

OPTIMUM OPERATING TEMPERATURE FOR REFINING LIGHT OIL
WITH SULFURIC ACID IN COKE OVEN BY-PRODUCT RECOVERY

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Signatures of Authors

Department of Chemical Engineering, January 23, 1943

Signature of Professor
in Charge of Research

Signature of Department Head

M.I.T. Station
Bethlehem Steel Co.
Lackawanna, New York
January 23, 1943

Professor Warren K. Lewis
Department of Chemical Engineering
Massachusetts Institute of Technology
Cambridge, Massachusetts

Dear Professor Lewis:

In accordance with the regulations of the Faculty, we are submitting this thesis entitled Optimum Operating Temperature for Refining Light Oil with Sulfuric Acid in Coke Oven By-Product Recovery, in partial fulfillment of the requirements for the degree of Bachelor of Science in Chemical Engineering Practice.

Respectfully yours,

Raymond F. Frankel, Jr.

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I. SUMMARY

Due to the present war emergency, it has become necessary to produce large quantities of benzene and toluene of a high degree of purity for nitration. For years the Bethlehem Steel Company in Lackawanna, New York has recovered from coke-oven gas, mixtures of these oils which were sold as motor benzol. Because of the emergency, however, in September, 1942, a new refining process was installed which enabled the plant to obtain benzene and toluene of relatively high purity. The new apparatus included an agitator in which the impurities were removed by an acid wash and several stills and fractionating columns to separate the various oils or fractions. During the warm months the process was very satisfactory, giving products that met all the requirements and specifications. When the cold weather set in, however, it became increasingly difficult to obtain the desired purity from the acid wash in the agitator.

The object of this investigation was to study this agitation under various conditions and to determine optimum conditions for the operation.

A rather intensive literature survey was carried out but only indicated that no investigation of this type had ever been published previously. It was therefore decided that runs would have to be made, taking into consideration such variables as temperature, acid concentration, acid-oil ratio, and time of agitation. A number of runs were made under the various conditions, using in each case samples of oil and acid obtained from the plant tanks.

The agitation was produced by a glass agitator in a large, well lagged Erlenmeyer flask. Oil at temperatures varying from 25° to 60°C. was agitated with acid added at increasing acid-oil ratios of 2% to 6%, and at concentrations of 96% and 88% acid. The product, after neutralization, was tested by the standard Barrett wash test for purity.

From these determinations, plots were drawn of purity vs. time for acid-oil ratios, purity vs. acid-oil ratio for various temperatures, purity vs. temperature for different ratios, and purity vs. temperature for different concentrations.

These graphs revealed the following facts: (1) that under any conditions of agitation the major portion of the sulfonation reaction takes place within a relatively short time, with the result that the purity rapidly approaches an asymptotic value. The time necessary to reach the asymptotic line is determinable for any given agitator. (2) that as the acid-oil ratio increases, wash number decreases at all temperatures. (3) that at any ratio, an increase in temperature up to 40°C. results in greater purity. Above 40° increased temperature decreases the purity. (4) that if the sulfuric acid used is diluted to any considerable extent, it is impossible to achieve any great degree of purity. (5) that the yield of washed oil is essentially constant under all conditions of agitation.

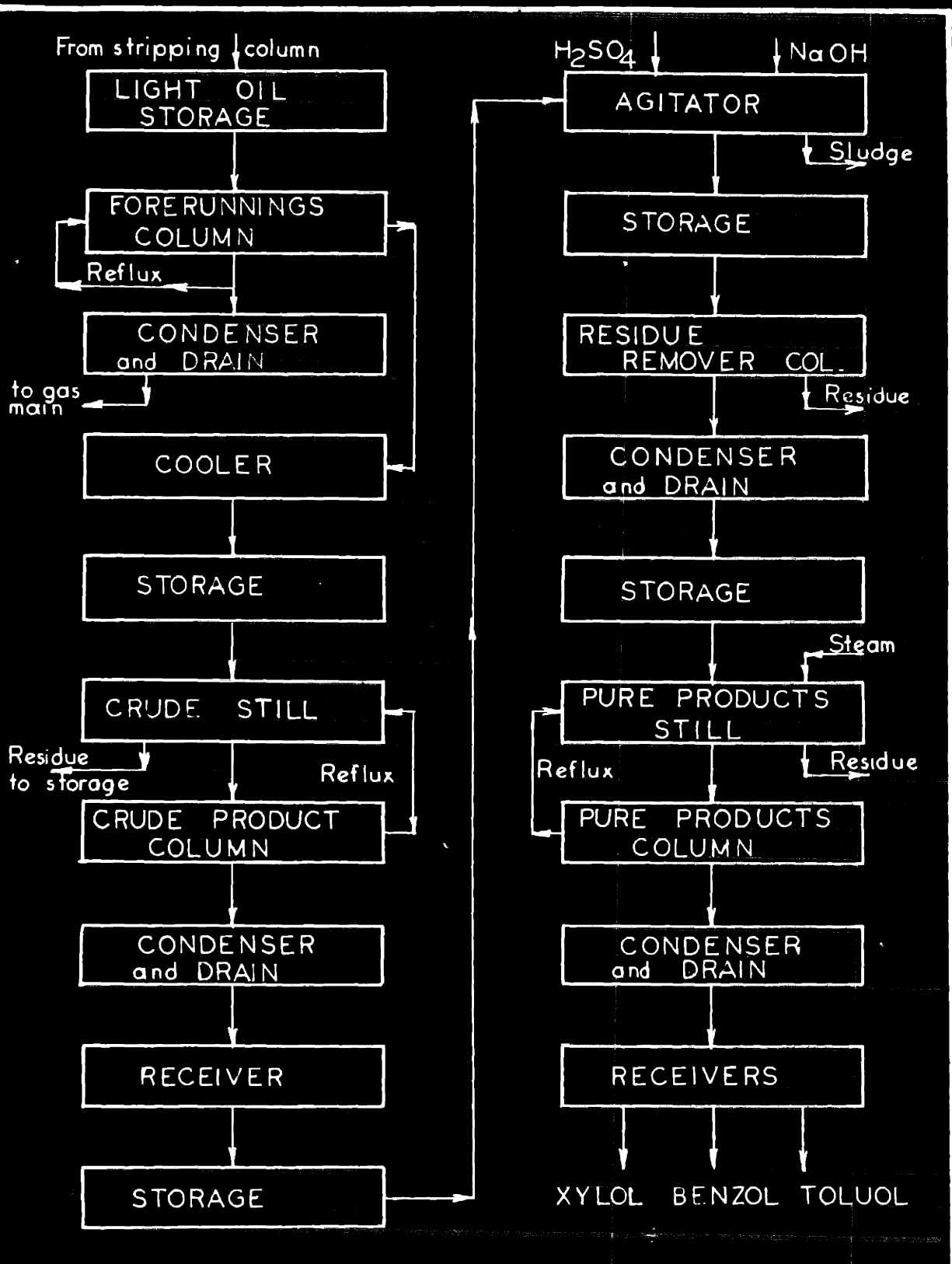
On the basis of the aforementioned conclusions, the following recommendations were made: (1) that the Lackawanna Plant be operated under these optimum conditions: acid-oil

ratio - 5%, temperature - 40°C., concentrated sulfuric acid. (2) that a purity vs. time curve be determined for the industrial agitator at the above conditions, and the agitator subsequently be operated at the minimum time determined. (3) that an investigation be made to determine whether addition of the acid in several batches will result in reduced acid consumption without increasing the agitation time excessively.

II. INTRODUCTION

In September, 1942, Bethlehem Steel Company set into operation at its Lackawanna Plant a new Process for the refining of benzol, toluol, and xylol obtained from coke oven gas. The new set-up as included in the Benzol plant has as its main components four rectifying columns and an agitator. (See Figure 1) The light oil, containing aromatics as well as olefins and paraffins, is brought to the Benzol plant where it is stripped from a solvent and charged to the forerunnings column. In this operation all the lighter, lower boiling impurities (forerunnings) are removed and sent to the coke oven gas main. The remainder is then charged to a pot still which feeds the crude products column. Here all the material which boils below 140°C . is removed and is known as the crude products. The crude products are then agitated, first with concentrated sulfuric acid and then with 18% sodium hydroxide. The purpose of this operation is to remove such olefinic impurities as would color the final products or produce gums. From the agitator, the washed oil goes to a residue removal column and thence to the pure products still and column, from which pure benzene (0.5° - 1.0° b.p. range), pure toluene (0.5° - 1.0° b.p. range) and xylenes (12° b.p. range) are obtained.

This thesis interests itself only in the sulfuric acid wash in the agitator. This operation as it is used now is as new as the four column installation. In previous operation, benzene was not produced for nitration, as it is now, and there-



FLOW SHEET
of
BENZOL PLANT

M. I. T. STATION
BETHLEHEM STEEL CO.

F33-3B42

1-23-43

FIGURE 1

S.E.G.-C.J.M.

fore did not have to be a highly refined product. Motor benzol was washed by the silica-gel method and the crude for making relatively pure toluene and xylenes was washed by the present method. The agitator is now operated as follows:

A charge of crude oil from the crude products storage is placed in the agitator and an amount of 66° Baumé (approximately 96%) commercial sulfuric acid is allowed to flow into the apparatus for a period of approximately ten minutes after agitation has been started. The amount of acid now used is 400 gallons for an 8000 gallon crude products sample. The agitator is timed after the last bit of the acid is run in and agitation is kept up for 30 minutes. After this time the agitator is stopped and after ten minutes (to allow settling) a sample is taken from the top. This is tested immediately by the standard Barrett Wash Test. (See page 30) The acid layer is allowed to settle to the bottom and is drained off after thirty minutes. If the wash color is acceptable, an amount of 18% sodium hydroxide solution (now 400 gallons) is added and the batch agitated again for thirty minutes and settled for thirty minutes. The caustic layer is then run off and the batch is ready to be sent to the residue removal column. If, however, the wash color was not acceptable, the acid sludge is drained off and a new charge of acid (50 gallons) is added and the operation repeated. This is done until the wash color is down to a value of 1 or 0-1.

With the advent of colder weather it was found that it took many extra washings to reduce the wash color to an acceptable value. This increased the cost of the washing operation considerably and thus the need for some form of heating

became apparent. After some experimenting, a closed steam coil was placed in the tank above the agitator in order to preheat the oil. This had the desired effect of giving the proper wash color with a reasonably normal amount of acid.

This investigation is concerned with finding the optimum conditions at which the oil should be agitated in order to achieve the proper wash color most economically. Consideration is taken of the effect of time of agitation, wash color, acid-oil ratio, and costs of acid, steam and loss of product. A theoretical discussion of the problem and its variables may be found in the Appendix of the thesis under the title SUPPLEMENTARY INTRODUCTION.

III. PROCEDURE

In order to study the interdependence of the variables and from this correlation to determine, subsequently, the optimum temperature of agitation, much experimental data was needed. It was decided to make the runs on a laboratory scale, for by so doing, runs could be made more frequently and with better control of the variables than would be possible on a commercial scale agitator. Consequently, a small agitator was constructed; its mixing action being very similar to the agitator in use at the Benzol plant. The mixer was lagged during yield runs to insure reproducible results. Yield was measured in a lagged graduate and standard Barrett Wash tests were made on all samples.

Of the five variables, - temperature, acid-oil ratio, concentration, time, and stepwise washing, - the first four were selected for the initial investigation. As the available time was limited, a test to determine the effectiveness of stepwise washing was omitted.

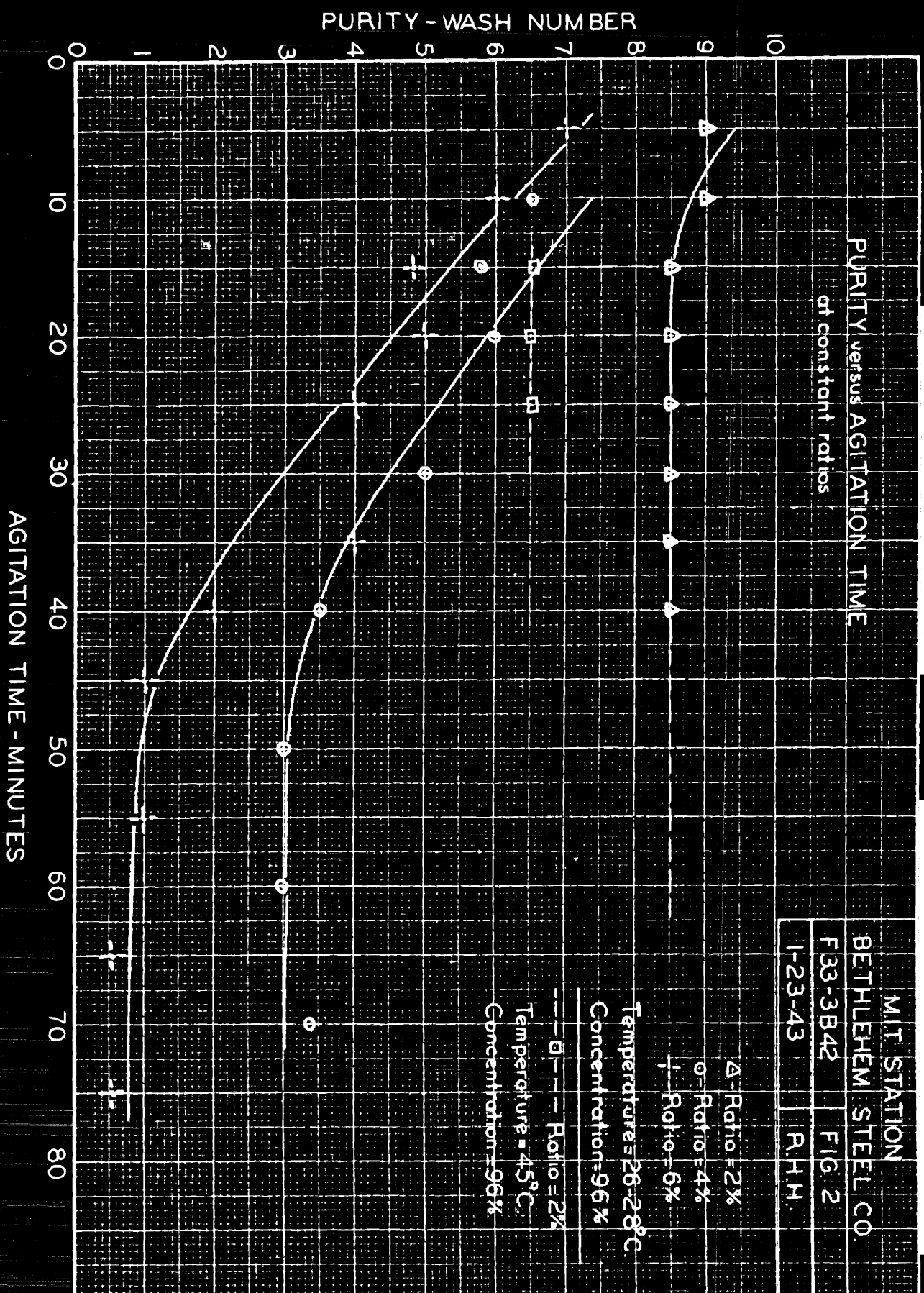
A literature search yielded some interesting information that simplified the procedure. It was noted that as time increased, purity approached a constant value, all other variables being fixed. To check this fact, time runs were made and curves of purity versus time were plotted; first at various acid-oil ratios, holding concentration and temperature constant; and then a few check points at a different temperature holding concentration and acid-oil ratio constant. The runs made at the various ratios were at

room temperature, which is below that to be used in future runs.

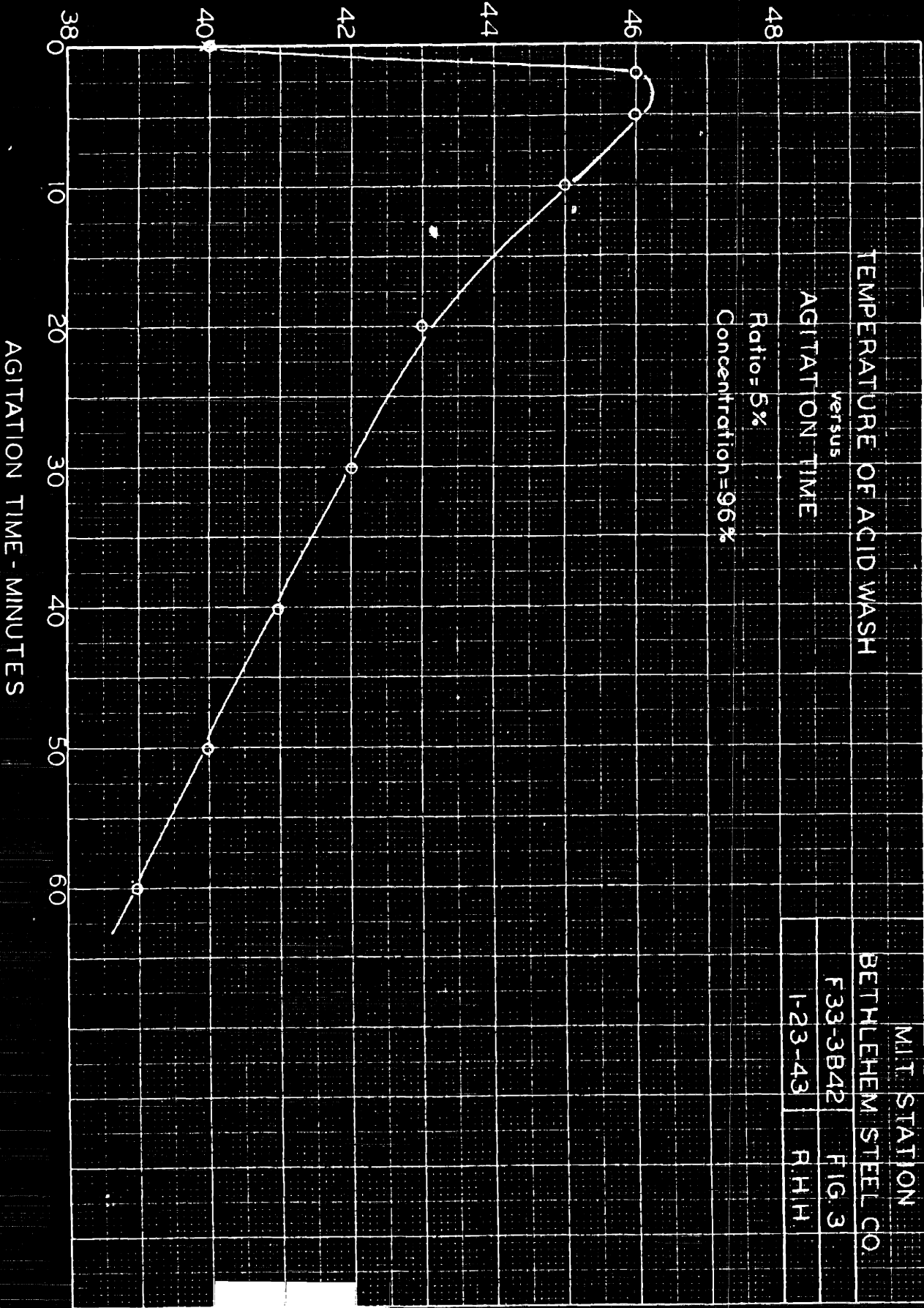
The yield data to determine the influence of temperature and acid-oil ratio were obtained by varying temperature and ratio at constant concentration. To obtain these data, samples were heated to the required temperature, placed in a lagged box, brought to the proper acid-oil ratio with 66° Baume sulphuric acid, and then agitated for one hour. One hour is more than the safe minimum time found in any of the time runs conducted at all the acid-oil ratios used. Yield was measured and Barrett Wash tests were made to determine purity. The data obtained from these runs permitted the selection of the optimum point by inspection.

Because of the limited time available, only a few runs at a lower concentration were made. During these runs, the effect on purity of a lower concentration, at one temperature and several ratios was noted.

IV. RESULTS



TEMPERATURE - DEGREES CENTIGRADE



TEMPERATURE OF ACID WASH

versus

AGITATION TIME

Ratio = 5%

Concentration = 96%

MIT STATION
BETHLEHEM STEEL CO.

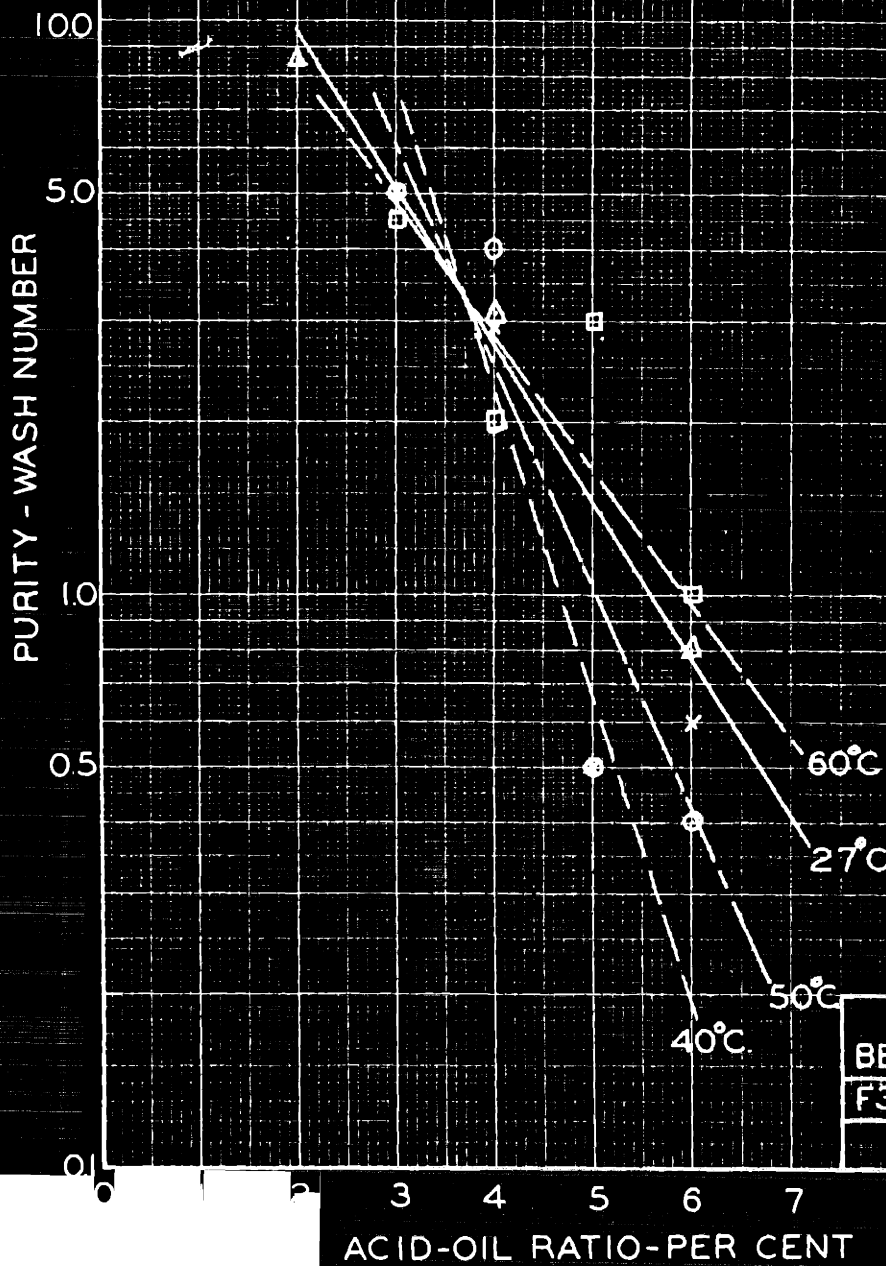
F33-3B42 FIG 3

1-23-43 R.H.H.

PURITY versus ACID-OIL RATIO
at constant temperature

Agitation time = 60 minutes
Concentration = 96 %

△ ————— 27°C
○ - - - - - 40°C
x - - - - - 50°C
□ - - - - - 60°C



M.I.T. STATION	
BETHLEHEM STEEL CO.	
F33-3B42	FIG. 4
1-23-43	R.H.H.

PURITY versus TEMPERATURE

M.I.T. STATION
BETHLEHEM STEEL CO.
F33-3842 | FIG 5
1-23-43 C.J.M.-R.H.H.

□ Ratio = 4%
△ Ratio = 5%
○ Ratio = 6%
Agitation time = 60 min.
Concentration = 96%

PURITY - WASH NUMBER

4

3

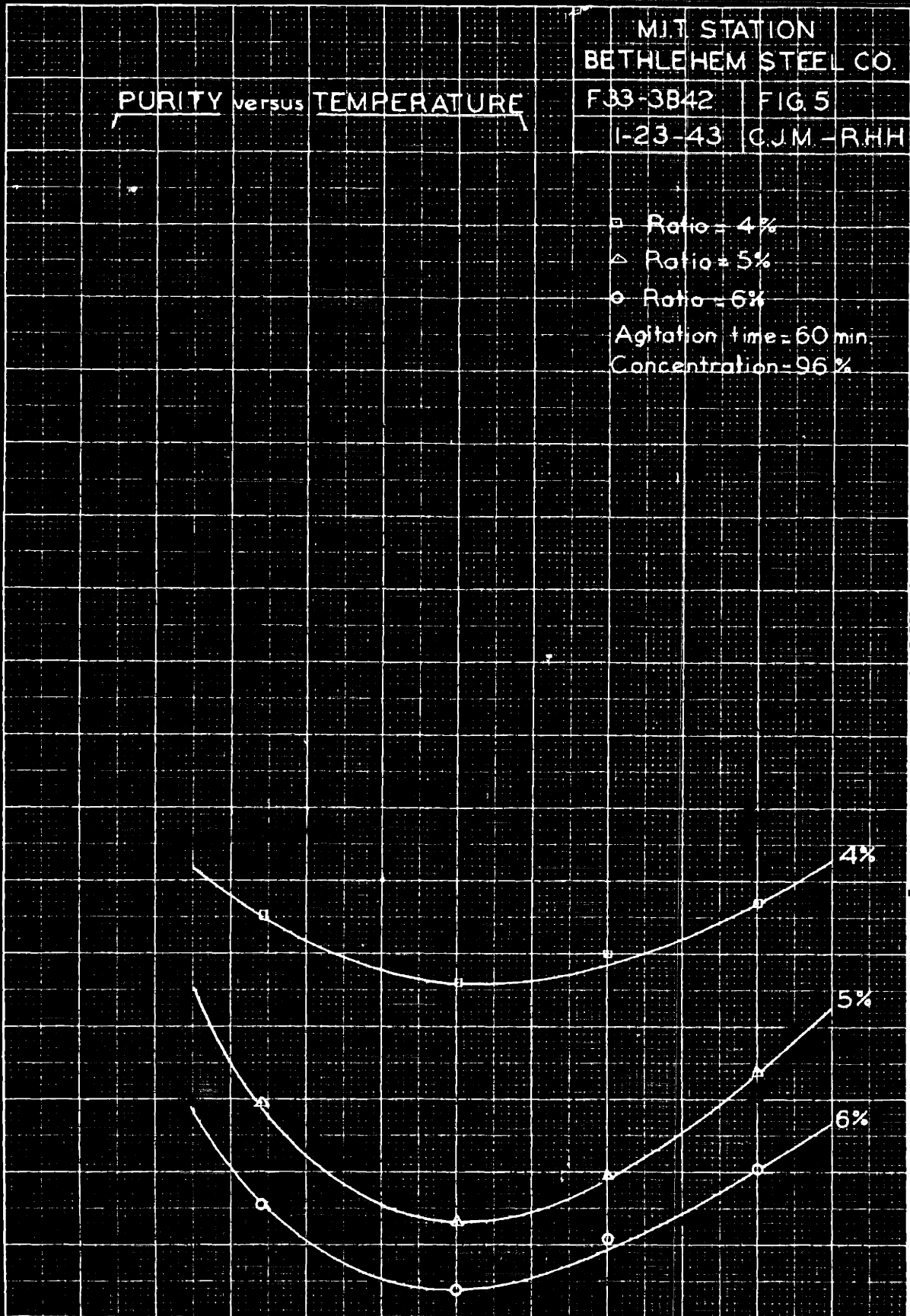
2

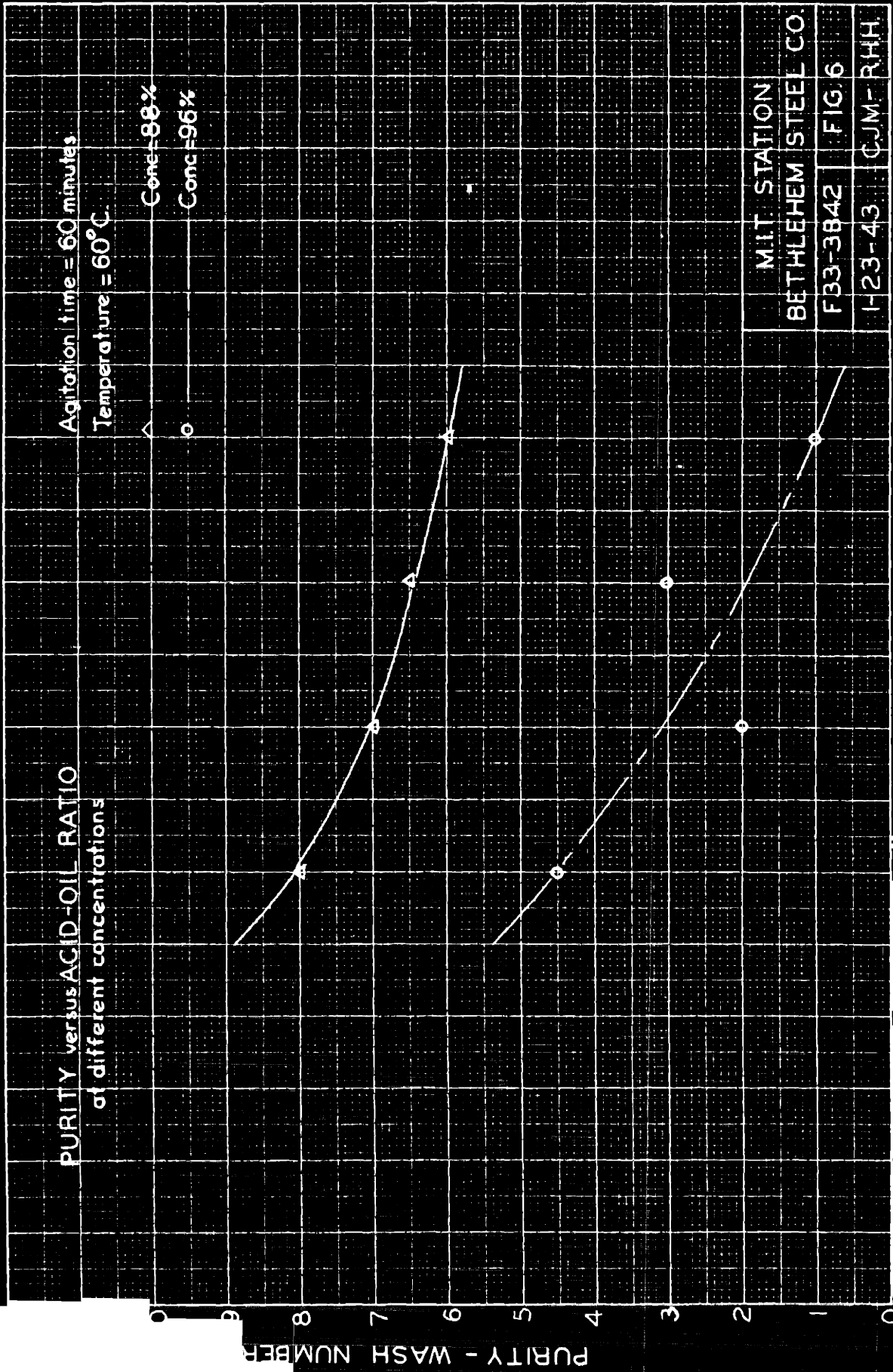
1

0

0 10 20 30 40 50 60 70

TEMPERATURE - DEGREES CENTIGRADE





MIT STATION
 BETHLEHEM STEEL CO.
 FB33-3842 FIG. 6
 1-23-43 C.J.M.-R.H.H.

3
ACID-OIL RATIO - PER CENT
 7

PURITY - WASH NUMBER

V. DISCUSSION OF RESULTS

To obtain the plots needed for the determination of optimum conditions, it was first necessary to make several intermediate charts. In order for the various "yield" runs to be comparable, it was essential that sufficient time of agitation be allowed for the reaction to go to completion. The possibility of setting an arbitrary time of agitation was inadvisable, since commercial agitation conditions were not reproducible on the laboratory scale, and the time values determined would not be applicable to the industrial agitator.

For this reason the first objective to determine was the time necessary for the reaction to go to completion under various conditions. Previous research by Eisner, Fein, and Fisher⁽²⁾ at high acid-oil ratios had indicated that the reaction of sulfuric acid with olefins approached a limiting value within a relatively short period of time. It was felt, therefore, that if a plot of purity versus time were drawn for any given temperature, ratio, and concentration, an asymptotic curve could be determined from which the time necessary for complete reaction could be found. Previous research (See page 23) having indicated that the limit of the reaction occurs when the acid has reached a certain dilution point, it was obvious that the concentrated acid would be longest in reaching its maximum reaction. Similarly, runs taken at room temperature would be slower to react than runs taken at any higher temperature. This being so, it

was decided to take purity versus time runs at various ratios (3%, 4%, 5%, and 6%) at constant limiting conditions of temperature and concentration (room temperature and 96% acid).

Purity was determined by the standard Barrett Wash test whereby 90% of the neutralized wash product is distilled off and shaken with a standard quantity of sulfuric acid. The color of the acid layer is then compared, after a settling period, with a group of 15 bottles of standard graduated color samples. The lower the number of the bottle to which the sample corresponds (wash number), the greater the purity of the sample. A wash number of 1 is the purity requisite for subsequent nitration.

Time runs were made for acid-oil ratios of 2%, 4%, and 6%, the results of which are plotted in Figure 2. As was expected, the curve for each ratio approached a definite, asymptotic value, the asymptotic value being reached in 15 minutes for a 2% ratio and in 55 minutes for a 6% ratio. Although periods of slightly less than 55 minutes were satisfactory for 3% to 5% ratios, the difference in time was so little that it was decided advisable to take all the yield runs at a constant period of 60 minutes, at which time complete reaction would be assured under all conditions.

The assumption that higher temperature runs would approach their asymptotic value sooner than those at low temperatures was checked by a short 2% run at 45° C. for 15, 20, and 25 minute periods. As can be observed from the graph, this curve has already reached its asymptote at 15 minutes, the time at which the room temperature and 2% run reaches

its asymptote.

It should also be mentioned that a test made on an unagitated sample gave a wash test which, if one roughly extrapolated the color comparisons, would range around a #40 wash color. Since within 5 minutes the color was reduced to 9 or less for all ratios, this indicates that the largest portion of the reaction takes place within the first several minutes.

Although the time curves taken were utilized in subsequent runs, it must be noticed that these times are not applicable to the commercial agitator inasmuch as agitation conditions are not quantitatively reproducible. It would be advisable, however, to have a similar series of time runs on the plant agitator to determine the minimum time necessary for complete reaction. Since the depreciation on the impeller and the other industrial apparatus is a direct function of time of agitation, the advantages of determining the exact time required for the conditions employed are obvious.

Fig.3 is a representative plot of the temperature of the wash vs. agitation time. For the lowest initial temperature ($40^{\circ}\text{C}.$), the curve usually rose to a peak approximately $6^{\circ}\text{C}.$ higher than the initial temperature, as seen in the diagram; for higher initial temperatures ($60^{\circ}\text{C}.$) the peak usually represented a rise of approximately $2^{\circ}\text{C}.$

This sudden rise initially seems to confirm the previous conclusion that the major portion of the reaction

occurs in the first five minutes. The gradual decrease in temperature is due to heat losses from the agitator, for although the container was placed in a rock wool insulated box, it was impossible to secure completely adiabatic conditions.

One exception to the temperature-time curve should be noted. Runs No. 46 and 55, both at the 5% ratio, 96% acid, and an initial temperature of 60°C., rose to a peak nearly 5° higher than their starting temperature, a point unusually high for an initial temperature of 60°C. The fact that the wash test of these runs also proved abnormal, gave this temperature rise a rather peculiar, but inexplicable significance.

The "yield" plot (purity vs. acid-oil ratio, Fig. 4) has been drawn so that representative purity values for different temperatures at various ratios may be determined for use in Figure 5, the purity-temperature chart. If the purity-ratio diagram is first plotted, the purity-temperature points determined by the curves thereon will be weighed by four other points, rather than by a single determination, thus giving a more representative diagram.

As can be observed from Figure 4, the purity at various acid-oil ratios at constant temperatures were determined. Inasmuch as purity values for low wash numbers, are of much greater precision than for higher wash numbers, this plot has been made on semi-log paper. Since the runs taken at 2% ratios for the various temperatures were not insulated, as were the other heated runs (40°, 50°, and 60° runs),

it was decided not to include these determinations on the charts, inasmuch as they would not be comparable to the other values.

Observation of the curves show that as acid-oil ratio is increased, wash number decreases at all temperatures.

Figure 5 of purity versus temperature has been determined by picking points off vertical lines on Figure 4. This gives a representative curve for each ratio at increasing temperatures. From the plot it can be seen that for each ratio an increase in temperature gives an increase in purity passing through a minimum wash number near $40^{\circ}\text{C}.$, after which further temperature increase results in reducing the purity. Since $40^{\circ}\text{C}.$ is the point of lowest wash number for each ratio, this is obviously the optimum operating temperature. The possibility that the curve may have a very steep slope below $30^{\circ}\text{C}.$, approaching a low point somewhere to the left of $40^{\circ}\text{C}.$ is conceivable, but even if this were so, it would still be advantageous to operate at $40^{\circ}\text{C}.$, since any cooling from the lower temperature under these conditions would result in a much higher wash number as a result of the rather critical slope.

Forty degrees Centigrade is, therefore, the temperature at which the agitation should be conducted. The temperature is not critical, so that insulation of the commercial agitator would be unfeasible. However, since lowering of the temperature does reduce the purity, it is advisable to agitate the oil while it still retains a 40° temperature.

In Figure 5, ratios less than 4% have not been drawn since the data do not permit accurate location of the curves of ratios below 3.7 in Figure 4. However, this had slight significance on the results of this thesis since the range of interest is around a wash number of 1.

By interpolation it appears that a ratio of about 4.7% would be the minimum acid-oil ratio with which a purity of 1 is obtainable. A slight safety factor is advisable, however, so that a 5% ratio is probably more feasible.

Explanation of the shape of the curves is rather difficult. It is possible that temperature increases below 40° give better olefinic sulfonation, thereby bettering the purity, but that above 40° C. increased temperature brings about the formation of soluble aromatic sulfonated compounds or decomposition products that contaminate the oil. Since no previous investigation has been done on this reaction, however, it is impossible to decide just why the curves should turn upward above 40°C.

Figure 6 shows a plot of purity versus acid-oil ratio for two different concentrations. Since the work of Eisner, Fein, and Fisher⁽¹⁾ had indicated that sulfuric acid above concentrations of 88% begin to react on aromatic hydrocarbons, it was desired to determine whether the equivalent purities could not be obtained at lower concentrations. The curves of Figure 6 show that nowhere in the range tested did the diluted acid give a wash number less than 6. From this fact it was felt that any dilution of the concentrated acid would be highly undesirable.

The possibility of step-wise washing, although it was not investigated, appears exceedingly feasible. The addition of the acid in several batches is practiced successfully at several light oil plants and there appears to be no reason why it should not be equally desirable at the Lackawanna plant. Since low ratio-agitations reach their asymptotic values much sooner than high ratio agitations, as shown by Figure 2, it appears that the actual time of agitation would probably be no more for step-wise washing than for single batch operation. Depreciation would be approximately the same, and the only increase in time would be that necessary for settling. An investigation of the feasibility of step-wise acid washing is highly recommended for future study.

The actual yield resulting from each run was measured and gave a value which was essentially constant within the precision of the measurements. Three hundred fifty cc. of oil were used in every run, and a washed oil yield after washing^{of} at least 98.5% was obtained in practically every case.

Certain aspects of the experimental set-up should perhaps be mentioned here in connection with the graphs and results previously discussed.

The light oil used in the experiment was obtained from storage tank No. 6 in the Lackawanna light oil plant. This and tank No. 7, with which it is connected, hold the oil from the Crude Products still, approximately 1-1/3 runs from the crude still being required to fill the two tanks. Thus the composition of the oil in the tanks will vary since they contain at times the light ends of one distillation and the

whole of another, and at other times the heavy ends of one distillation with the whole of another. Two five gallon oil samples were used in this experiment, the first batch being used in the time runs, the second batch being used for all the "yield" runs. The average "90's" value (temperature at which 90% of the washed oil distills over) for the time run sample was 112°C. and for the "yield" run sample, 118°C. Both of these values are a bit higher than the usual "90's" point (101°C.), showing that a greater portion of xylol and toluol than is usual was present. It is not likely that this difference in composition had any effect on the experimental results, however.

Agitation was done in the apparatus described previously. It was found, however, that the rotational rate of the impeller varied somewhat as the air pressure changed, giving slightly different agitation conditions over the series of runs. Completely adiabatic conditions were also lacking, although the agitator was surrounded by rock-wool insulation in a wooden container. Heat losses were thus greatly reduced but not entirely eliminated as is evident from Figure 3. It should also be noted that the acid was added all at once, instead of slowly, over a period of time, as is done industrially. This change in method of addition should affect the length of time necessary, but will not exert an appreciable effect on the optimum temperature data.

The "90's" distillation was done with an electric heater and a standard condenser. The temperatures at which each 10% distilled over were remarkably consistent, all runs

giving readings within 1°C. of the corresponding points for the other distillations. The following is a result of a typical distillation during the "yield" runs:

1 st drop at		84.0°
10%	-	86.5°
20%	-	87.5°
30%	-	88.5°
40%	-	90.0°
50%	-	91.5°
60%	-	94.0°
70%	-	98.0°
80%	-	105.0°
90%	-	116.0°

As previously mentioned, these temperatures are somewhat higher than commonly obtained by the plant operators on an average oil batch.

The wash tests were made by comparison with the plant's standard Barrett solutions. Any errors in wash number would probably be in an upward direction since any incidental impurities, such as cork, probably tend to deepen the wash color. Greater precision is also possible at the lower numbers since differences in color are more easily observable in this range. It would be advisable for any similar experiments conducted in the future to make up several intermediate standard color solutions for the range between 0 and 1.

The purpose of all these runs was to determine the optimum conditions for the acid-oil wash. It was expected to combine steam cost, acid cost, and loss of product in curves illustrating cost of product versus the temperature necessary to obtain the desired purity at various ratios and

concentrations. Heating cost was calculated to be 18 cents per 10° rise for an 8,000 gallon batch, and the cost of increasing the ratio 1% was computed to be \$8 per 8,000 gallon batch. Depreciation and labor would necessarily be considered as fixed costs since the time factor in the laboratory was not comparable to the industrial apparatus.

It was found unnecessary to make the cost chart, however, inasmuch as certain factors proved constant over the entire range of conditions. Yield was found to be essentially constant thereby eliminating this cost factor. Dilute acid solutions were found incapable of giving the requisite purity so that there was no possibility of using a weaker acid. Furthermore, a temperature in the range of 40° was found to be the optimum for all ratios, so that the heating cost was determined at a constant value. It remains only to consider the minimum acid-oil ratio necessary to obtain the desired purity and, allowing a proper safety factor, this has been found to be 5%.

VI. CONCLUSIONS

From the previous discussion of results several conclusions are evident:

1. Under any conditions of agitation, the major portion of the sulfonation reaction takes place within a relatively short time with the result that the purity rapidly approaches an asymptotic value. The time necessary to reach the asymptotic line is determinable for any given agitator.
2. As the acid-oil ratio decreases, wash number decreases at all temperatures.
3. At any ratio, an increase in temperature up to 40° results in greater purity. Above 40° increased temperature decreases the purity.
4. If the sulfuric acid used is diluted to any considerable extent, it is impossible to achieve any great degree of purity.
5. Step-wise washing is a possible means of achieving better, cheaper sulfonation.
6. The yield of washed oil is essentially constant under all conditions of agitation.

VII. RECOMMENDATIONS

It is recommended that:

1. The agitator at the Lackawanna plant be operated at the following optimum conditions:
 - a. Acid-oil ratio - 5%
 - b. Temperature - 40°C
 - c. Concentrated sulfuric acid
2. A purity time curve be determined for the industrial agitator at the above conditions, and the agitator subsequently be operated at the minimum time determined from these data.
3. An investigation be made to determine whether addition of the acid in several batches will result in reduced acid consumption without increasing the agitation time excessively.

VIII. APPENDIX

A. SUPPLEMENTARY INTRODUCTION

The necessity of improving the purity of the benzol and toluol light oil fractions brought about an investigation of what variables in the refining process could be altered to achieve greater purity. The possibility of taking a smaller temperature cut of benzol and toluol from the pure products still presented itself, but the fractions already being taken were limited to a 0.5° - 1.0° Centigrade range. Furthermore, previous attempts at the Lackawanna plant to eliminate impurities by this method had indicated that no further purification could be achieved by narrowing the distillation temperature cut.

Since most of the crude light oil impurities are removed through the sulfonation or agitation action, this was the obvious point to achieve greater purity. Experience had shown that in order to achieve benzene and toluene in the final product of sufficient purity for nitration, a Wash No. of 1 was necessary for the product of the acid wash. Five variables in the agitation procedure were evident: (1) time of agitation, (2) temperature, (3) acid-oil ratio, (4) acid concentration, and (5) possible addition of acid in several batches. It was decided, therefore, to investigate these variables so as to determine the optimum conditions of operation but emphasizing the effect of temperature variation. Although the caustic neutralization may also affect the final product, no attempt was made to investigate this possibility.

The crude light oil consists of olefins, aromatics, and saturated hydrocarbons, the olefins and saturates being present in relatively small amounts as impurities. It has been shown (ref. 3,4,6,7) that sulfuric acid reacts selectively with olefins, aromatics, and saturates usually in the order named. The purification consists of the sulfonation of the olefinic compounds along with some aromatic sulfonation, these sulfonation products being drained off in an acid sludge. Practically all the saturates remain as impurities.

Investigation of the effect of agitation time revealed that periods of agitation ranging from 15 minutes to seven hours had been used at the Lackawanna plant. Inasmuch as the deterioration of the impeller and other equipment is a direct function of the time of agitation, it was deemed advisable to determine the effect of agitation time on the wash number. The fact that any quantity of acid added to the oil soon appeared to lose its purifying effect, whereas additional fresh acid still had considerable effect, - a result born out by the previous experiment of Elsner, Fein, and Fisher⁽²⁾ - led to the belief that the acid approached a point of dilution beyond which it was ineffective. These data revealed that even with an acid-oil ratio of 3 to 1, (300%) after 13 extractions, considerable amounts of olefins were still extracted. Since relatively low acid-oil ratios are used in the light oil agitation employed at the Lackawanna plant, it was felt unlikely that practically complete elimination of the olefins was the limiting factor in the sulfonation process.

With this premise in mind, it was believed that by determining the wash number of the light oils at increasing time intervals and at various acid-oil ratios, a series of asymptotic curves would result for the various ratios when wash number was plotted against time at constant concentration and temperature.

Although the experimental times determined in a laboratory apparatus were not strictly applicable to the commercial process, it was felt that proof of the proposed premise would aid in setting the actual time of commercial agitation. Also, it was deemed necessary to know the effect of time before the influence of the other variables was determined.

The next variable to be considered was temperature, increased temperature having already been successfully employed in operations at the Lackawanna plant. Experience there indicated that higher temperatures brought about greater purity for a given ratio and concentration. Since the purity necessary was standardized by commercial demands at Barrett Wash No. 1, the effect of increased temperature, within limits, would be to lower the necessary acid-oil ratio or acid concentration. Since the cost of heating is relatively small, this, of course, was highly desirable. Accordingly it was decided to determine the purities (at constant concentration) obtained using various acid-oil ratios at various temperatures. Total yield was also to be taken, since optimum conditions would of course, be dependent on the amount of product obtained.

Finally, it was decided to investigate the effect of acid concentration on the purification. The Lackawanna plant had always employed a 66° Baumé (approximately 96%)

commercial sulfuric acid for its sulfonation reaction. Nevertheless, from previous work (ref 1,3,4,5,6,7) with pure olefinic and aromatic hydrocarbons it appears likely that olefins are the principal hydrocarbons removed with acid concentrations up to about 88% and that removal of aromatics is the main reaction occurring with acids of concentration greater than 88%. Accordingly, it was decided to determine another set of ratio versus temperature curves at a lower acid concentration of 88%, concentrated acid (96%) having been used in the previous experimental work.

In order to determine the optimum operating conditions, cost considerations would finally have to be made. Steam costs could be determined from the temperatures employed; the cost of acid would depend on the acid-oil ratio; and the loss of product on the yield measurements.

Since the length of agitation necessary, as determined in this investigation, would not be comparable with the actual conditions, the cost of operating the agitator must be considered as a fixed cost.

By plotting the sum of the variable costs versus temperature, the optimum operating conditions can then be determined.

B. DETAILED PROCEDURE

Original Samples of Oil and Acid

The oil used in this investigation was the product obtained from the crude still and column at the Benzol plant of the Bethlehem Steel Co. in Lackawanna, New York. Five gallon samples of the oil were obtained on two different days from the interconnected storage tanks No.'s 6 and 7. The capacity of these tanks is approximately equal to the volume of the products obtained in one and one half complete batches in the crude still and column. At the time each sample was taken, the tanks were almost full, so that the samples should be representative of the oil in a particular batch. Since the samples were taken on different days, however, their compositions did vary. This did not affect the procedure, since they were used in two different parts of the investigation.

The sulphuric acid used in this study was also obtained at the Benzol plant. A one half gallon sample of the 66° Baume' commercial sulfuric acid was obtained by lowering a container into the storage tank.

Acid Wash

Throughout this investigation, a 350 cc sample of oil was used for each run. The acid wash was carried out in a well lagged one liter Erlenmeyer flask to prevent heat losses. Agitation was produced in the flask by means of a glass impeller driven by a compressed air jet.

In the first part of this study, the wash was carried out at room temperature and with a constant acid concentration

of 66° Baumé. Runs were made at acid-oil ratios of 2%, 4% and 6% from five minutes to seventy minutes in length to obtain curves of purity versus time at the constant acid-oil ratios. The object of these runs was to determine the length of time necessary for the reaction of the acid with impurities, for use in subsequent yield runs.

A series of 12 runs was then carried out with acid-oil ratios of 3%, 4%, 5% and 6% and with preheated oil temperatures of 40°C., 50°C., and 60°C. In each case, 66° Baumé acid was used, (96%) and the agitation was carried on for one hour.

Another series of four runs was made with the same four acid-oil ratios, but all at a temperature of 60° C. and with 88% acid.

Settling and neutralization

At the end of the agitation period, the mixture was allowed to stand, separating into two layers. At first, this separation was allowed 30 minutes and took place in a graduate insulated with magnesia lagging. In subsequent investigations, however, it was found that the separation required but one or two minutes, thus making the lagging unnecessary. Measurement was then made of the number of cc in the oil layer.

An 80 cc sample of the oil layer was then drawn off into a small separatory funnel. In order to neutralize any acid entrained in the oil, approximately 80 cc of 5% NaOH was also added to the funnel and the mixture was shaken vigorously by hand. After complete neutralization, it was again allowed to stand and separate into two layers. This operation

required from three to twenty minutes. At the end of this time, the heavier caustic layer was drawn off and the oil layer passed through a filter. The purpose of this operation was to remove any water that might have been entrained in the oil. The resulting oil was usually pale yellow or straw colored.

Distillation

In all the tests, a 50 cc sample of the filtered oil was collected for distillation. For the first few runs, the distillation was carried out in a standard Engler 100 cc distilling flask heated by an electric heater, and the vapors were condensed in a water cooled glass jacket. It was found that the temperatures obtained with this apparatus for the first drop of distillate varied as much as ten degrees from those obtained by the plant laboratory with a standard condenser. This, of course, made it necessary for us to adopt a similar condenser in order to get consistent results and run standard specification tests on the distillates. The final condenser jacket used, was a copper trough filled with cold water and lay at an angle of 75° with the vertical. The hot vapors passed through a glass tube which ran through the trough and which was surrounded by the cold water. Ninety percent of the oil sample was distilled off and collected for the standard color tests. Temperature readings were then taken at the first drop and at the end of the 90% sample.

Wash Test

In order to determine the relative purity of the distilled oil, the Barrett Standard Wash Test was employed.

The standard Barrett Test consists of the following: Seven cc of 96% laboratory CP sulfuric acid is placed in a small glass-stoppered bottle to which is added approximately 21 cc of the oil. The mixture is shaken vigorously for 15 seconds and then allowed to stand for 15 minutes. At the end of this period, the bottle is inverted once or twice to give the acid layer a uniform color and it is then compared with a set of 15 standard Barrett color solutions. The wash number is determined by the number of the standard solution which it most closely resembles as regards to color.

C.SUMMARIZED DATA

Time runs at 96% Sulfuric Acid Concentration

Run No.	Time (min)	Temperature Cent.	Acid-Oil Ratio %	Wash No.
1	5	24(room temp)	6%	7
2	10	24(room Temp)	6%	6
3	15	25(room temp)	6%	4-5
4	20	25(room temp)	6%	5
5	25	26(room temp)	6%	4
6	30	26(room temp)	6%	-
7	35	27(room temp)	6%	4
8	40	27(room temp)	6%	2
9	40	25(room temp)	2%	8-9
10	35	27(room temp)	2%	8-9
11	30	27(room temp)	2%	8-9
12	25	28(room temp)	2%	8-9
13	20	28(room temp)	2%	8-9
14	15	28(room temp)	2%	8-9
15	10	28(room temp)	2%	9
16	5	27(room temp)	2%	9
17	10	55	6%	4
18	20	35	2%	8
19	20	45	2%	6-7
20	20	55	2%	<u>6-7</u>
21	25	45	2%	<u>6-7</u>

SUMMARIZED DATA

Time runs at 96% Sulfuric Acid Concentration

Run No.	Time (min)	Temperature °Cent.	Acid-Oil Ratio %	Wash No.
22	15	25(room temp)	6%	0- <u>1</u>
23	15	55	6%	3-4
24	15	45	2%	<u>6</u> -7
25	20	65	2%	<u>6</u> -7
26	55	27(room temp)	6%	1
27	20	27(room temp)	4%	6
28	30	27(room temp)	4%	5
29	40	27(room temp)	4%	4-5
30	50	27(room temp)	4%	4
31	65	26(room temp)	6%	0-1
32	75	27(room temp)	6%	0-1
33	60	27(room temp)	4%	3
34	70	27(room temp)	4%	3- <u>4</u>
35	15	27(room temp)	4%	5-6
36	10	27(room temp)	4%	<u>6</u> -7

SUMMARIZED DATA

Yield runs at One hour elapsed time.

Run No.	Concentration of Acid %	Temperature Cent.	Acid-Oil Ratio %	Wash No.
37	96%	40	3%	5
38	96%	50	3%	5
39	96%	60	3%	4-5
40	96%	40	4%	4
41	96%	50	4%	2- <u>3</u>
42	96%	60	4%	2
43	96%	60	3%	4-5
44	96%	40	5%	0-1
45	96%	50	5%	0-1
46	96%	60	5%	3
47	96%	40	6%	0-1
48	96%	50	6%	0- <u>1</u>
49	96%	60	6%	1
50	88%	60	6%	6
51	88%	60	5%	6-7
52	88%	60	4%	7
53	88%	60	3%	8
54	96%	60	4%	6-7
55	96%	60	5%	2- <u>3</u>

SUMMARIZED DATA

Typical 90% Distillations of Washed and Unwashed Samples.

Temperatures in Degrees Centigrade

PerCent of Sample	Sample "A" * (unwashed)	Sample "A" #21 (washed)	Sample "B" ** (unwashed,	Sample "B" #37 (washed)
1 st drop	82.0	82.5	84.0	84.0
10%	84.8	84.0	86.0	86.0
20%	85.0	84.6	87.5	87.0
30%	86.0	85.5	88.0	88.0
40%	87.0	86.3	90.0	89.5
50%	88.0	87.5	91.5	91.5
60%	90.0	89.5	94.0	94.0
70%	92.5	92.3	97.5	98.5
80%	97.0	97.0	104.0	105.5
90%	110.0	111.0	116.0	115.5

*Sample "A" used for obtaining data for time runs.

**Sample "B" used for obtaining data for yield runs.

D. LOCATION OF ORIGINAL DATA

The complete data for this thesis can be found in Data Book # 73, pages 47 through 87. This book is filed at the Buffalo Station of the M.I.T. School of Chemical Engineering Practice at the Bethlehem Steel Company, Lackawanna, New York.

E. LITERATURE CITATIONS

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