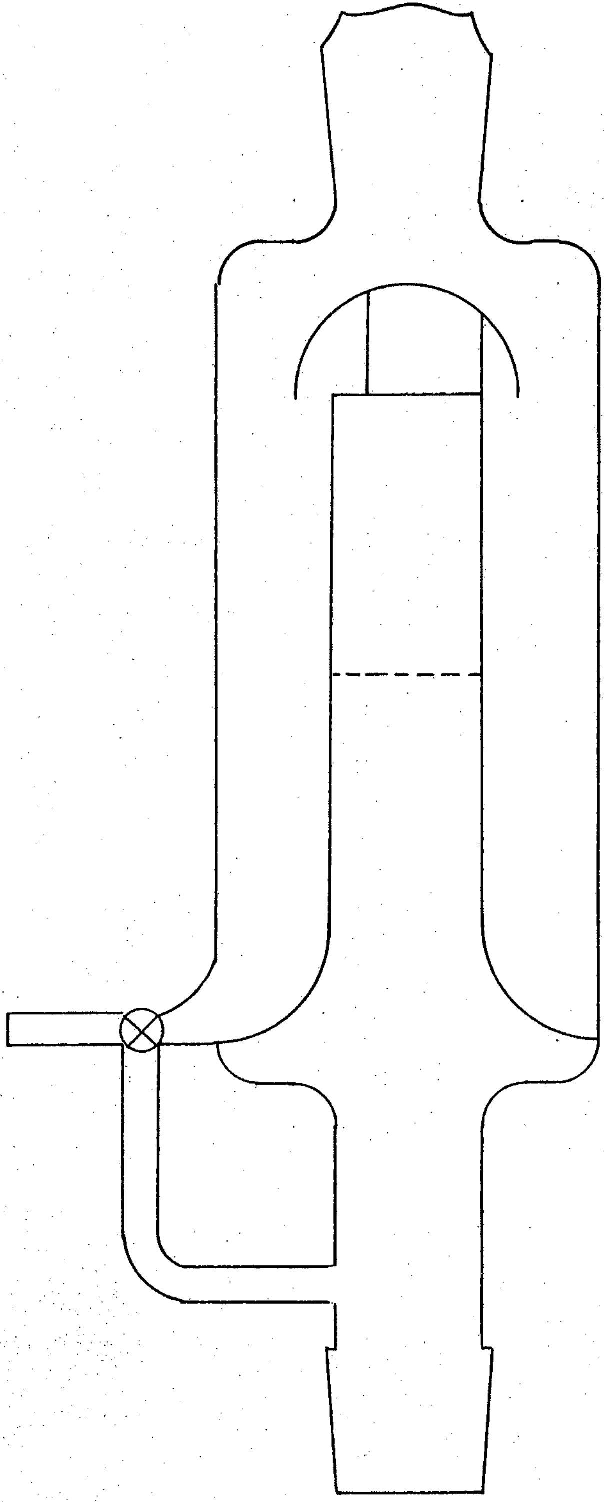


Figure 3. Reflux Rate Apparatus

The reboiler was a 1000 ml three necked flask with 29/42 \$ ground glass joints. One of the necks was used as a thermometer well and another was used as a method of introducing the pulse into the column. The reboiler was heated by a Glass-Col electric heating mantle and insulated with glass wool.

The pulse was introduced through a side arm on the reboiler. It was produced by the pulsation of a column of liquid in a glass tube. This liquid was of the same composition as that in the reboiler. The schematic of this system can be seen in Figure 4. The pulsing pump was a model CPS - 1 Lapp Pulsafeeder, manufactured by the Lapp Insulator Company. It was driven by a Graham variable speed drive which was connected to a Graham transmission. The motor of the unit was ¼ hp. and allowed an input frequency to the pulsafeeder of 0 - 235 cycles per minute. For this application the check valves in the head of the pulsafeeder were removed to allow simple pulsation without net flow of liquid. The pulse volume was variable from 0 to 12.5 ml per pulse and Claybaugh (9) reported that the frequency was reproducible to within 0.4 cpm at the highest frequency.

The pulsafeeder was constructed of stainless steel and teflon. The reagent head was constructed of stainless steel and the diaphragm was constructed of teflon. The diameter of the diaphragm was six inches. An overall view of the apparatus is shown in Figure 5.

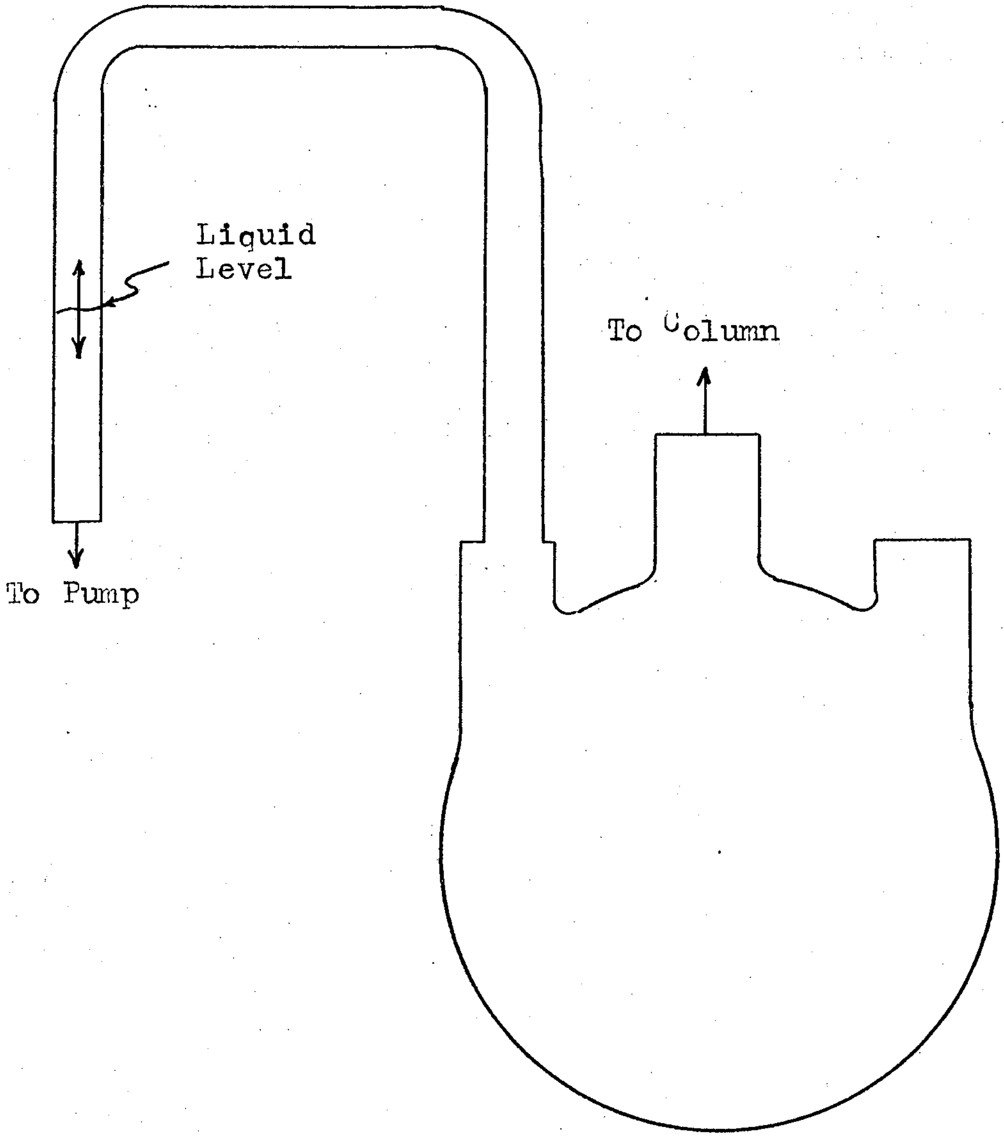


Figure 4. Pulse Apparatus

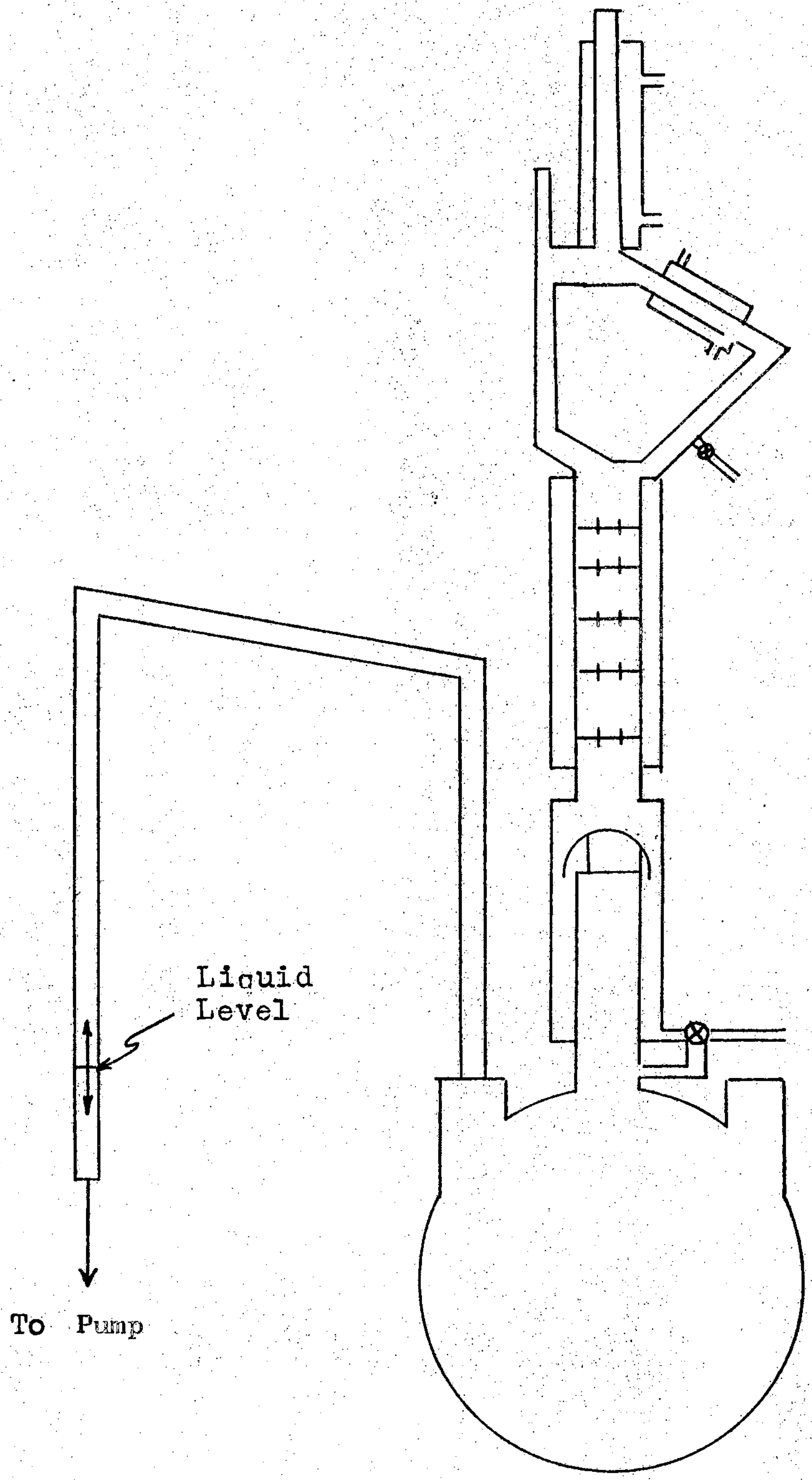


Figure 5. Pulsed Distillation Apparatus

CHAPTER III

EXPERIMENTAL PROCEDURE

Prior to beginning a series of runs the reboiler was filled with a solution of carbon tetrachloride and benzene of known composition. About 600 ml of this solution was normally used as a charge to the reboiler. The heating mantle was turned to sixty volts and the column was allowed to come to equilibrium. The pulsing unit was turned on after the column reached equilibrium. The desired frequency and amplitude of the pulse had previously been set. Sufficient time was allowed for the column to come to equilibrium under pulsation. Equilibrium was considered achieved when two samples taken several minutes apart had the same composition. After the column reached equilibrium the stopcock on the reflux rate apparatus was closed and the time necessary to collect 50 ml of reflux was measured. This time was converted into a reflux rate for the column.

Following this more time was allowed for the column to return to equilibrium. This additional time was deemed necessary because the collection of reflux in the reflux trap altered the composition of the reboiler liquid and this caused the column to depart from the steady state.

During all this time the column was operating under conditions of total reflux. Total reflux conditions were used because in a batch type distillation column the only steady state situation is at total reflux. This also simplified the calculations greatly. In the non-total reflux case the efficiency might have been a function of time which would not have been desirable. The steady state requirement could have been met with a continuous distillation column but the equipment available made it desirable to use a batch type column.

After the column had reached steady state, samples of the reflux and of the liquid draining from the bottom plate were taken. The reflux trap made it possible to sample the liquid coming from the bottom tray and this made it possible to avoid making any assumption about the type and operation of the reboiler. This assured that the results obtained were attributable only to the operation of the plates and were in no way dependent on the operation of the reboiler.

The reflux sample was withdrawn through a stopcock. The sample was withdrawn at a slow rate to avoid altering the composition at the top and causing an unsteady state situation. The rate at which it was possible to remove the overhead was less than one drop per three seconds. If the reflux was removed at any faster rate the composition was changed and the results were not reproducible. Normally two samples were removed from the top of the column. If the samples had an identical composition it was assumed that the column was at equilibrium. If there was a noticeable difference in the two samples more time was allowed for the column to come to equilibrium. Two samples were considered identical if their refractive indices differed by no more than 0.0002. If the difference was greater the column was assumed not to be in equilibrium and time was allowed for the column to reach equilibrium before further samples were withdrawn. At first two samples were also taken of the bottoms product. These samples appeared to always have the same composition and after the first few times only one sample was removed.

Method of Analysis

The analysis of the products was made by refractive index. The instrument used was an Abbe' type refractometer manufactured by the American Optical Company. This instrument can be read directly to ± 0.001 and can be estimated accurately to ± 0.0002. Readings were normally taken to ± 0.0001 in order to eliminate the possibility of any rounding off errors.

The refractometer was kept at 25.0 ± 0.2 degrees centigrade by the use of a constant temperature bath. The bath consisted of a LaPine temperature controller with built in pump and heater. Cooling coils were inserted in the bath and water from a cold sink was run through these coils, allowing the bath to be cooled. The source of the cold sink was provided by a tank of water placed in a refrigerator in which the temperature was about 40°F.

Selection of the System

The system of carbon tetrachloride - benzene was used. This system was chosen because it is a standard system for determining the efficiency of distillation columns and because Oldershaw used it in his original work on this type of column (15). This system was also chosen because the refractive indices of these compounds differ sufficiently to make analysis by refractive index accurate.

Quick, relatively accurate analysis by refractive index was believed necessary to determine when the column had reached equilibrium. A refractive index-mole fraction plot was constructed after the measurements had been made on the materials which were to be used in the experiment. The carbon tetrachloride was Fisher certified reagent grade which is at least 99 per cent pure. The benzene used was Phillips pure grade benzene which is guaranteed to be at least 99 per cent pure.

CHAPTER IV

RESULTS AND DISCUSSION

The raw data which were taken were used to obtain the efficiency of the distillation column. The McCabe-Thiele method of determining the number of trays in the distillation column was used (14). The main assumption involved in the use of the McCabe-Thiele method is that of constant molal overflow. For the carbon tetrachloride-benzene system the use of this assumption is well justified. The molal heat of vaporization of benzene is 7340 cal/gm mole and that of carbon tetrachloride is 7150 cal/gm mole (16). In a normal run the composition of the liquid changed from 30 per cent carbon tetrachloride at the top of the column to 20 per cent at the bottom of the column. The difference in the amount of heat necessary to vaporize one mole of each of these mixtures is 25 cal. This means that the molal overflow could have changed by 0.334 per cent from the top to the bottom of the column which is definitely negligible.

The other main assumption is that the column is adiabatic. It is safe to assume that this vacuum jacketed, silvered column is close to adiabatic. In this case a small departure from adiabaticity would tend to cause the molal overflow to be more nearly constant because the molal heat of vaporization of the product is less than that of the original feed. Since the column only changed the composition by about 10 per cent the scale of the McCabe-Thiele diagram was expanded to insure greater accuracy in determining the number of stages. The equilibrium data used for the diagram were taken from Chu (17).

The efficiency of the Oldershaw column without pulsing was first determined as a function of flow rate. These data are presented in Tables I and II in Appendix A and shown graphically in Figure 6. As was expected, the efficiency of the column decreased with increasing flow rates above a certain minimum which was necessary to insure the stability of the column.

The minimum flow rate necessary to insure the stability of the column was found to be between 800 and 1000 ml of reflux per hour. At 1000 ml per hour the column was definitely stable and at rates below 800 ml per hour the column was definitely unstable. Between these two limits the stability of the column seemed to depend on chance or on factors which could not be measured. Apparently a slight change in the conditions caused the system to be either stable or unstable. At a liquid reflux rate of over 2500 ml per hour the column was still operating but the condenser and reflux rate timing apparatus began to flood. The results of any runs taken above about 2800 ml per hour would be questionable. For this reason no readings were taken with the flow rate higher than this.

After the efficiency of the column without pulsing had been definitely determined the runs with pulsation were begun. The first series of runs were made with the maximum available amplitude of 12.5 ml per pulse. The efficiency - flow rate curves at this

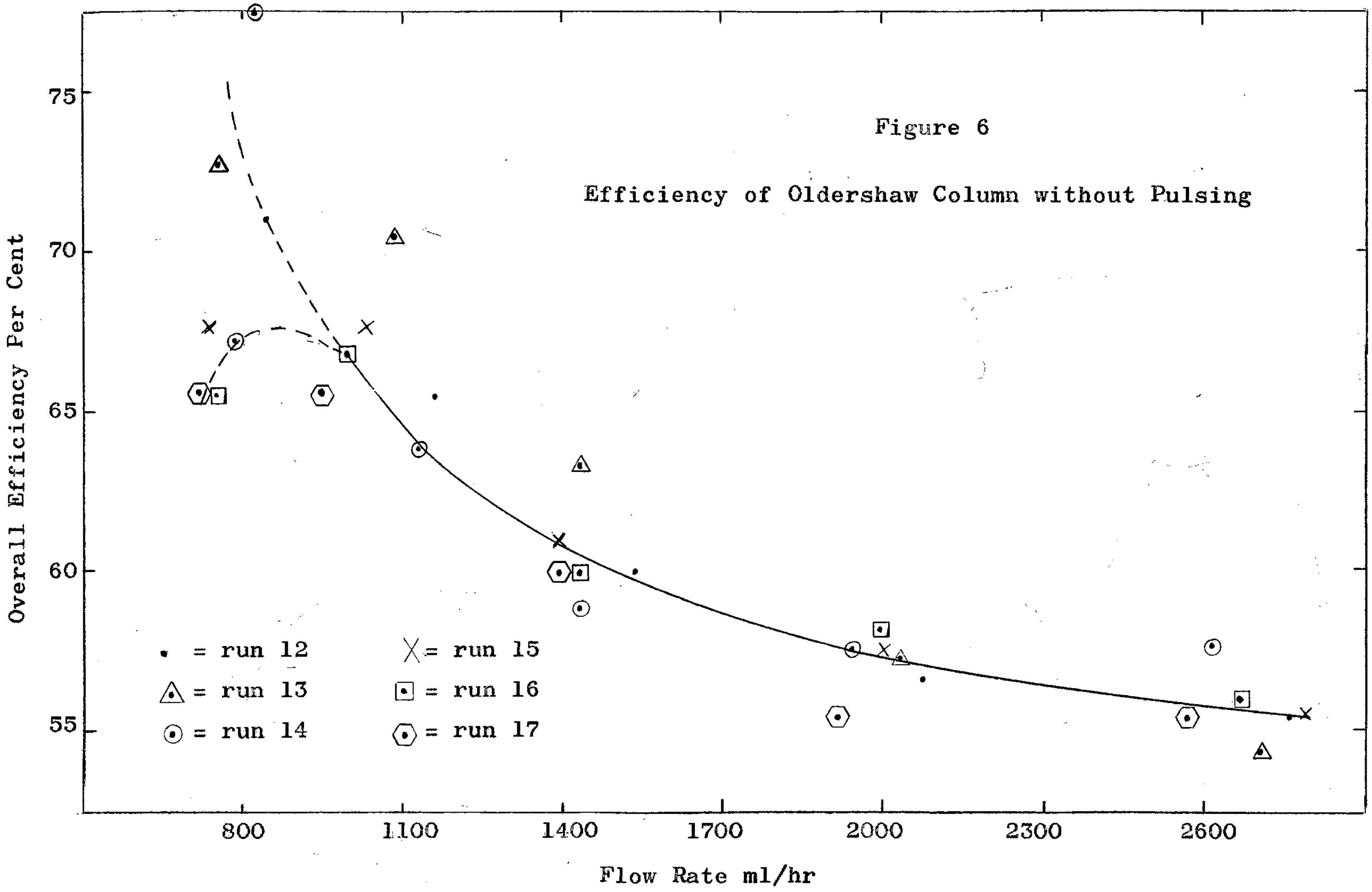


Figure 6

Efficiency of Oldershaw Column without Pulsing amplitude were taken for several different frequencies. Frequencies of 2, 4, 8, 15, 30, 60, 120, and 220 cycles per minute were all investigated.

Results of Initial Pulsed Runs

The results of these runs are presented in Tables III - VIII, Appendix A, and shown graphically in Figures 8-15, Appendix B. A typical curve is shown in Figure 7. In most cases, the efficiency of the column was considerably higher with pulsation than without. The data for the runs at two cycles per minute (cpm) were widely scattered and no conclusions could be drawn. It is probable that this low pulse frequency disturbs the column only enough to make it unstable. At a pulse frequency of 4 cpm a definite increase in the efficiency of the column was noted. This increase in efficiency was from one to three per cent and varied with the flow rate. Eight cpm provided a similar increase. A frequency of 15 cpm caused a notably greater increase than was noted at 4 cpm. This increase was from three to six per cent above the corresponding values obtained without pulsation. This value is about twice that which was observed at lower pulse frequencies. A similar but slightly lesser increase was observed at 30 cpm and a still lower increase was noted at 60 cpm. At both 120 and 220 cpm a different effect was noticed. At low flow rates there was a marked decrease in the efficiency of the column. In fact, the column was considerably less efficient than in the case of no pulsation. At 220 cpm this effect extended to higher flow rates than it did for 120 cpm.

After the completion of the above series of runs, an

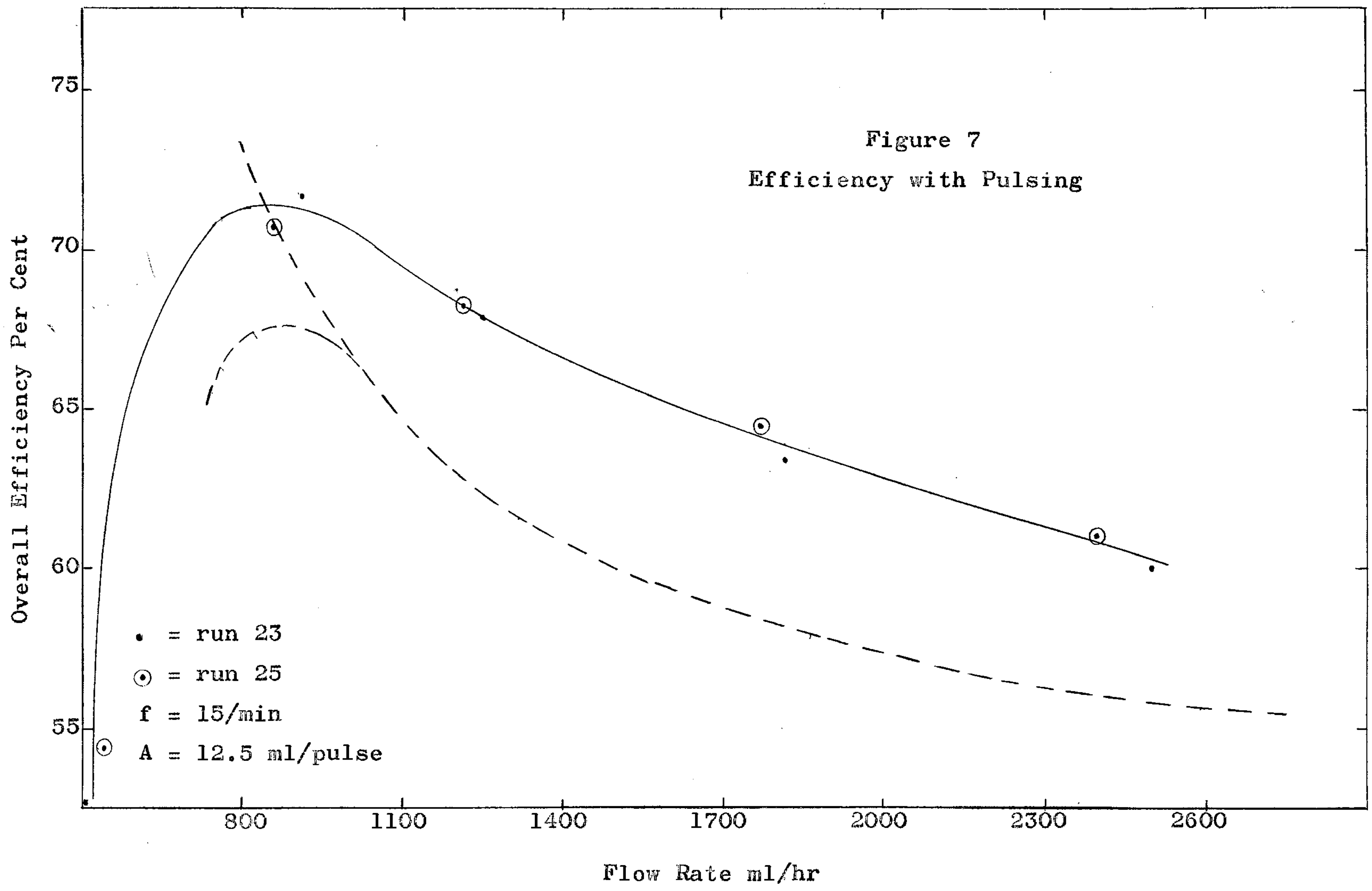


Figure 7

Efficiency with Pulsing

investigation of the effect of pulse amplitude on the increase in efficiency was undertaken. The study was made to determine if the same sort of behavior with variation in frequency occurred at other amplitudes. A pulse amplitude of 6 ml was chosen for this series of runs. The results of this series of runs are presented in Tables IX and X, Appendix A, and are shown graphically in Figures 16-18, Appendix B. At a frequency of 4 cpm an increase in the efficiency of one to two per cent was noticed. The dependence of this increase on flow rate was noticeable only at low flow rates. At a frequency of 30 cpm the efficiency increase was from three to four and one-half per cent. This increase seemed to grow with increasing flow rate. At a frequency of 220 cpm the increase in efficiency decreased to one and one-half to two per cent above the non-pulsed value.

The next logical step in the investigation was to go to a very small pulse amplitude and determine if the effect still existed there and, if so, how great it was. The amplitude was chosen as one ml per pulse. This was small enough to show any different effect that might occur but large enough to be accurately reproducible. At a frequency of 30 cpm some effect was noticeable. At this frequency the efficiency increased one to two per cent at medium flow rates but appeared to be lower at the extreme flow rates. Finally the pulsation frequency was raised to 220 cpm and at this high frequency a strong increase in the efficiency was noted. This increase was from three to five per cent and seemed to increase with increasing flow rate. The data from this series of runs are presented in Tables XI-XIII, Appendix A, and shown graphically in Figures 19-21, Appendix B. The amount of data collected to this point was thought sufficient for the scope of this study.

Correlation of Efficiency with Variables

The effect of frequency on efficiency at various flow rates and specific amplitudes was determined. The results were plotted and appear in Figures 22-24, Appendix B. At 1 ml amplitude the effect of pulsing increased with increasing frequency. At low frequencies there was no noticeable effect due to pulsing. At slightly higher frequencies there was a definite but slight increase in efficiency. At the highest frequency there was a substantial increase in the efficiency of the column.

At six ml per pulse there was a similar effect. In this case, however, there was a noticeable effect even at the lowest frequency of 4 cpm. There was also a greater effect at 30 cpm. This was in agreement with what would be expected from the first results. When the frequency was increased to 220 cpm the increase in efficiency was less than that observed at 30 cpm. This increase in efficiency was still greater than that of 4 cpm.

At a pulse amplitude of 12.5 ml there was again a similar effect. The efficiency at 4 cpm was notably greater than that of no pulsing and greater than the similar effect at 6 ml per pulse. At 15 cpm the effect was very large and was of the order of 5 to 6 per cent for the entire range of flow rates. By the time 60 cpm is reached the trend tends to reverse itself and the efficiency is lower than that reported for 15 cpm. At a frequency of 220 cpm the efficiency was actually less than in the case of no pulsing at all but the highest flow rate. This decrease was more than 10 per cent at some flow rates and was greater than four per cent at any flow rate less than 1800 ml per hour.

The effect of amplitude on efficiency at various flow rates and selected frequencies was also determined. The results of this are shown in Figures 25-27, Appendix B. At a frequency of 4 cpm the efficiency increased with increasing amplitude throughout the entire range of amplitudes available in the experiment. This same phenomenon was evident at a frequency of 30 cpm. The efficiency steadily increased although most of the increase took place in the lower amplitudes and the change of amplitude from 6 to 12.5 ml per pulse made very little difference in the efficiency.

At a frequency of 220 cpm an effect appeared which was analogous to the effect reported in the case of various amplitudes. There was a great increase in efficiency between 0 and 1 ml per pulse and between one and six ml the effect was somewhat negated. Actually the effect was only about one-half of that which appeared at one ml per pulse. When the amplitude was further increased to 12.5 ml there was a sharp decrease in efficiency, and for most flow rates it was lower than that for the non-pulsed case.

The phenomenon of passing through a maximum brought up the possibility that the efficiency might be a function of the frequency-amplitude product. This has been previously suggested for the similar phenomenon in pulsed extraction (3). The frequency-amplitude product was plotted against efficiency for various flow rates. This is shown in Figure 28, Appendix B. In every case the efficiency was found to pass through a maximum as the frequency-amplitude product increased. For the flow rate of 1100 ml per hour the initial efficiency was 64.4 per cent and the efficiency passed through a maximum of 69.6 per cent at a frequency-amplitude product of about 600 ml per minute of vapor. Similar behavior was exhibited at all the other flow rates.

The maximum efficiencies for the various flow rates were reached at different points. The maximum for 1400 ml per hour was reached at about 480 ml/min. The maximum for the 2000 ml per hour flow rate was reached at about 300 ml/min. while the maximum for 2600 ml per hour was reached at 240 ml/min. Thus, it is seen that with increasing flow rate the maximum increase in efficiency occurs at continuously smaller frequency-amplitude products.

Correlation Attempt

An attempt was made to explain the increased efficiency through the use of the A.I.Ch.E. tray efficiency correlation. The overall efficiency of a distillation column is given by the equation

$$\frac{-1}{2.3 \log (1-E_{og})} = \frac{1}{N_{og}} + \frac{\lambda}{N_l} \qquad (1)$$

Where N_{og} is the number of gas phase transfer units and N_l is the number of liquid phase transfer units. λ is the ratio of the amount of resistance in the gas phase to that in the liquid phase.

Both of the transfer units are functions of the gas and liquid flow rates. In its study the A.I.Ch.E. found that the following equations expressed these units adequately.

$$N_g = \frac{(0.776 + 0.116\ W - 0.290\ F + 0.0217\ L)}{N_{sc}^{0.5}} \qquad (2)$$

$$N_l = (1.064 \times 10^4\ D_l)^{0.5}\ (0.26\ F + 0.15)T_l \qquad (3)$$

In these equations W is weir height, F is the F factor which is the velocity in feet per second times the square root of the density of the gas. L is the volumetric flow rate in gallons per minute per average foot of flow width. D_l is the liquid diffusivity and T_l is the residence time in seconds.

The A.I.Ch.E. correlation was developed for large scale distillation columns and the constants do not necessarily apply to a small column such as was used in this work. Through appropriate assumptions and substitutions the equations in this case were reduced to:

$$N_l = K_1 + K_2'\ F \qquad (4)$$

$$N_g = K_5' + K_6'/F \qquad (5)$$

Substitution of this into equation 1 gives

$$\frac{1}{2.303 \log\ (1-E_{og})} = \frac{1}{K_1 + K_2'\ F} + \frac{1}{K_5' + K_6'/F} \qquad (6)$$

An attempt was made to use the A.I.Ch.E. developed constants. This attempt failed when the answers it gave were not reasonable. The constants for equation 4 were reasonable and these values were accepted. The experimental data of this investigation were then used to determine the values of the constants in equation 5. In order to do this it was assumed that the constants had the same ratio as they had in the original correlation.

These constants turned out to be variables with flow rate. This made it clear that a quantitative answer could not be easily obtained. The average values of the constants were taken in order to try to obtain a qualitative explanation of the increase in efficiency. The problem was set up on the analog computer in the hope of using this to determine the actual constants if the method predicted the observed increase. A hand calculation showed that the A.I.Ch.E. correlation predicted the same efficiency for the case of a pulsed vapor flow as it did for the case of no pulsing. At that point the attempt to use the correlation was abandoned. A more complete description of the work which was done on this correlation may be found in Appendix C.

Effects Noticed and Their Possible Causes

Several effects have been noted in this investigation. At low flow rates the column becomes unstable even in the absence of pulsation. By unstable is understood that the efficiency is considerably lower than expected. The probable explanation for this lies in the fact that at low vapor flow rates the liquid on the sieve trays is able to leak through them and thus the gas-liquid residence time is small. This phenomenon is known as weeping and occurs in all distillation columns if the vapor flow rate becomes small enough (17).

In this column weeping is observed at a reflux flow rate of about 800 ml per hour if the column is not being pulsed. This is at a vapor velocity of about one centimeter per second. With pulsation, instability often occurs at higher flow rates than without pulsing. In all of the runs with a pulse amplitude of either 1 or 6 ml per pulse this occurs at a flow rate of approximately 1000 to 1100 ml per hour. The instability in this flow rate range normally occurs at pulse frequencies of 30/min. or greater.

In the limiting case of a pulse amplitude of 12.5 ml this effect also occurs at higher flow rates. At 120 cpm the column is unstable up to a flow rate of 1700 ml per hour. In the case of 220 cpm the column is unstable at every point except the terminal point of 2600 ml per hour.

Visual observation does not detect any significant amount of liquid on the trays of the column during the regime of unstable operation. Apparently the liquid is either blown up into the downcomer or seeps through the trays. Both of these effects are probably present in the column. The large increase in the point where stability first occurs is probably due mainly to a small amount of liquid which is blown upward and drains down the downcomers. This probably occurs at high pulse amplitudes where the clear liquid is actually bumped up over the downcomer. The lesser increase in flow rate necessary to establish stability at lower pulse amplitudes is probably due to the lowering of the vapor flow rate in part of the pulse which allows weeping to occur. Since the vapor velocity is not a constant the weeping occurs at higher average vapor velocities than in the case of no pulsation.

The Increase Noted in Efficiency

The increase in efficiency that has been noted as a result of pulsation is more difficult to explain. There are two ways that it is possible to increase the efficiency of a distillation column. One of these would be to raise the residence time of the gas in the liquid. If this could be raised indefinitely a perfect plate could be achieved. The other way to increase the efficiency is to increase the mass transfer rate by decreasing the resistance to mass transfer.

Some writers have said that most of the mass transfer takes place in the froth above the clear liquid on the plate (12). Some of the mass transfer also takes place in the clear liquid layer. If it is true that the majority of the mass transfer takes place in froth then the residence time in the froth should be a reasonable criterion for measuring the approach to equilibrium.

If the residence time in the froth is longer then the efficiency should be higher, other effects being negligible.

The A.I.Ch.E. tray efficiency study showed that the froth height is approximately proportional to the square of the F factor, where the F factor is the product of the superficial linear velocity and the square root of the density of the gas. A sinusoidal pulse imposed on the vapor flow rate will then increase the average froth height without increasing the throughput of the column because $(A + B \sin CT)^2$ is greater than A^2 by $B^2 \sin^2 CT$. With all other factors held constant this will increase the average residence time of the vapor in the froth on each tray. This will make possible a closer approach to equilibrium, and therefore a higher efficiency will be achieved.

When the column is being pulsed the turbulence on the trays and in the froth will be increased and this might decrease the boundary layer which controls the resistance to mass transfer.

This would increase the mass transfer coefficient which would in turn increase the efficiency of the plate.

Similar to this is another possible effect. One of the reasons that efficiency decreases with increasing flow rate has been reported to be that the bubbles coming from the sieves tend to channel (12). That is, they tend to form a column through the clear liquid as well as through the froth. This means that it is possible for the vapor to pass a tray without ever coming into close contact with the liquid on that tray. During pulsation the vapor flow rate through the trays is not a constant and therefore since the actual flow rate is less than the average for part of the pulse there would be little tendency to form the columns of vapor at the lower vapor flow rate. Then the columns would have less chance to establish themselves in the high rate period. The net result would then be a lessening of the tendency for the vapor to channel. This would result in an increase in the efficiency of the column.

There are therefore three effects which may be the cause of the increased efficiency which has been noted in the column under conditions of pulsing. An increase in the effective residence time, an increase in turbulence resulting in a decrease in the resistance to mass transfer, and a decrease in the tendency to channel. All tend to increase the efficiency of the column under conditions of pulsation.

Difficulties Encountered in Experimentation

A number of difficulties were encountered during the course of this investigation. Two of these stand out as major difficulties. The most important of these was obtaining reproducible results. The other important difficulty was the tendency of the system to leach stopcock grease from the joints and collect it in the reboiler. This caused the boiling stones in the reboiler to clog up and caused the reboiler charge to superheat. The loss of grease also caused leaks in the system.

Obtaining reproducibility was the most important difficulty encountered. When the column was first put into operation the primary condenser cooled the reflux to its bubble point, and allowed it to drain back into the column. Between the reflux takeoff and the point where the sample was actually collected the liquid passed through another cooler to insure that it would be enough below its bubble point that an appreciable amount of sample would not be lost to vaporization, which might have affected the composition of the sample.

Unfortunately it was necessary to drain almost 1/2 ml of sample to be sure that the liquid was actually the reflux which was being formed at the time. The removal of this large amount of sample caused a change in the composition at the top of the column. Because of this it was impossible to achieve good, reproducible results. After the difficulty was analyzed this sampling arrangement was replaced. The new sampling arrangement subcooled all of the liquid and then had only a very short length of capillary bore glass tubing between the reflux line and the sampling point. The short length of tubing between the sampling point and the stopcock was emptied between the taking of samples so that no sample would have to be discarded. The sample was also removed at a very slow rate so that the composition at the top of the column would not change during the collection of the sample. The rate of taking the sample was held to one drop per three seconds or less and this, combined with the equipment modification, allowed reproducible results to be achieved.

The clogging of boiling stones and the resultant superheating in the reboiler liquid caused a lesser difficulty. This occurred mainly in the later runs. The reboiler temperature was noted to be rising from its normal 178°F to as high as 188°F. This caused some of the results to be erratic because the column was not in stable, steady state operation. When this occurred it was necessary to disassemble the column and thoroughly clean it. This was done with standard sulfuric acid cleaning solution. The petroleum base stopcock grease which had been in use was replaced with Non-Aq stopcock grease. After the cleaning and change of stopcock grease no further superheating was observed. Another problem was also cured by this change. The leaking of stopcocks which had ruined several runs was entirely eliminated.

Accuracy of Experimental Results

The accuracy of the experimental results obtained in this investigation has several limiting factors. The primary limitation is the accuracy of analysis which can be achieved by refractive index with the refractometer that was employed for this investigation. This refractometer is readable to 0.0001 and the results are reproducible to the same degree of accuracy. The smallest of the actual divisions on the scale is 0.001 and thus the accuracy was only as good as could be obtained with this refractometer.

This degree of accuracy still left something to be desired. The spread between the refractive index of the reflux and the bottoms product was usually about 0.004 and therefore it was possible to make an error of two per cent and still be within the accuracy of the refractometer. In practice the error was often one per cent or less but on occasion there were runs which deviated from one another by as much as three per cent which is still within the overall accuracy of the experiment.

The other main limitation on the accuracy of the results was the accuracy of the McCabe-Thiele method of analyzing the distillation column. This method allowed duplication, when done on expanded graph paper, to within about one per cent. Many times it was possible to reproduce the results exactly with the McCabe-Thiele diagram and other times the error was about one per cent. The overall accuracy of the experiment was within three per cent. In practice this accuracy was often bettered and there are numerous cases of identical reproduction. Thus, since the effect measured was of the order of five or six per cent, the increase in efficiency can be said to be significant although not enough runs were made at any given conditions to prove this statistically.

CHAPTER V

RECOMMENDATIONS AND CONCLUSIONS

The following are the conclusions which can be logically drawn from this investigation.

1. There is an increase in the efficiency of a column which occurs when the column is pulsed.
2. There are probably several causes for this increased efficiency.
    (a) The increase in the effective residence time on each plate.
    (b) The decrease in the resistance to mass transfer caused by increased turbulence.
    (c) A lessened tendency to channel which is caused by the fluctuations in the vapor rate.
3. The instability which occurs at low vapor flow rates is probably due to a tendency of the tray to weep.
4. The instability which occurs at higher pulse amplitudes and higher reflux rates is probably due to liquid being blown over the downcomers during the upward pulse and then being drawn into the downcomers during the downward pulse.

There are several paths open for further study in this field. Among them are the following:

1. The expansion of this experiment to large scale distillation columns. This would determine if the process has any potential commercial value.
2. The definite determination of the causes of the increase in efficiency which has been noted. This would involve the construction of a column where it would be possible to study froth height and determine if the proposed mechanism is valid.
3. The extension of this work to a continuous column. If there is to be any commercial use of this phenomenon it will be necessary to discover what happens when a continuous distillation column is pulsed.

A SELECTED BIBLIOGRAPHY

1. Armstrong, W. D. and R. M. Wood, "An Introduction to the Theoretical Evaluation of the Frequency Response of a Distillation Column to a Change in Reflux Flow", Transactions of the Institute of Chemical Engineers, Vol. 39, 80 (April, 1961).

2. Armstrong, W. D. and R. M. Wood, "The Dynamic Response in a Distillation Column to Changes in the Reflux and Vapour Flow Rates", Transactions of the Institution of Chemical Engineers, Vol. 39, 65 (April, 1961).

3. Beyer, G. H. and R. M. Cohen, "Performance of a Pulsed Extraction Column", Chem. Eng. Prog., 50, 278 (1954).

4. Beyer, G. H. and R. B. Edwards, "Flooding Characteristics of a Pulse Extraction Column", A.I.Ch.E. Journal 2, (1956).

5. Ceaglske, N. H., "Dynamics of Fractional Distillation", A.I.Ch.E. Journal, 7, 653, (1961).

6. Chantry, W. A., "Pulse Columns in Liquid-Liquid Extraction", Ind. Eng. Chem., 47, 1153, (1955).

7. Chu, J. C., et. al., Vapor Liquid Equilibrium Data, Ann Arbor, Michigan (1956).

8. Bubble Tray Design Manual, A.I.Ch.E., New York (1958).

9. Claybaugh, W. E., "Limiting Flow Capacities in a Pulse Extraction Column", M.S. Thesis, Oklahoma State University (1959).

10. Claybaugh, W. E., "Effects of Backmixing on Concentration Profiles in a Pulse Column", Ph.D. Thesis, Oklahoma State University (1961)

11. Foss, A. S. and J. A. Gerster, "Liquid Film Efficiencies on Sieve Trays", Chem. Eng. Prog., 52, 28, (1956).

12. Garner, F. H. and K. E. Porter, "Mass Transfer Stages in Distillation", Proceedings of the International Symposium on Distillation, The Institution of Chemical Engineers, London (1960).

13. McAllister, R. A. and C. A. Plank, "Pulsations in Sieve Tray and Bubble Cap Distillation Columns", A.I.Ch.E. Journal, 4, 282, (1958).

14. McCabe, W. L. and J. C. Smith, Unit Operations of Chemical Engineering, McGraw-Hill, New York, (1955).

15. Oldershaw, C. F., "Perforated Plate Columns for Analytical Batch Distillations", Ind. Eng. Chem. Analytical Edition, 13, 265, (1941).

16. Perry, J. H., editor, Chemical Engineers Handbook, McGraw-Hill, New York, (Third ed. 1951).

17. Prince, R.G.H., "Characteristics and Design of Bubble Plate Columns", Proceedings of the International Symposium on Distillation, The Institution of Chemical Engineers, London, (1960).

NOMENCLATURE

The units on many of the quantities are often given in two systems. The English system is the original system used by the A.I.Ch.E. Tray Efficiency Committee in their correlation while the metric units were used in this work.

A = bubbling area, sq. ft., cm^2.

a = interfacial area per unit volume of holdup, $ft.^{-1}$. cm^{-1}.

E_{og} = overall point efficiency in vapor terms.

E_{ol} = overall point efficiency in liquid terms.

F = F factor, the square root of the gas density times the superficial linear gas velocity.

G_m = gas flow rate per unit bubbling area, # moles/hr. $ft.^2$, gm. moles/hr. cm^2.

K_{og} = overall gas mass transfer coefficient, # moles/hr. $ft.^2$, atm., gm. moles/hr. cm^2 atm.

L = liquid volume flow rate factor, gal./min. ft., cm^3/min cm.

L_m = liquid flow rate per unit bubbling area, # moles/hr. $ft.^2$, gm moles/hr cm^2.

N = rate of diffusion, # moles/hr., gm moles/hr.

N_g = gas film transfer unit.

N_l = liquid film transfer unit.

N_{og} = overall gas transfer unit.

N_{ol} = overall liquid transfer unit.

p = partial pressure, atmospheres.

p_g = gas phase partial pressure, atm.

p = total absolute pressure, atm.

S = interfacial area, $ft.^2$.

t_l = true liquid residence time, seconds.

t_g = true gas residence time, seconds.

W = weir height, inches, mm.

y = mole fraction in gas phase.

y^* = equilibrium mole fraction.

Z = height in column ft., cm.

Z_c = measured clear liquid height, in., cm.

λ = ratio of the mass transfer resistance in the gas to that in the liquid.

ρ = molal density of the liquid phase, # $moles/ft^3$, gm $moles/cm^3$.

APPENDIX A

EXPERIMENTAL DATA

TABLE I

EXPERIMENTAL DATA RUNS 12, 13, 14

Run Number 12, Pulse Frequency 0/min., Amplitude 0 cm^3

Sample #	R.R.ml/hr	RI Top	RI Bot.	# Plates	Eff. %
1	845	1.4812	1.4864	3 10/18	71.1
2	1160	1.4816	1.4864	3 5/18	65.5
3	1540	1.4820	1.4864	3	60.0
4	2070	1.4821	1.4863	2 15/18	56.7
5	2760	1.4821	1.4862	2 14/18	55.6

Run Number 13, Pulse Frequency 0/min., Amplitude 0 cm^3

Sample #	R.R.ml/hr	RI Top	RI Bot.	# Plates	Eff. %
1	760	1.4810	1.4863	3 12/19	72.6
2	1090	1.4810	1.4862	3 10/19	70.5
3	1430	1.4817	1.4862	3 3/18	63.3
4	2040	1.4818	1.4861	2 16/18	57.3
5	2700	1.4820	1.4860	2 14/19	54.6

Run Number 14, Pulse Frequency 0/min., Amplitude 0 cm^3

Sample #	R.R.ml/hr	RI Top	RI Bot.	# Plates	Eff. %
1	820	1.4834	1.4886	3 7/9	77.7
2	1130	1.4839	1.4884	3 7/36	63.8
3	1430	1.4842	1.4884	2 17/18	58.9
4	1936	1.4843	1.4884	2 7/9	57.7
5	2610	1.4843	1.4884	2 7/9	57.7

TABLE II

EXPERIMENTAL DATA RUNS 15, 16, 17

Run Number 15, Pulse Frequency 0/min., Amplitude 0 cm^3

Sample #	R.R.ml/hr	RI Top	RI Bot.	# Plates	Eff. %
1	742	1.4840	1.4886	3 6/18	66.7
2	1035	1.4840	1.4886	3 6/18	66.7
3	1396	1.4845	1.4886	3 1/18	61.1
4	2000	1.4845	1.4886	2 15/18	57.6
5	2790	1.4847	1.4886	2 14/18	55.7

Run Number 16, Pulse Frequency 0/min., Amplitude 0 cm^3

Sample #	R.R.ml/hr	RI Top	RI Bot.	# Plates	Eff. %
1	750	1.4844	1.4889	3 5/18	65.6
2	1025	1.4842	1.4890	3 3/8	67.5
3	1430	1.4846	1.4888	3	60.0
4	1990	1.4848	1.4888	2 32/35	58.3
5	2670	1.4850	1.4888	2 27/34	56.0

Run Number 17, Pulse Frequency 0/min., Amplitude 0 cm^3

Sample #	R.R.ml/hr	RI Top	RI Bot.	# Plates	Eff. %
1	720	1.4845	1.4890	3 5/18	65.6
2	945	1.4844	1.4890	3 5/18	65.6
3	1395	1.4849	1.4890	3	60.0
4	1910	1.4851	1.4890	2 14/18	55.5
5	2570	1.4851	1.4890	2 14/18	55.5

TABLE III

EXPERIMENTAL DATA RUNS 18, 19, 20

Run Number 18, Pulse Frequency 60/min., Amplitude 12.5 cm^3

Sample #	R.R.ml/hr	RI Top	RI Bot.	# Plates	Eff. %
1	740	1.4854	1.4894	3	60.0
2	1000	1.4847	1.4895	3½	70.0
3	1330	1.4849	1.4896	3 13/36	67.2
4	1820	1.4853	1.4895	3 1/18	61.0
5	2400	1.4856	1.4896	3	60.0

Run Number 19, Pulse Frequency 60/min., Amplitude 12.5 cm^3

Sample #	R.R.ml/hr	RI Top	RI Bot.	# Plates	Eff. %
1	710	1.4853	1.4894	3 9/36	65.0
2	868	1.4847	1.4895	3½	70.0
3	1200	1.4849	1.4896	3 13/36	67.2
4	1580	1.4851	1.4896	3 2/10	64.0
5	2300	1.4856	1.4897	3 1/20	61.0

Run Number 20, Pulse Frequency 60/min., Amplitude 12.5 cm^3

Sample #	R.R.ml/hr	RI Top	RI Bot.	# Plates	Eff. %
1	650	1.4859	1.4899	2 16/17	59.0
2	885	1.4852	1.4899	3½	70.0
3	1210	1.4860	1.4900	3	60.0
4	1720	1.4859	1.4900	3 3/36	62.0
5	2410	1.4860	1.4900	3	60.0

TABLE IV

EXPERIMENTAL DATA RUNS 21, 22, 23

Run Number 21, Pulse Frequency 30/min., Amplitude 12.5 cm^3

Sample #	R.R.ml/hr	RI Top	RI Bot.	# Plates	Eff. %
1	690	1.4836	1.4890	3 15/19	75.8
2	900	1.4841	1.4892	3 11/19	71.6
3	1220	1.4847	1.4894	3 7/19	67.3
4	1710	1.4851	1.4895	3 8/37	64.3
5	2500	1.4853	1.4894	3	60.0

Run Number 22, Pulse Frequency 30/min., Amplitude 12.5 cm^3

Sample #	R.R.ml/hr	RI Top	RI Bot.	# Plates	Eff. %
1	545	1.4859	1.4899	3	60.0
2	880	1.4851	1.4900	3 11/18	72.2
3	1260	1.4852	1.4899	3 7/17	68.2
4	1760	1.4857	1.4900	3 3/18	63.4
5	2480	1.4859	1.4899	3	60.0

Run Number 23, Pulse Frequency 15/min., Amplitude 12.5 cm^3

Sample #	R.R.ml/hr	RI Top	RI Bot.	# Plates	Eff. %
1	500	1.4857	1.4896	2 11/17	53.0
2	900	1.4851	1.4900	3 11/19	71.7
3	1250	1.4855	1.4900	3 7/18	67.8
4	1800	1.4859	1.4901	3 3/18	63.3
5	2500	1.4861	1.4900	3	60.0

TABLE V

EXPERIMENTAL DATA RUNS 24, 25, 26, 27

Run Number 24, Pulse Frequency 15/min., Amplitude 12.5 cm^3

Sample #	R.R.ml/hr	RI Top	RI Bot.	# Plates	Eff. %
1	This run failed				

Run Number 25, Pulse Frequency 15/min., Amplitude 12.5 cm^3

Sample #	R.R.ml/hr	RI Top	RI Bot.	# Plates	Eff. %
1	540	1.4851	1.4888	2 12/17	54.2
2	860	1.4849	1.4897	3 10/19	70.6
3	1200	1.4851	1.4898	3 7/17	68.2
4	1770	1.4854	1.4898	3 2/9	64.4
5	2400	1.4857	1.4898	3 1/18	61.0

Run Number 26, Pulse Frequency 4/min., Amplitude 12.5 cm^3

Sample #	R.R.ml/hr	RI Top	RI Bot.	# Plates	Eff. %
1	580	1.4853	1.4896	3 3/36	61.7
2	950	1.4848	1.4895	3 8/17	69.5
3	1320	1.4854	1.4898	3 4/18	64.4
4	2110	1.4858	1.4899	3 1/36	60.6
5	2560	1.4859	1.4897	2 13/18	54.5

Run Number 27, Pulse Frequency 4/min., Amplitude 12.5 cm^3

Sample #	R.R.ml/hr	RI Top	RI Bot.	# Plates	Eff. %
1	613	1.4859	1.4896	2 12/17	54.2
2	923	1.4851	1.4898	3 7/17	68.2
3	1390	1.4855	1.4898	3 7/36	63.9
4	1850	1.4859	1.4900	3 1/18	61.0
5	2500	1.4859	1.4898	2 14/18	56.0

TABLE VI

EXPERIMENTAL DATA RUNS 28, 29, 30

Run Number 28, Pulse Frequency 2/min., Amplitude 12.5 cm^3

Sample #	R.R.ml/hr	RI Top	RI Bot.	# Plates	Eff. %
1	680	1.4859	1.4900	3 4/18	64.5
2	1000	1.4858	1.4900	3 13/36	67.2
3	1330	1.4859	1.4900	3 5/36	62.8
4	1870	1.4860	1.4900	3 1/18	61.0
5	2540	1.4861	1.4900	3	60.0

Run Number 29, Pulse Frequency 2/min., Amplitude 12.5 cm^3

Sample #	R.R.ml/hr	RI Top	RI Bot.	# Plates	Eff. %
1	723	1.4858	1.4897	3	60.0
2	1000	1.4858	1.4900	3 4/18	64.5
3	1390	1.4860	1.4900	3 3/36	62.0
4	1900	1.4861	1.4901	3	60.0
5	2630	1.4837	1.4870	2 7/17	48.0

Run Number 30, Pulse Frequency 2/min., Amplitude 12.5 cm^3

Sample #	R.R.ml/hr	RI Top	RI Bot.	# Plates	Eff. %
1	675	1.4851	1.4898	3 13/36	67.2
2	953	1.4850	1.4898	3 17/36	69.3
3	1305	1.4855	1.4900	3 6/18	66.7
4	1820	1.4859	1.4900	3 3/18	63.3
5	2600	1.4859	1.4900	3 3/18	63.3

TABLE VII

EXPERIMENTAL DATA RUNS 31, 32, 33

Run Number 31, Pulse Frequency 8/min., Amplitude 12.5 cm^3

Sample #	R.R.ml/hr	RI Top	RI Bot.	# Plates	Eff. %
1	600	1.4858	1.4900	3 4/18	64.5
2	895	1.4857	1.4900	3 5/18	65.5
3	1290	1.4859	1.4900	3 3/36	61.7
4	1940	1.4860	1.4900	3	60.0
5	2610	1.4861	1.4900	2 32/35	58.3

Run Number 32, Pulse Frequency 8/min., Amplitude 12.5 cm^3

Sample #	R.R.ml/hr	RI Top	RI Bot.	# Plates	Eff. %
2	600	1.4860	1.4902	3 7/37	63.8
3	860	1.4858	1.4901	3 5/18	65.4
4	1275	1.4860	1.4902	3 7/37	63.8
5	1820	1.4862	1.4902	3	60.0
6	2550	1.4863	1.4902	2 11/12	58.3

Run Number 33, Pulse Frequency 220/min., Amplitude 12.5 cm^3

Sample #	R.R.ml/hr	RI Top	RI Bot.	# Plates	Eff. %
1	500	1.4869	1.4903	2 8/17	48.3
2	780	1.4870	1.4904	2 11/18	52.2
3	1150	1.4872	1.4906	2 11/18	52.2
4	1710	1.4870	1.4906	2 29/34	57.2
5	2400	1.4870	1.4908	2 19/20	59.0

TABLE VIII

EXPERIMENTAL DATA RUNS 34, 35, 36

Run Number 34, Pulse Frequency 220/min., Amplitude 12.5 cm^3

Sample #	R.R.ml/hr	RI Top	RI Bot.	# Plates	Eff. %
1	600	1.4860	1.4898	2 14/18	55.5
2	825	1.4867	1.4900	2 11/18	52.3
3	1200	1.4868	1.4901	2 11/18	52.3
4	1730	1.4865	1.4901	2 13/18	54.5
5	2500	1.4866	1.4904	2 31/34	58.3

Run Number 35, Pulse Frequency 120/min., Amplitude 12.5 cm^3

Sample #	R.R.ml/hr	RI Top	RI Bot.	# Plates	Eff. %
1	670	1.4871	1.4906	2 7/9	55.6
2	860	1.4852	1.4888	2 29/36	55.6
3	1200	1.4865	1.4908	3 6/17	67.0
4	1800	1.4866	1.4908	3 4/17	64.7
5	2500	1.4869	1.4908	3	60.0

Run Number 36, Pulse Frequency 120/min., Amplitude 12.5 cm^3

Sample #	R.R.ml/hr	RI Top	RI Bot.	# Plates	Eff. %
1	600	1.4872	1.4908	2 26/35	54.9
2	905	1.4875	1.4908	2 22/35	52.7
3	1240	1.4869	1.4908	3 1/18	61.0
4	1760	1.4869	1.4910	3 7/34	64.2
5	2500	1.4871	1.4910	3	60.0

TABLE IX

EXPERIMENTAL DATA RUNS 37, 38, 39

Run Number 37, Pulse Frequency 30/min., Amplitude 6 cm^3

Sample #	R.R.ml/hr	RI Top	RI Bot.	# Plates	Eff. %
1	663	1.4864	1.4900	3½	70.0
2	983	1.4864	1.4908	3 15/36	68.2
3	1290	1.4869	1.4909	3 7/35	64.0
4	1800	1.4871	1.4910	3 1/9	62.2
5	2430	1.4871	1.4910	3 1/9	62.2

Run Number 38, Pulse Frequency 30/min., Amplitude 6 cm^3

Sample #	R.R.ml/hr	RI Top	RI Bot.	# Plates	Eff. %
1	700	1.4857	1.4900	3 7/18	67.8
2	975	1.4858	1.4904	3 17/34	70.0
3	1330	1.4863	1.4907	3 12/35	66.6
4	1910	1.4867	1.4907	3 1/7	62.8
5	2610	1.4868	1.4906	2 8/9	58.0

Run Number 39, Pulse Frequency 220/min., Amplitude 6 cm^3

Sample #	R.R.ml/hr	RI Top	RI Bot.	# Plates	Eff. %
1	700	1.4863	1.4899	2 23/36	52.5
2	975	1.4855	1.4901	3 4/9	68.7
3	1360	1.4841	1.4886	3 5/18	65.5
4	1920	1.4859	1.4899	3	60.0
5	2610	1.4864	1.4902	2 35/37	59.0

TABLE X

EXPERIMENTAL DATA RUNS 40, 41, 42

Run Number 40, Pulse Frequency 220/min., Amplitude 6 cm^3

Sample #	R.R.ml/hr	RI Top	RI Bot.	# Plates	Eff. %
1	715	1.4867	1.4900	2 10/17	51.8
2	1000	1.4869	1.4904	3 7/17	68.3
3	1330	1.4862	1.4905	3 4/17	64.7
4	1870	1.4866	1.4905	3	60.0
5	2610	1.4868	1.4906	2 17/18	59.0

Run Number 41, Pulse Frequency 4/min., Amplitude 6 cm^3

Sample #	R.R.ml/hr	RI Top	RI Bot.	# Plates	Eff. %
1	740	1.4859	1.4901	3 3/18	63.3
2	990	1.4855	1.4900	3 1/3	66.7
3	Lost due to leak				
4	1370	1.4855	1.4898	3 1/6	63.3
5	1875	1.4863	1.4902	3	60.0
6	2610	1.4869	1.4906	2 16/18	57.7

Run Number 42, Pulse Frequency 4/min., Amplitude 6 cm^3

Sample #	R.R.ml/hr	RI Top	RI Bot.	# Plates	Eff. %
1	695	1.4866	1.4907	3 7/35	64.0
2	985	1.4854	1.4896	3 3/36	61.6
3	1330	1.4869	1.4909	3 1/6	64.0
4	1850	1.4870	1.4908	3 1/36	60.6
5	2610	1.4859	1.4897	2 13/17	55.3

TABLE XI

EXPERIMENTAL DATA RUNS 43, 44, 45

Run Number 43, Pulse Frequency 30/min., Amplitude 1 cm^3

Sample #	R.R.ml/hr	RI Top	RI Bot.	# Plates	Eff. %
1	725	1.4862	1.4907	3 15/35	68.7
2	970	1.4861	1.4908	3 21/36	71.3
3	1360	1.4862	1.4898	2 13/18	54.5
4A	1880	1.4844	1.4881	3 1/9	62.2
5	2500	1.4852	1.4890	2 7/9	56.0
6	1360	1.4859	1.4900	3 7/36	64.0

Run Number 44, Pulse Frequency 30/min., Amplitude 1 cm^3

Sample #	R.R.ml/hr	RI Top	RI Bot.	# Plates	Eff. %
1	695	1.4844	1.4890	3 3/18	63.4
2	1025	1.4859	1.4901	3 5/36	62.8
3	1360	1.4869	1.4908	3 1/18	61.0
4	1880	1.4871	1.4908	3	60.0
5	2620	1.4860	1.4890	2 4/18	45.0

Run Number 45, Pulse Frequency 30/min., Amplitude 1 cm^3

Sample #	R.R.ml/hr	RI Top	RI Bot.	# Plates	Eff. %
1	745	1.4860	1.4906	3 1/3	66.7
2	1015	1.4857	1.4901	3 5/18	65.5
3	1380	1.4866	1.4907	3 5/36	62.8
4	1930	1.4868	1.4907	3	60.0
5	2630	1.4870	1.4907	2 15/18	56.7

TABLE XII

EXPERIMENTAL DATA RUNS 46, 47, 48

Run Number 46, Pulse Frequency 220/min., Amplitude 1 cm^3

Sample #	R.R.ml/hr	RI Top	RI Bot.	# Plates	Eff. %
1	755	1.4880	1.4936	5 1/9	110
2	1035	1.4801	1.4852	3 19/36	70.5
3	1396	1.4829	1.4875	3	60.0
4	1935	1.4839	1.4884	3 3/18	63.2
5	2630	1.4843	1.4886	3 1/18	61.1

Run Number 47, Pulse Frequency 220/min., Amplitude 1 cm^3

Sample #	R.R.ml/hr	RI Top	RI Bot.	# Plates	Eff. %
1	780	1.4837	1.4886	3 11/18	72.2
2	1070	1.4839	1.4886	3 7/18	67.8
3	1460	1.4843	1.4888	3 2/9	64.4
4	1950	1.4846	1.4888	3 1/9	62.2
5	2730	1.4846	1.4888	3 1/9	62.2

Run Number 48, Pulse Frequency 220/min., Amplitude 1 cm^3

Sample #	R.R.ml/hr	RI Top	RI Bot.	# Plates	Eff. %
1	800	1.4839	1.4890	3 11/18	72.2
2	1090	1.4841	1.4890	3½	70.0
3	1450	1.4849	1.4890	3 1/18	61.0
4	2020	1.4845	1.4888	3 3/18	63.2
5	2730	1.4848	1.4890	3	60.0

TABLE XIII

EXPERIMENTAL DATA RUNS 49, 50, 51

Run Number 49, Pulse Frequency 4/min., Amplitude 1 cm^3

Sample #	R.R.ml.hr	RI Top	RI Bot.	# Plates	Eff. %
1	715	1.4848	1.4890	3 3/36	61.7
2	1000	1.4843	1.4892	3 7/18	67.8
3	1360	1.4850	1.4891	2 16/18	57.8
4	1950	1.4850	1.4891	2 15/18	56.7
5	2610	1.4850	1.4890	2 7/9	55.7

Run Number 50, Pulse Frequency 4/min., Amplitude 1 cm^3

Sample #	R.R.ml/hr	RI Top	RI Bot.	# Plates	Eff. %
1	790	1.4841	1.4890	3 19/37	70.3
2	1090	1.4821	1.4870	3 6/19	66.3
3	1460	1.4832	1.4878	3 1/12	61.7
4	2000	1.4840	1.4881	2 8/9	57.8
5	2730	1.4845	1.4884	2 13/18	54.5

Run Number 51, Pulse Frequency 4/min., Amplitude 1 cm^3

Sample #	R.R.ml/hr	RI Top	RI Bot.	# Plates	Eff. %
1	740	1.4843	1.4892	3½	70.0
2	1045	1.4847	1.4894	3 2/9	64.5
3	1400	1.4801	1.4844	2 17/18	58.9
4	2000	1.4818	1.4860	2 11/12	58.3
5	2650	1.4825	1.4865	2 25/34	54.7

APPENDIX B

GRAPHICAL PRESENTATION OF RESULTS

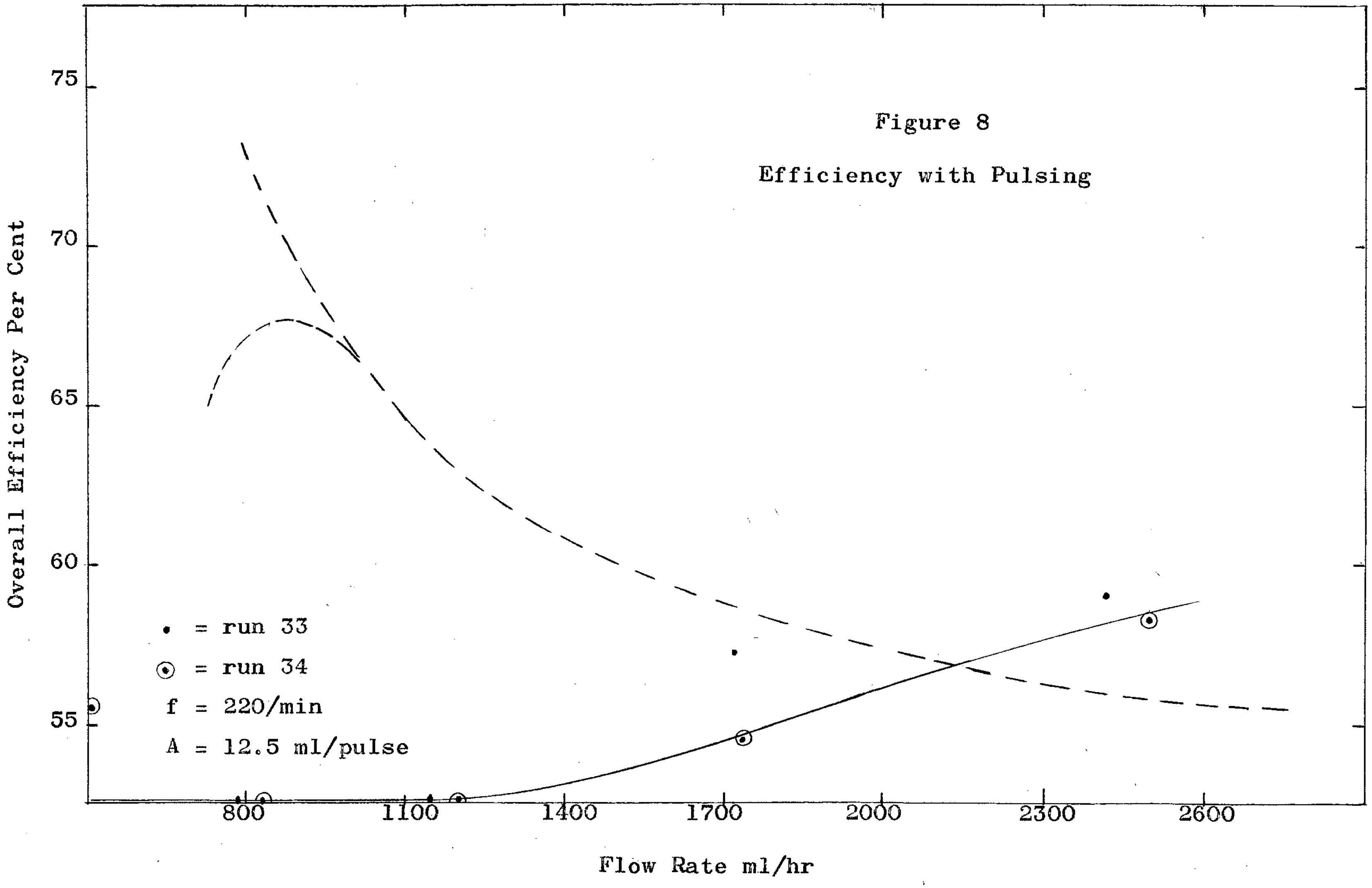


Figure 8

Efficiency with Pulsing

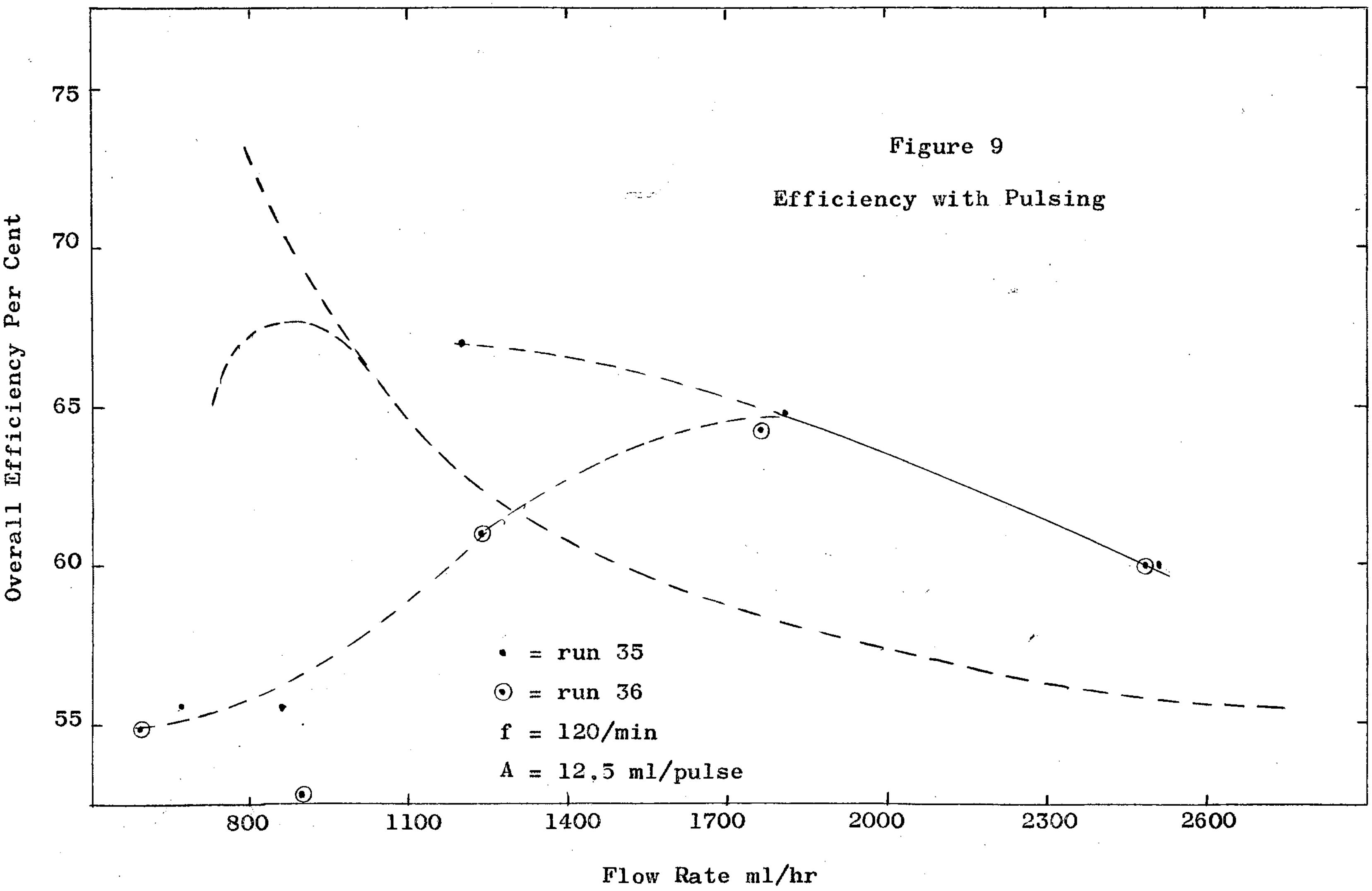


Figure 9

Efficiency with Pulsing

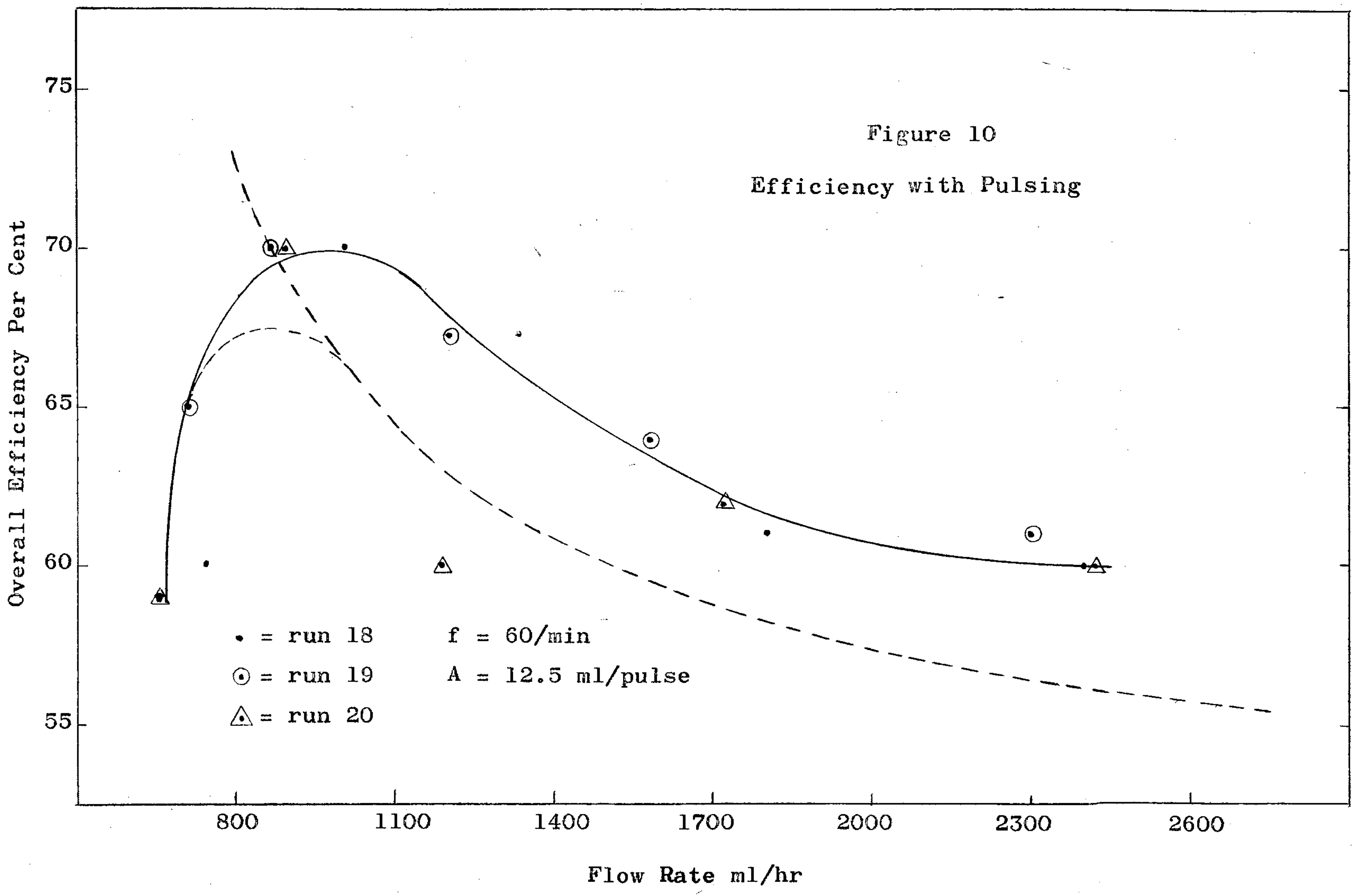


Figure 10

Efficiency with Pulsing

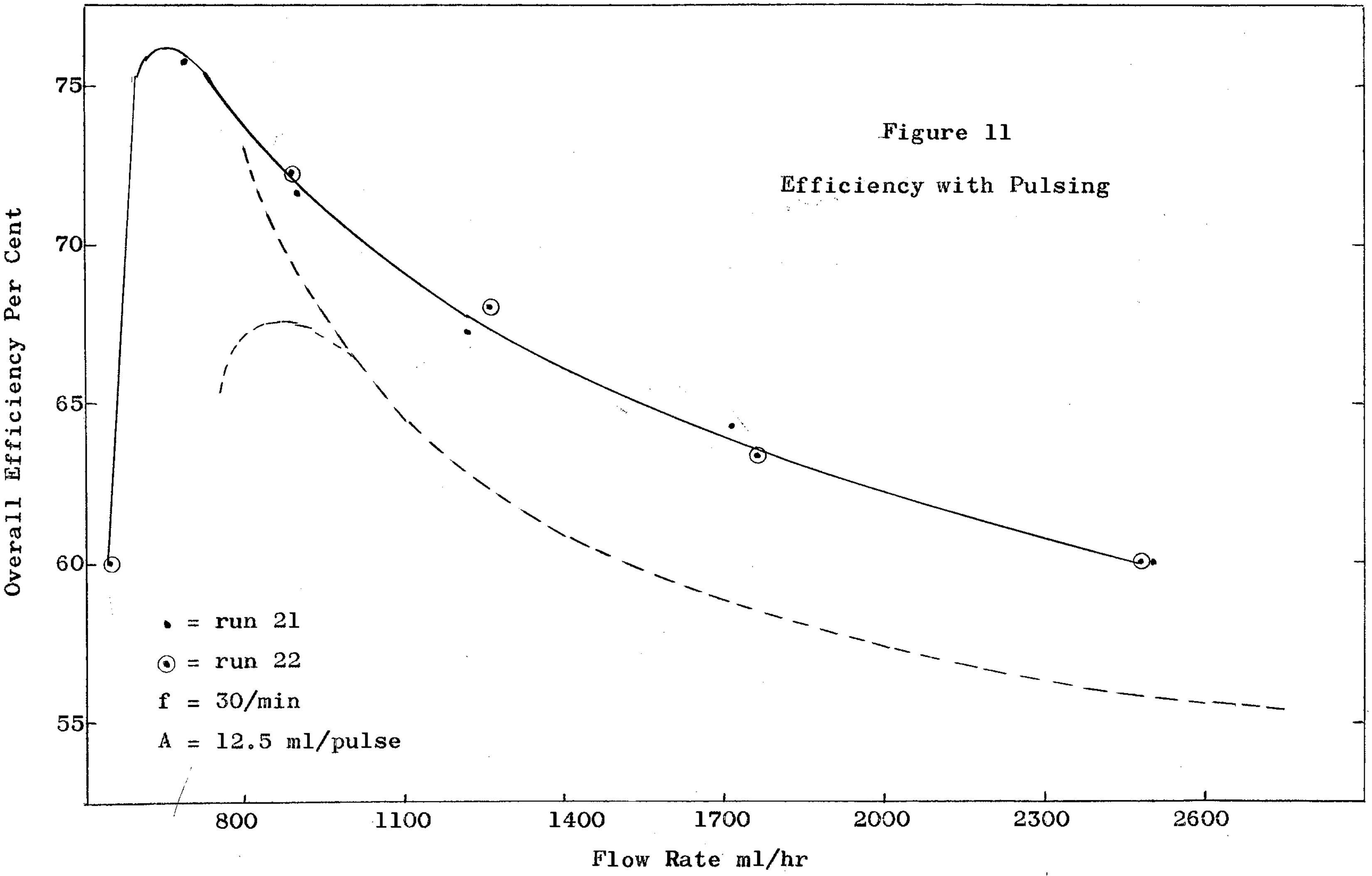


Figure 11

Efficiency with Pulsing

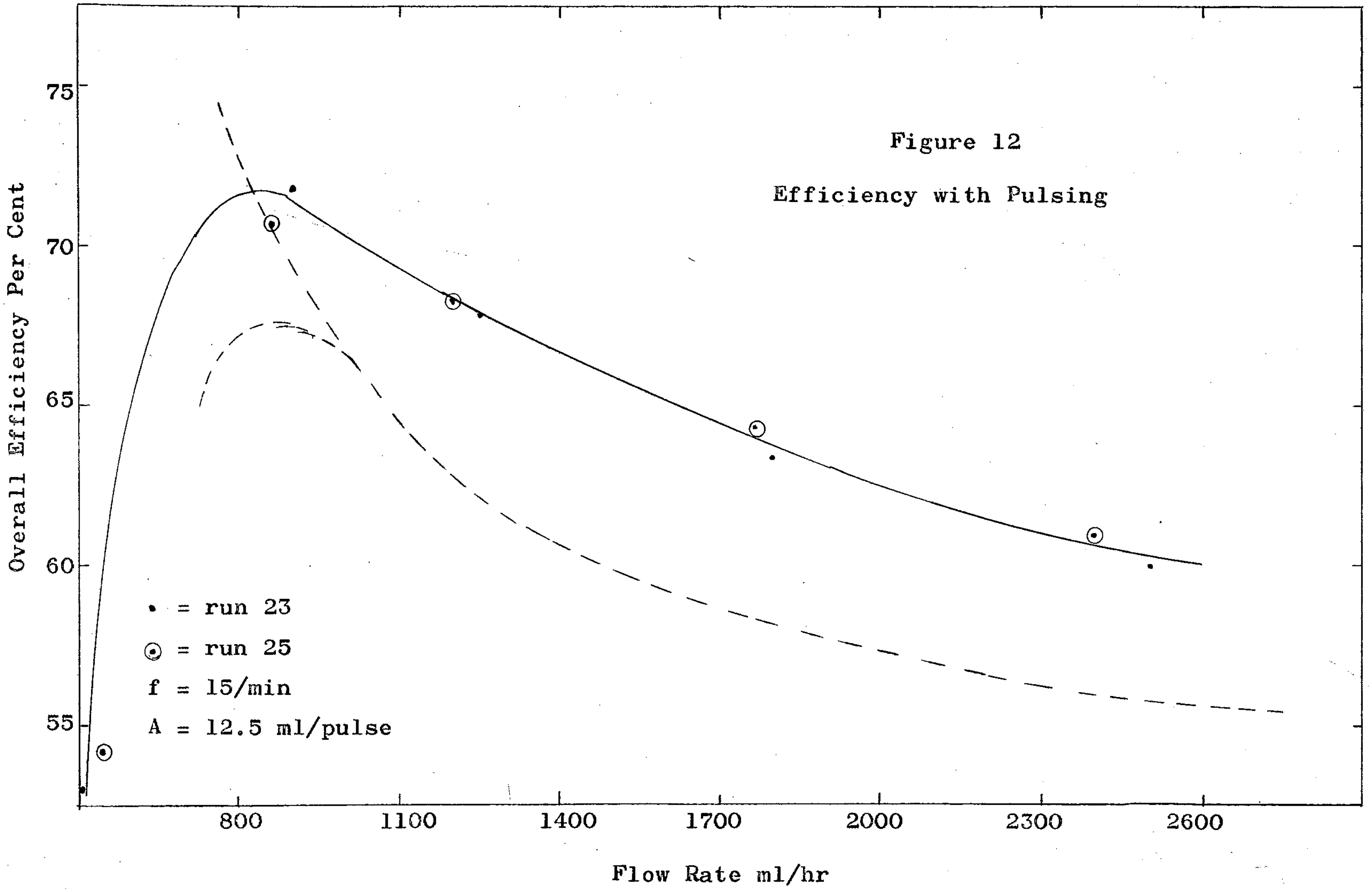


Figure 12

Efficiency with Pulsing

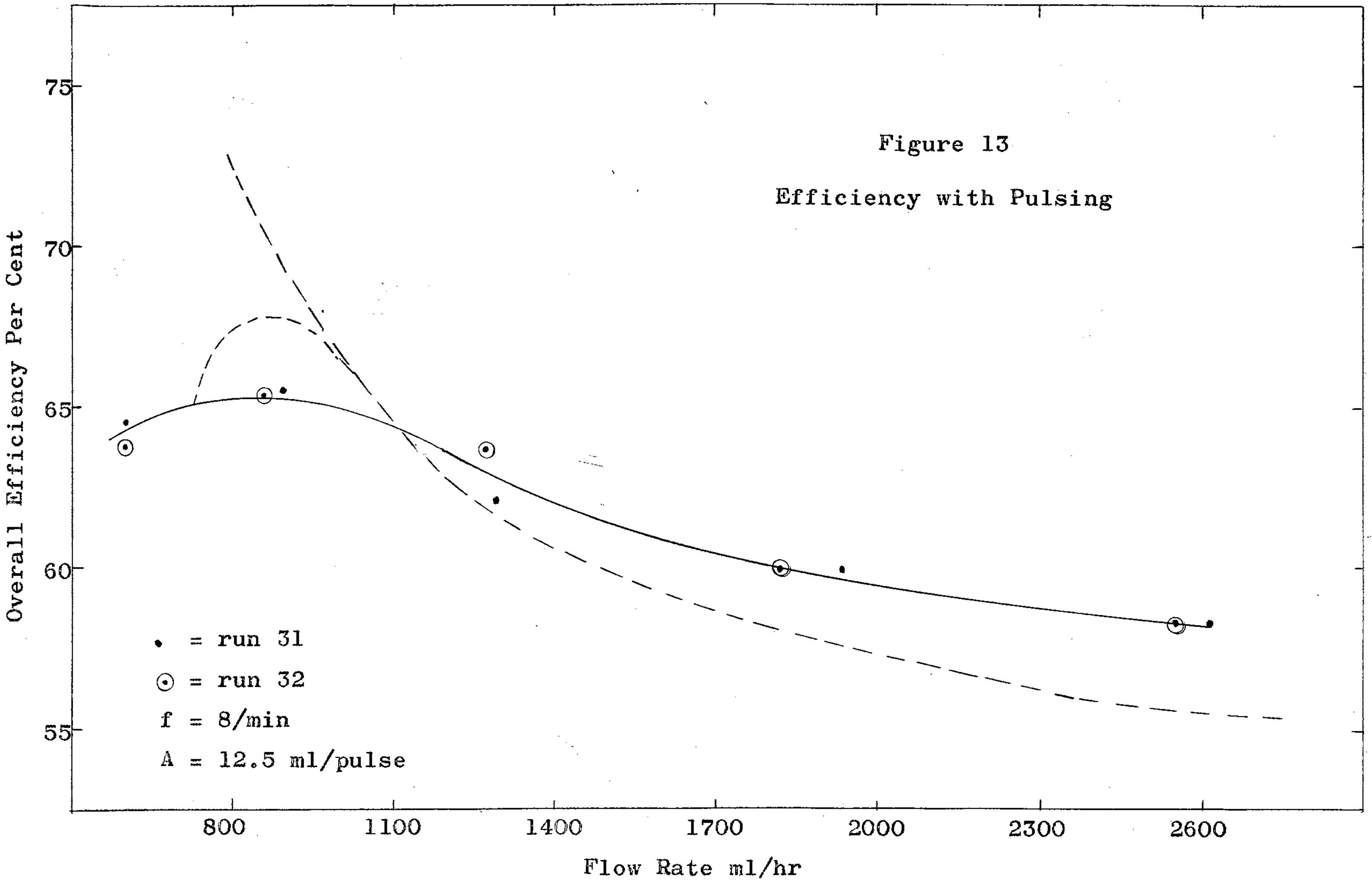


Figure 13

Efficiency with Pulsing

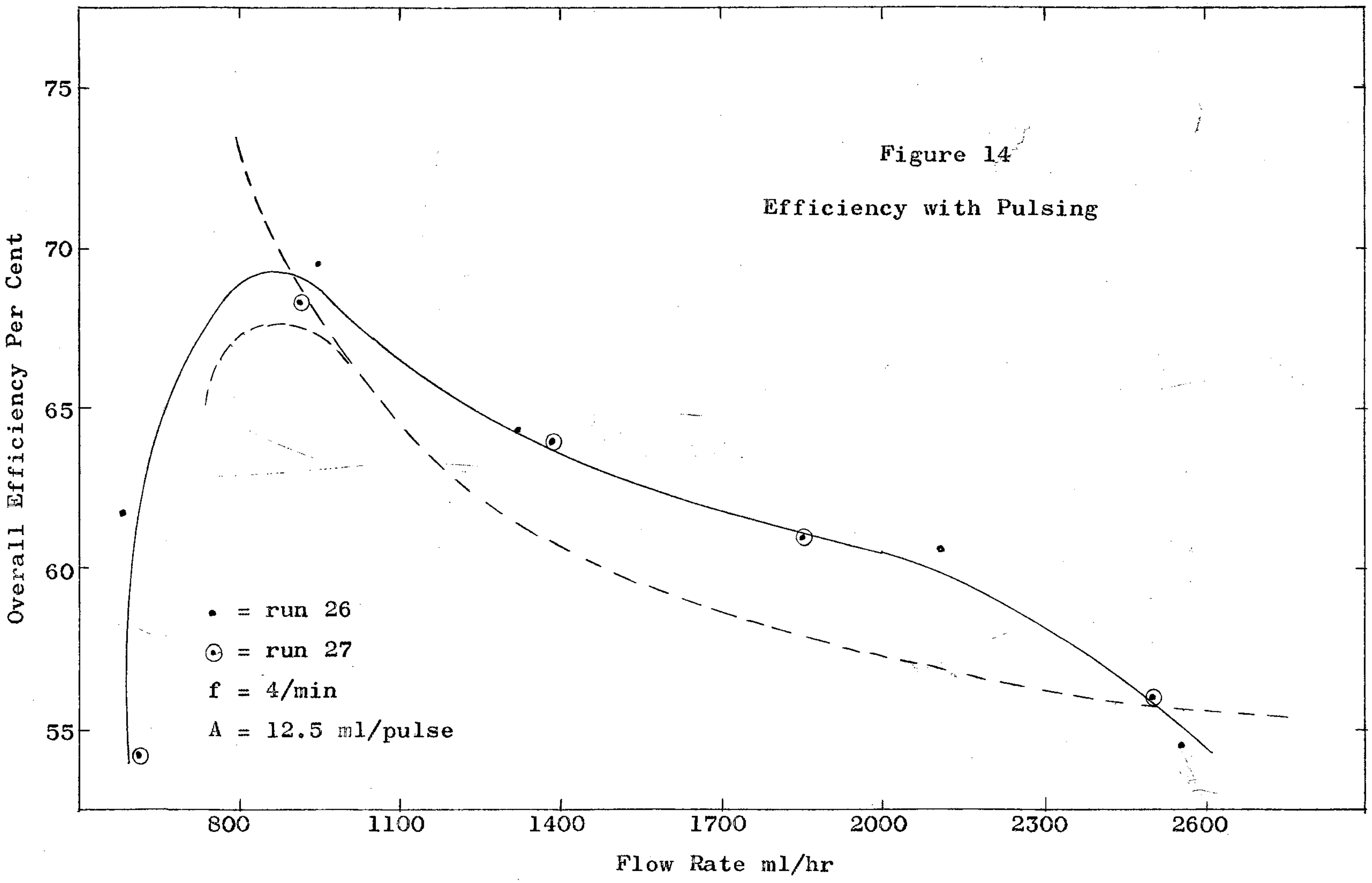


Figure 14

Efficiency with Pulsing

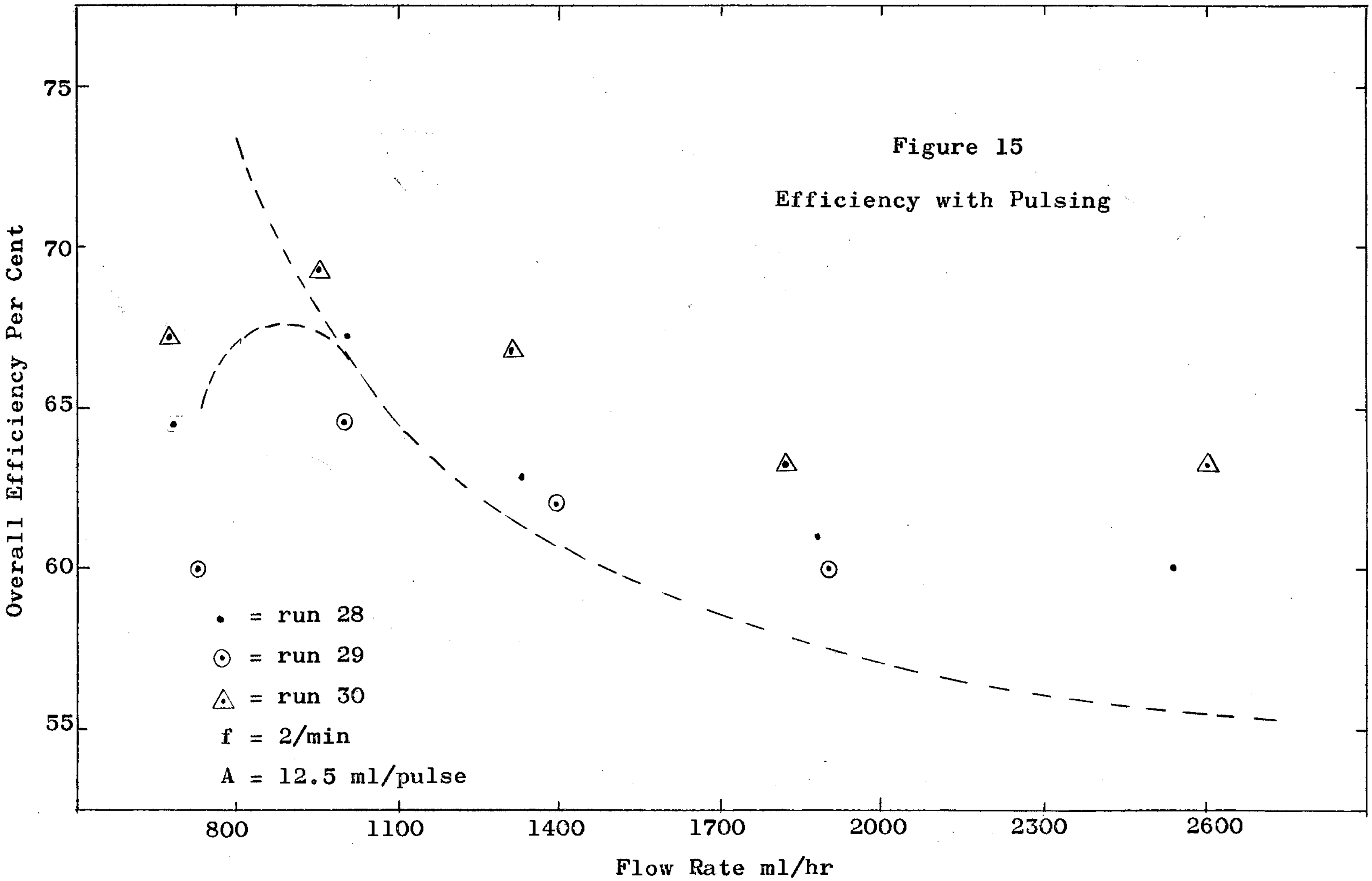


Figure 15

Efficiency with Pulsing

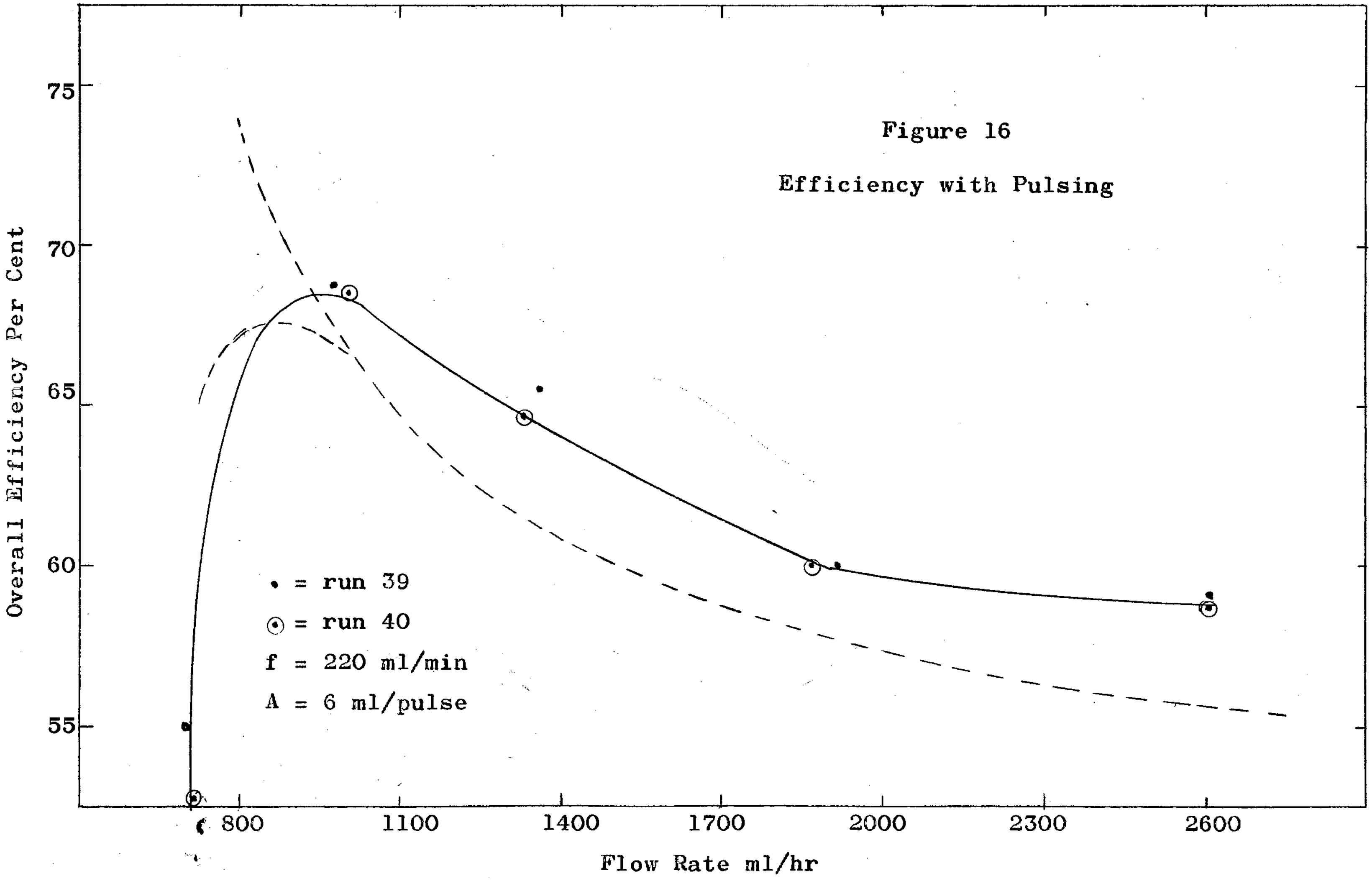


Figure 16

Efficiency with Pulsing

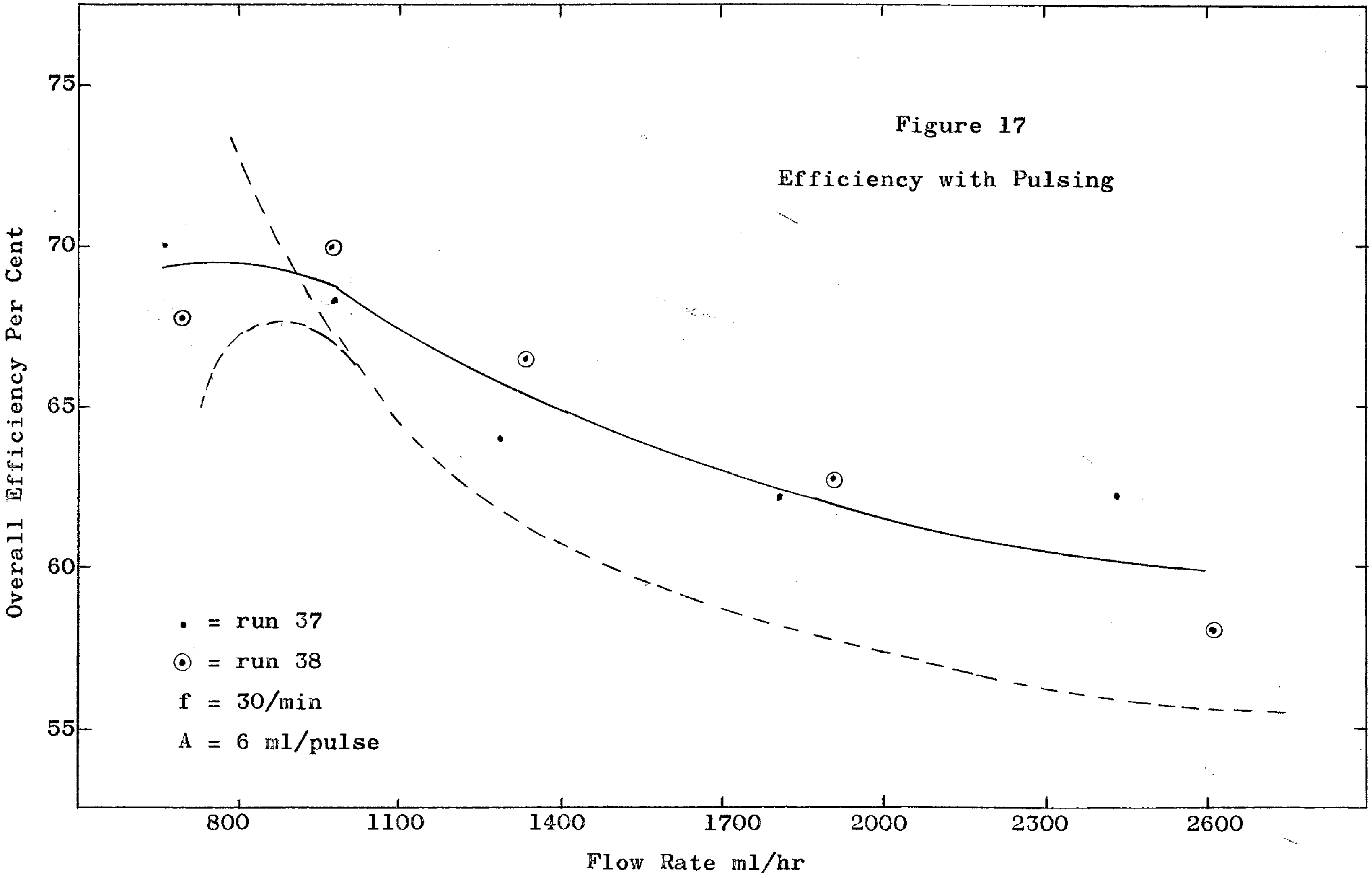


Figure 17

Efficiency with Pulsing

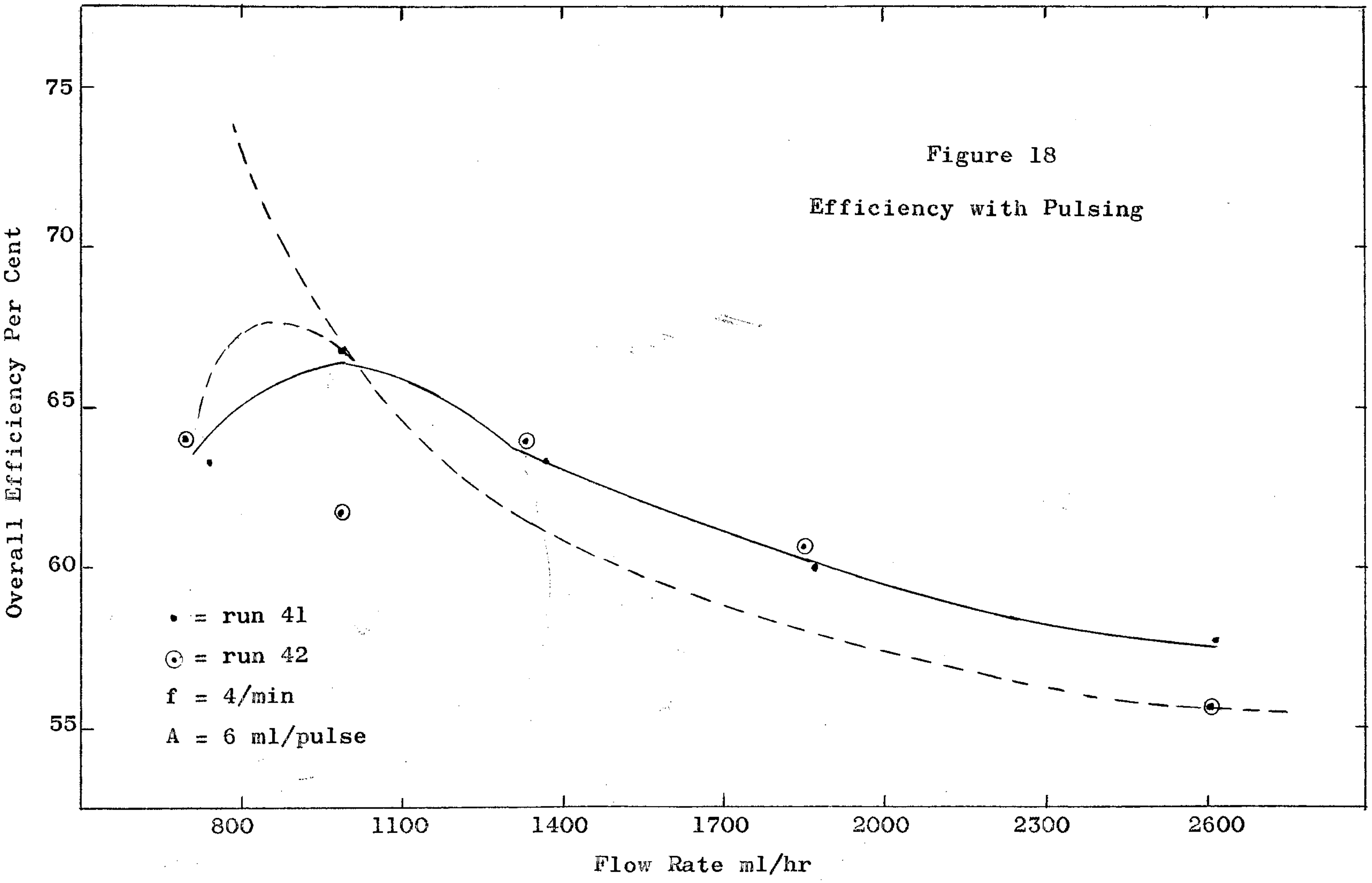


Figure 18

Efficiency with Pulsing

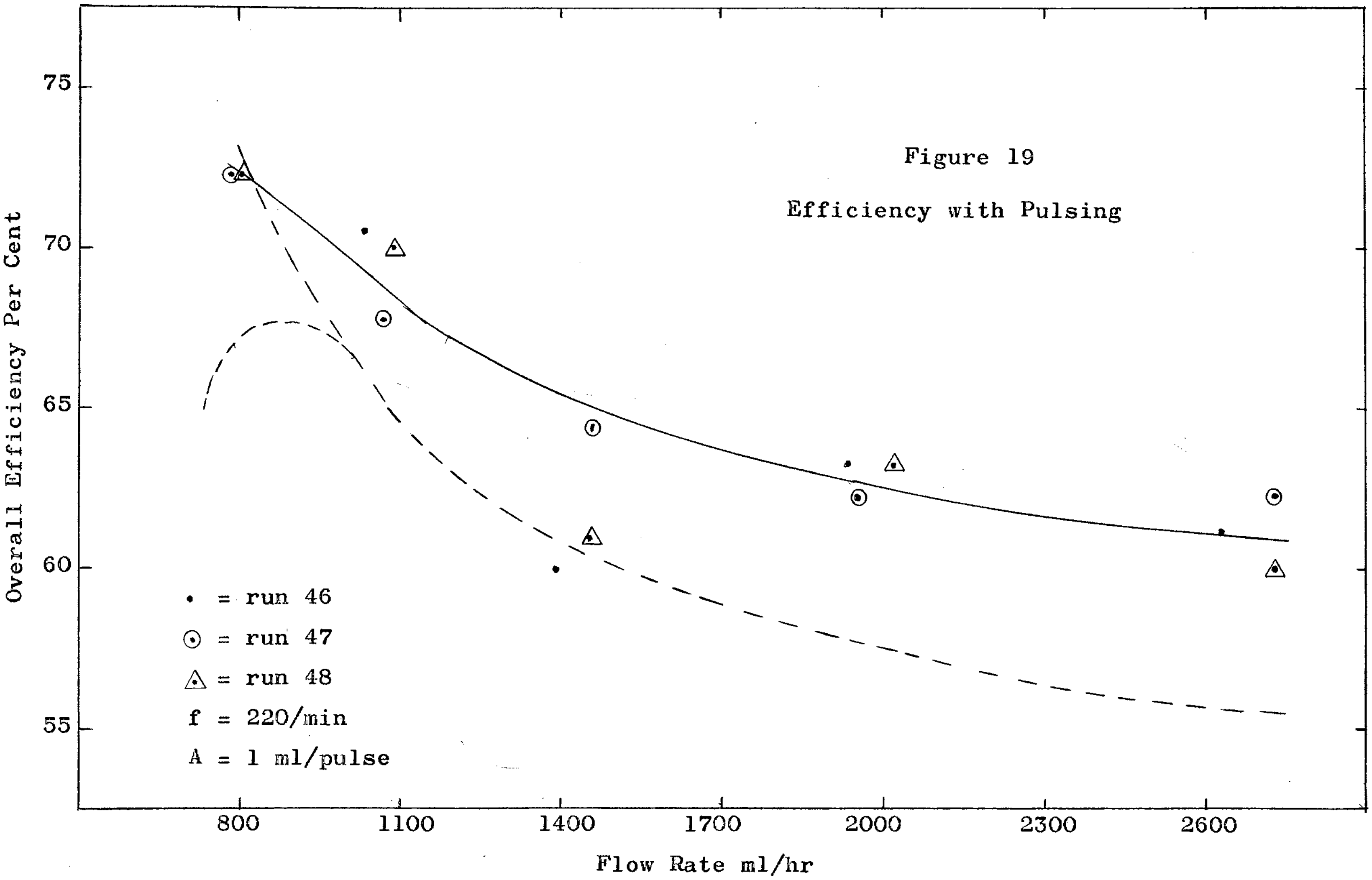


Figure 19

Efficiency with Pulsing

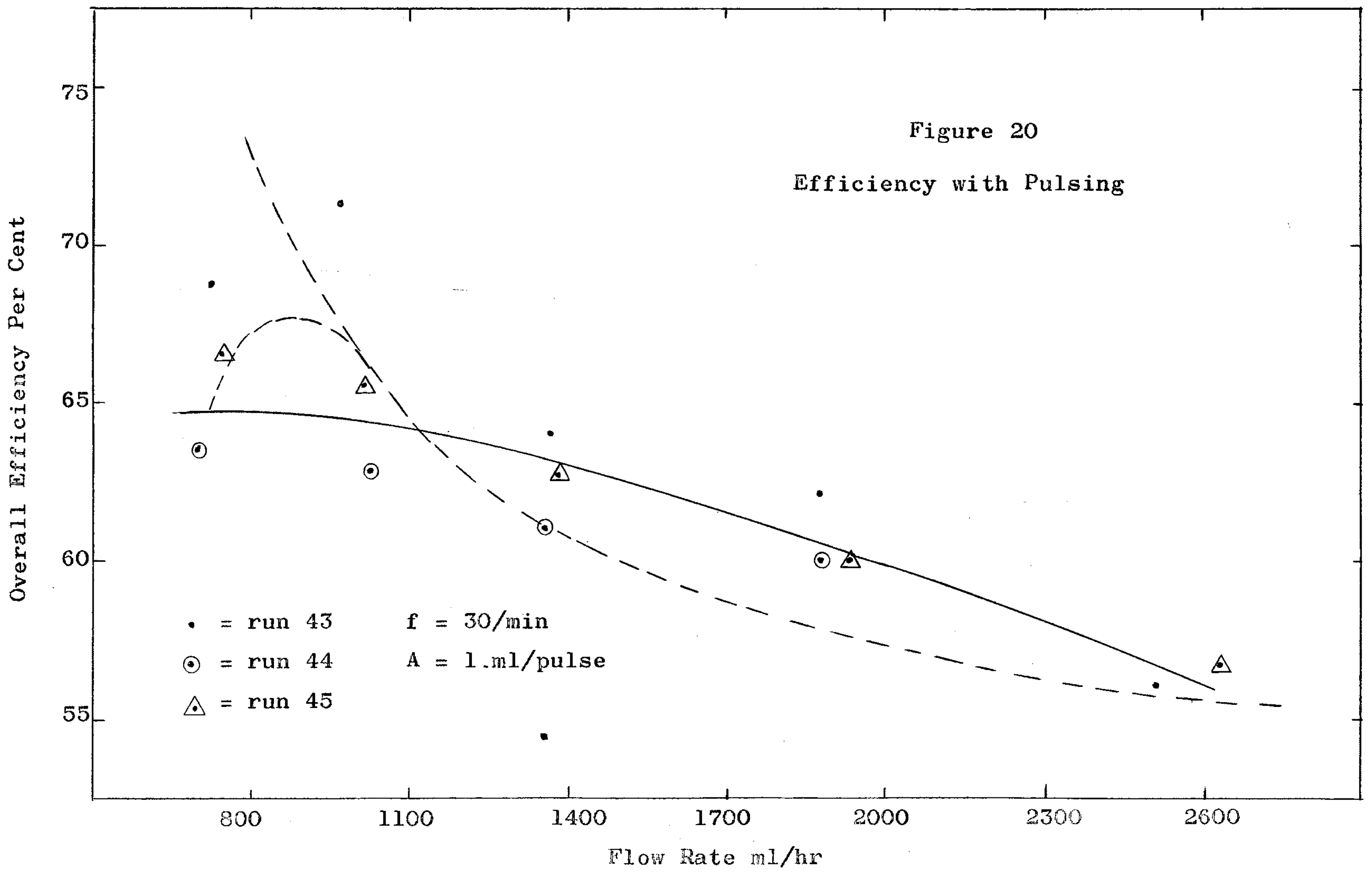


Figure 20

Efficiency with Pulsing

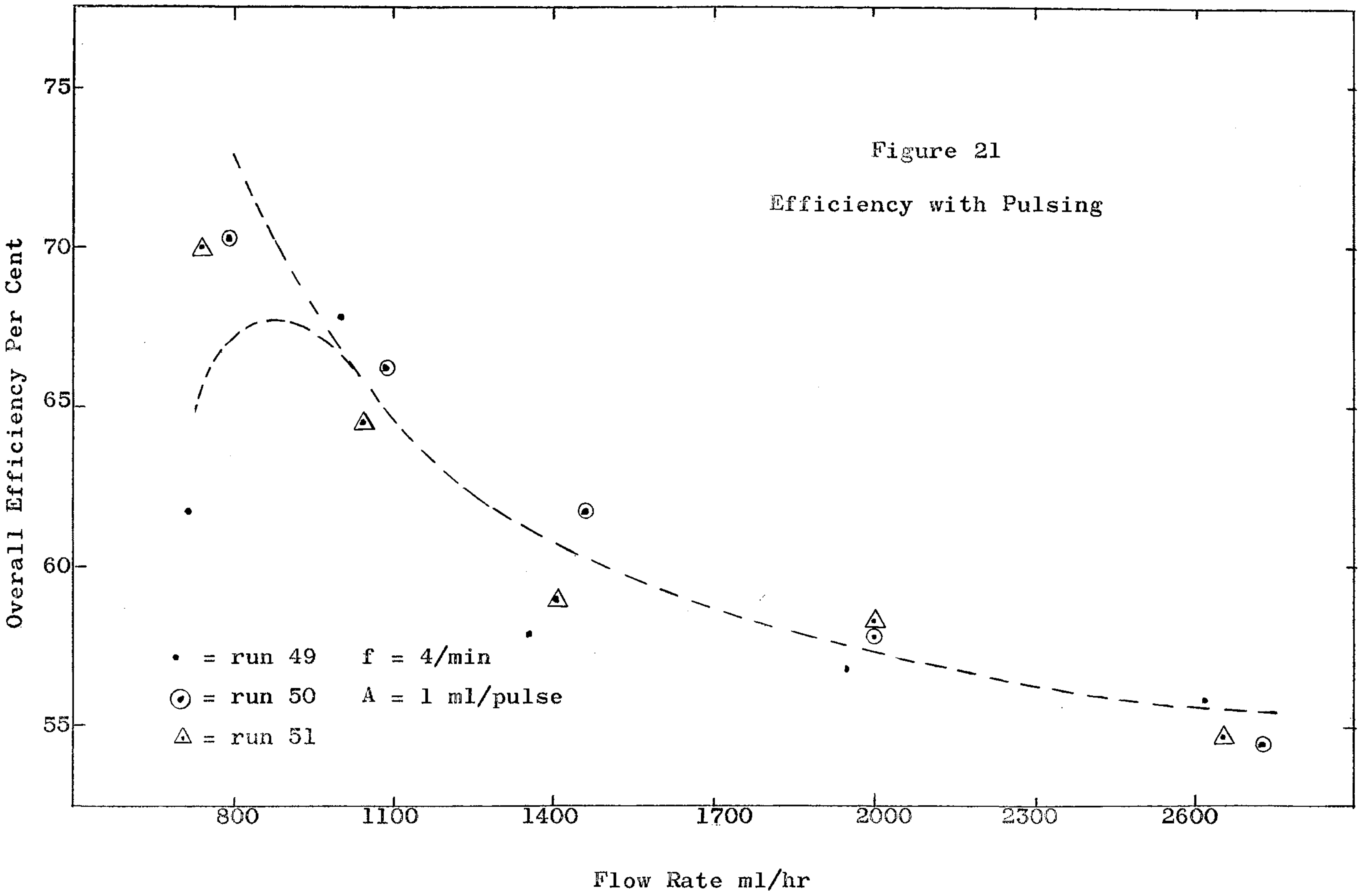


Figure 21

Efficiency with Pulsing

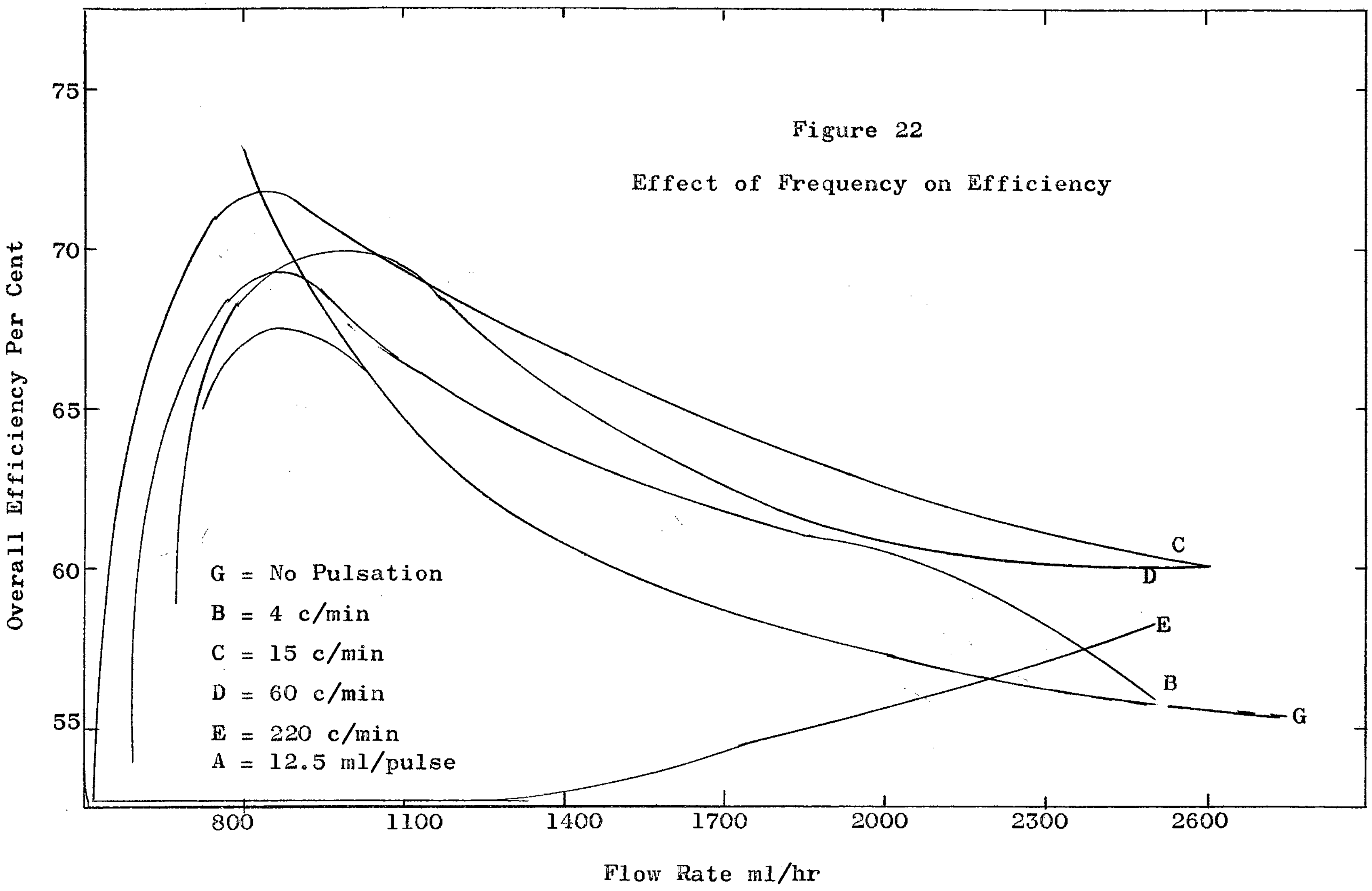


Figure 22

Effect of Frequency on Efficiency

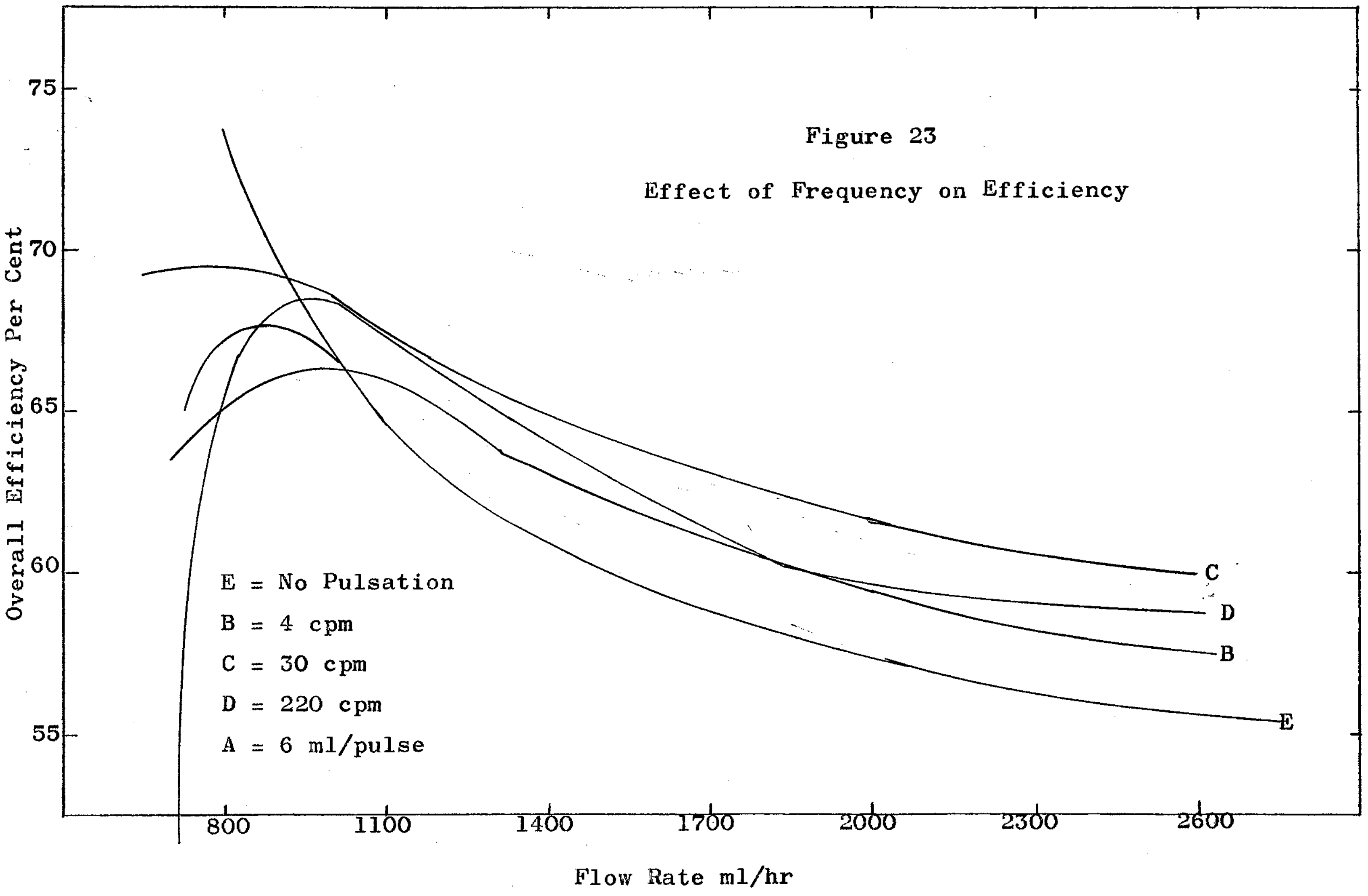


Figure 23

Effect of Frequency on Efficiency

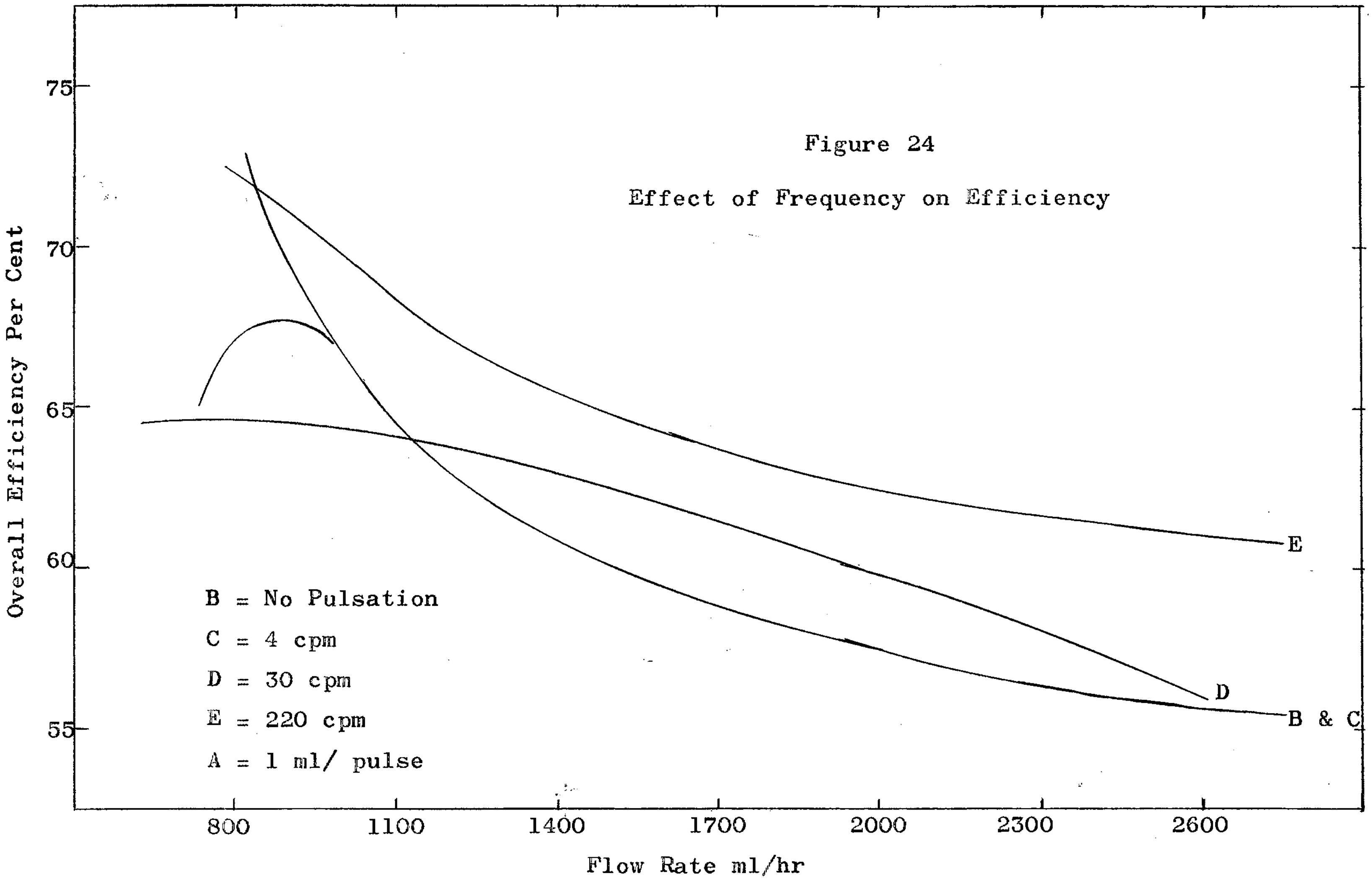


Figure 24

Effect of Frequency on Efficiency

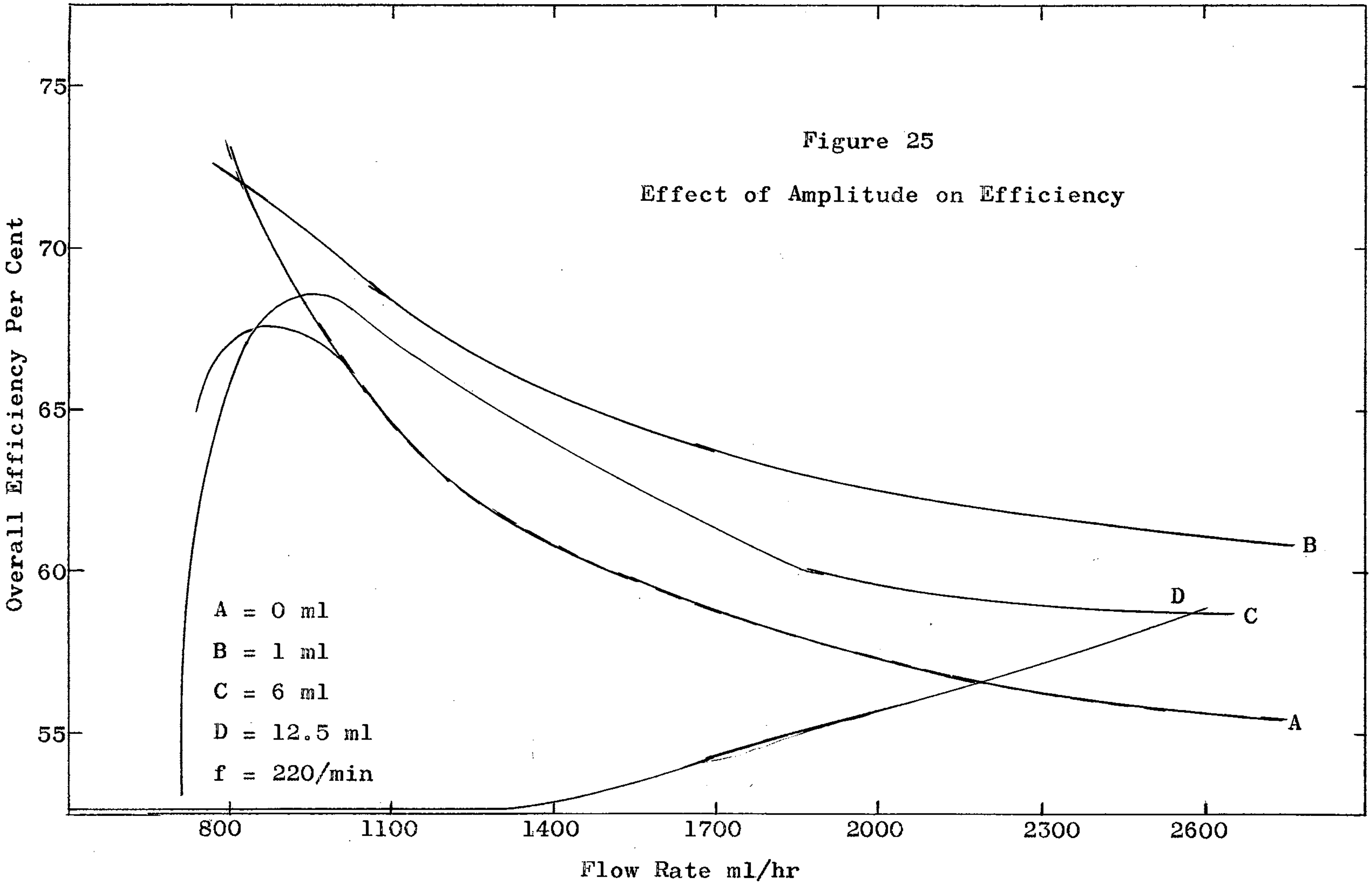


Figure 25

Effect of Amplitude on Efficiency

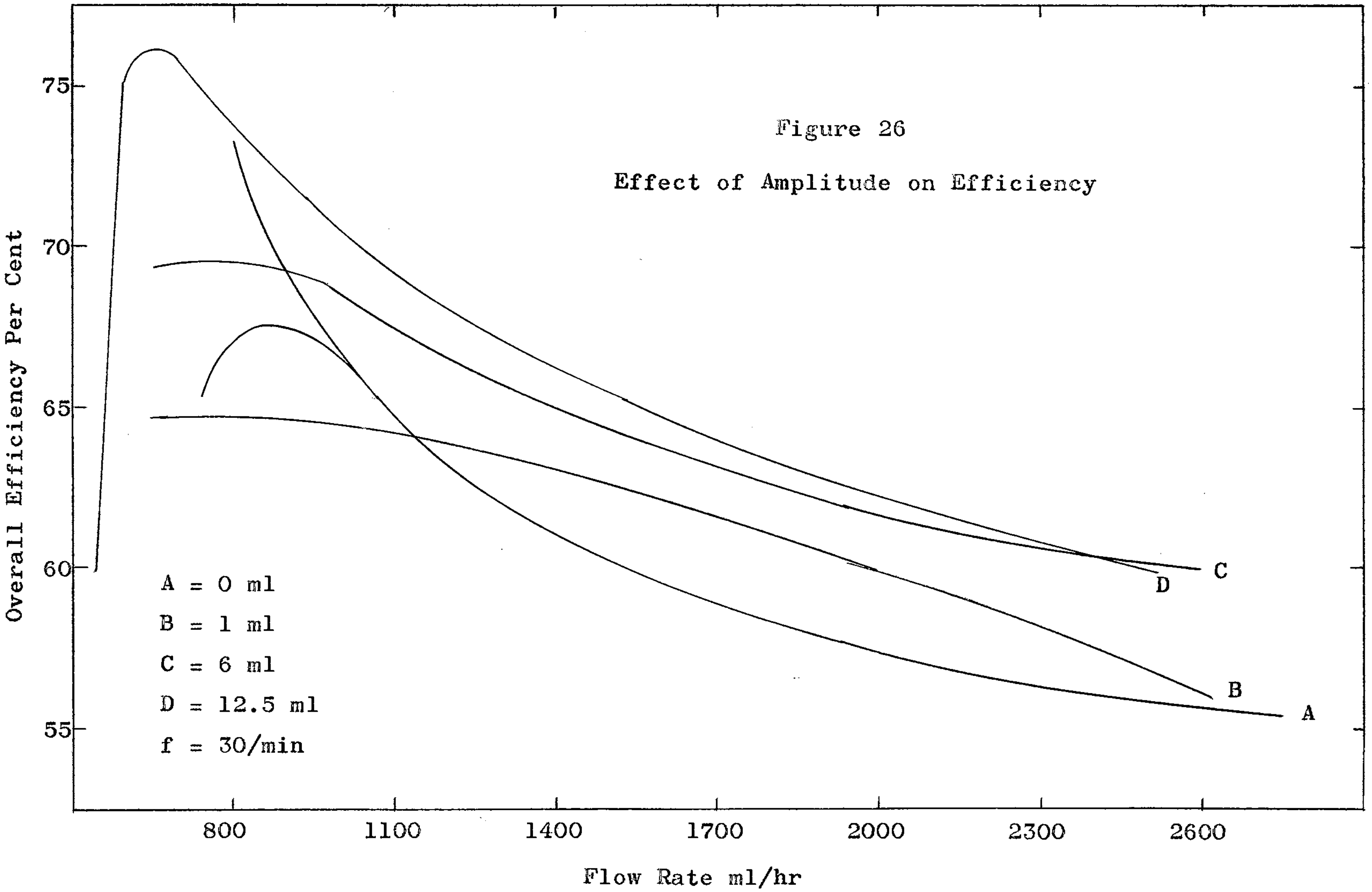


Figure 26

Effect of Amplitude on Efficiency

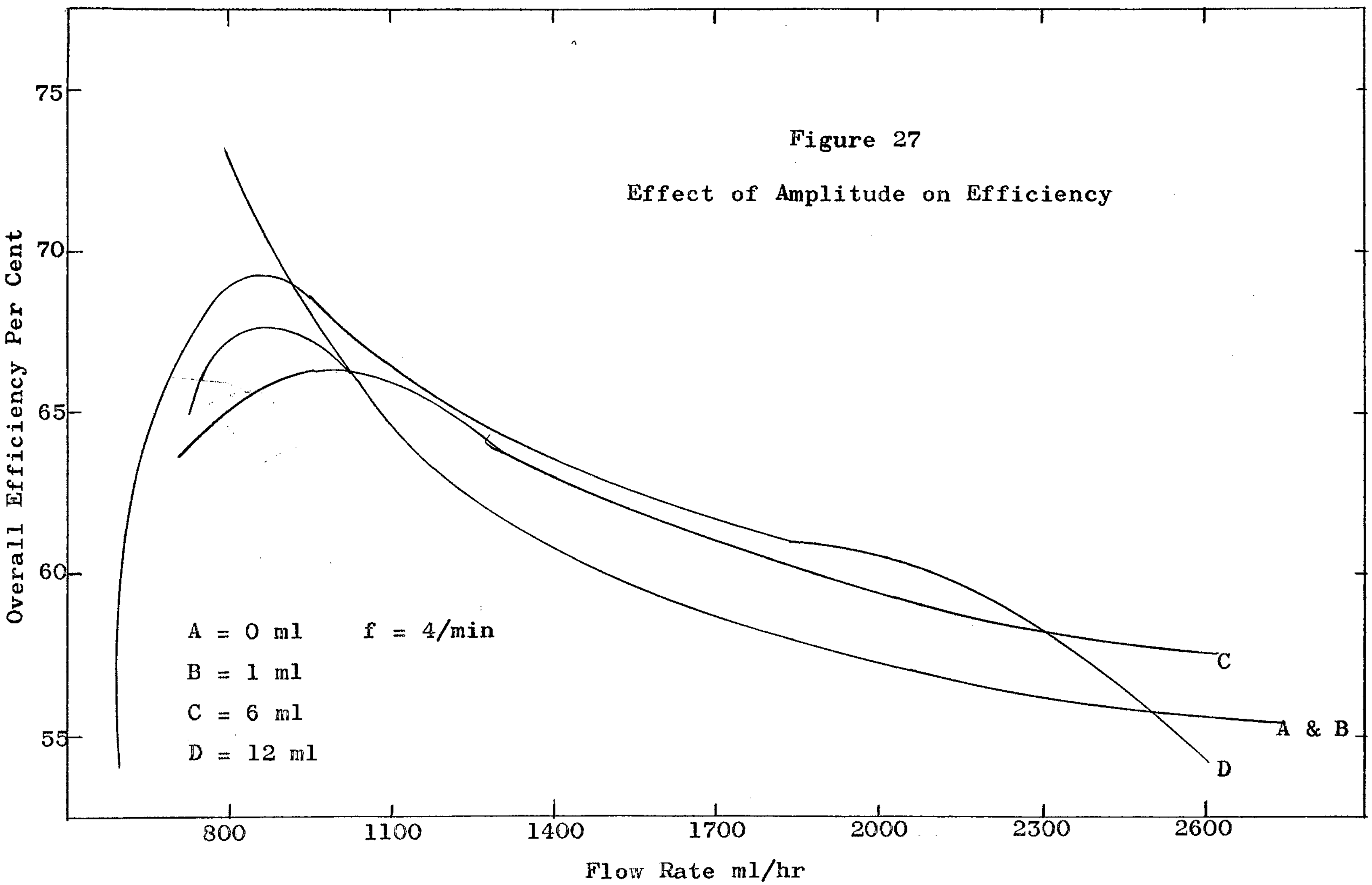


Figure 27
Effect of Amplitude on Efficiency
Overall Efficiency Per Cent
75
70
65
60
55
800
1100
1400
1700
2000
2300
2600
Flow Rate ml/hr
A = 0 ml
f = 4/min
B = 1 ml
C = 6 ml
D = 12 ml
C
A & B
D

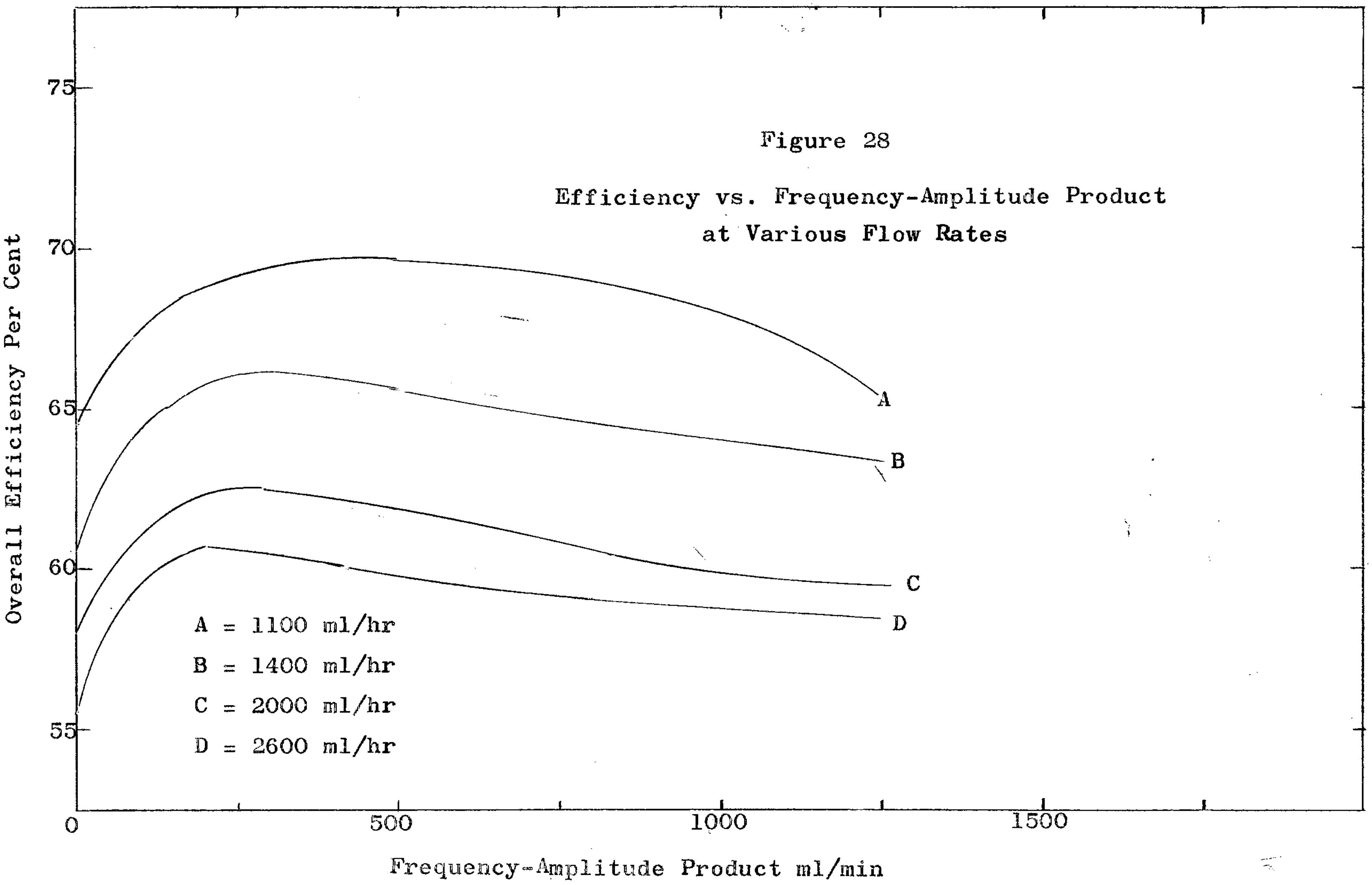


Figure 28
Efficiency vs. Frequency-Amplitude Product at Various Flow Rates
Overall Efficiency Per Cent
75
70
65
60
55
0
500
1000
1500
Frequency-Amplitude Product ml/min
A
B
C
D
A = 1100 ml/hr
B = 1400 ml/hr
C = 2000 ml/hr
D = 2600 ml/hr

APPENDIX C

DETAILED EFFICIENCY CORRELATION

For an ideal gas the equation for mass transfer is:

$$\frac{N}{S} = K_{og}(p^{*} - p_g) \qquad (1)$$

The differential expression for this is:

$$dN = K_{og}\, a(y^{*} - y)\ PA\ dZ \qquad (2)$$

For a fluid stream in a distillation column with the assumption of equimolal countercurrent transport:

$$dN = G_m\ A\ dY \qquad (3)$$

Combining equations 2 and 3 gives:

$$\frac{K_{og}\ a\ P\ dZ}{G_m} = \frac{dy}{y^{*} - y} \qquad (4)$$

Making the assumption that all terms on the left side of this equation are constant except dZ and integrating gives:

$$\frac{K_{og}\ a\ PZ}{G_m} = \int \frac{dy}{y^{*} - y} = N_{og} \qquad (5)$$

The above equation defines a transfer unit. In an entirely analogous way it is possible to define N_l, N_{ol}, and N_g.

In the mass transport in a distillation column the contact time of the gas and liquid is important. The actual time of vapor liquid contact on a tray is:

$$t_l = 3600\ \frac{Z_c\ l}{L_m} \qquad (6)$$

Combining equation 6 with the equations for N_l and N_g.

$$N_l = k_l \ a \ t_l/3600 \qquad (7)$$

$$N_g = k_g \ a \ t_g/3600$$

The relationship between N_g, N_l, and N_{og} may be expressed as:

$$\frac{1}{N_{og}} = \frac{1}{N_g} + \frac{\lambda}{N_l} \qquad (9)$$

The efficiency in gas terms may be defined as

$$E_{og} = \frac{y - y_{n+1}}{y^* - y_{n+1}} \qquad (10)$$

Carrying out the integration indicated in equation 5 leads to:

$$1 - E_{og} = e^{-\frac{K_{og} \ A \ PZ}{G_m}} = e^{-N_{og}} \qquad (11)$$

Taking the log of equation 11 and rearranging gives:

$$\frac{1}{-\ln \ (1 - E_{og})} = N_{og} = \frac{1}{N_g} + \frac{\lambda}{N_l} \qquad (12)$$

In its study the A.I.Ch.E. Tray Efficiency Committee found a relationship between these transfer units and the liquid and gas flow rates. They expressed the correlation in the form:

$$N_g = (0.776 + 0.116W - 0.290F + 0.0217L)/N_{Sc}^{0.5} \qquad (13)$$

$$N_l = \left[(1.065 \times 10^4)(D_l)\right]^{0.5} (0.26F + 0.15)t_l \qquad (14)$$

Equations 13 and 14 in the case of this experiment can be reduced. Since the weir height is a constant for this system its effect can be combined with the constant in equation 13. For this system the Schmidt number will also be a constant and can be incorporated into the constants. Likewise the diffusivity is a constant for the system under study. Since the system is at total reflux the F factor will just be a constant multiple of L.

$$L = 26.1\ F \qquad (15)$$

This will allow simplification of equations 13 and 14:

$$N_g = K_1 + K_2\ F \qquad (16)$$

$$N_1 = K_5 + K_6/F \qquad (17)$$

The values for the constants were determined.

$K_1 = 1.03$ $\qquad K_2 = 0.08$

$K_5 = 0.00935$ $\qquad K_6 = 0.0212$

When these constants were used in equation 12 the value obtained for N_g was about 1.1 at an F factor of 0.473. The value for N_1 was 0.054. This gave impossible results. The value for N_g was reasonable and the constants for this were accepted. The value for N_1 was unreasonable and another method had to be devised to determine the constants for equation 17.

Actual experimental data were then used to determine the constants in equation 17. The assumption that the constants were in the same ratio as those of the original A.I.Ch.E. equation was made in order to simplify the calculations.

In this case:

$$K_6 = 0.6\ K_5 = A \tag{18}$$

This leads to the equation:

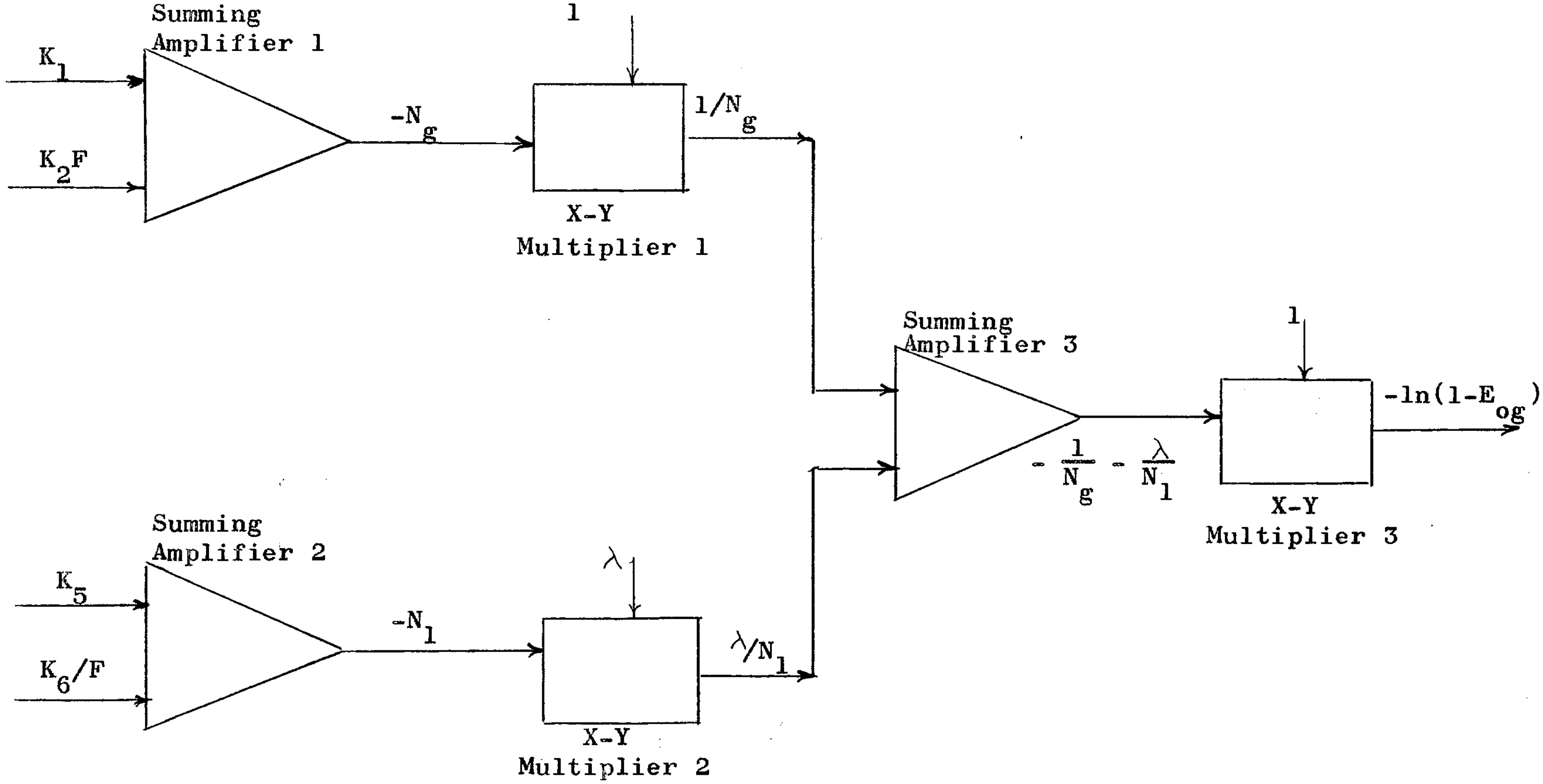
$$\frac{1}{\ln (1 - E_{og})} = \frac{1}{1.03 + 0.08F} + \frac{1}{0.933\ t_1 (AF + .6A)} \tag{19}$$

When actual experimental data are used in the equation, the constant A turns out to be a variable constant. In this case it is impossible to get a quantitative description of the change in efficiency but it was hoped that through the use of an average value for the constant the change in efficiency with pulsation could be explained at least qualitatively. The average value for A is 52.7.

Equation 19 was programmed for the analog computer. This program requires three summers and three multipliers in order to work. The program is shown in Figure 29. Each multiplier requires three amplifiers. To make the program simpler the form indicated by equations 16 and 17 was used. In order to put a sinusoidal input into this a function generator was used. The block diagram for this problem is shown in Figure 29. If the correlation would account for the increase in efficiency the use of the analog computer would allow determination of the correct coefficients by a trial and error procedure. The analog computer used was a Donner Model 3400 with 10 operational amplifiers. Two of these units were available. Before the analog computer was used to solve this equation a hand calculation was made to first determine if there was any

Figure 29

Analog Computer Program



chance that the correlation would account for an increase in efficiency in this system. The trial was made at an F factor of 0.973. A sinusoidal pulse with a maximum amplitude of one half of the steady state flow rate was imposed on the system. The equation was evaluated at 18° increments. The efficiency was found to vary by about two per cent with flow rate. The average for the complete sinusoidal pulse was identically equal with that for the case of no pulsation. This result indicated that it was not possible to account for the increased efficiency by the A.I.Ch.E. Correlation and further attempts to do so were abandoned.

VITA

Gilbert Vincent McGurl, Jr.

Candidate for the Degree of

Master of Science

Thesis: A PULSED LABORATORY DISTILLATION COLUMN

Major Field: Chemical Engineering

Biographical:

Personal Data: Born in Newark, New Jersey, April 22, 1941, the son of Gilbert V. and Marceline F. McGurl.

Education: Attended grade school in Newark, New Jersey and Pittsburgh, Pennsylvania; graduated from Central Catholic High School, Pittsburgh, Pennsylvania in 1957; received the Bachelor of Science degree in Chemical Engineering from Carnegie Institute of Technology, Pittsburgh, Pennsylvania in June, 1961; completed the requirements for the Master of Science degree in May, 1962.

Professional Experience: Employed in the summers of 1959 and 1960 by Koppers Company in their Research Laboratories at Verona, Pennsylvania as a summer trainee.