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SOLVENT RECOVERY
FROM A
COMPLEX PROCESS SOLVENT STREAM
BY
JOHN BUDAVARI

A THESIS
PRESENTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE
OF
MASTER OF SCIENCE IN CHEMICAL ENGINEERING
AT
NEWARK COLLEGE OF ENGINEERING

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Newark, New Jersey
May, 1974

ABSTRACT

This work deals with the recovery of solvents from a complex process waste stream containing methylene chloride, chloroform, n-propyl alcohol, isopropyl alcohol, heptane and butyl acetate. In addition to the above-mentioned solvents, the mixture is saturated with water (ca. 1%), hydrochloric acid, and contains organic and inorganic process impurities. The objective was to develop the simplest economical recovery process utilizing vapor-liquid equilibrium data, distillation and extraction procedures. Considerable effort was expended to develop precise and reliable assay methods. A process which met the necessary requirements of maximum solvent recovery with minimum waste disposal, was developed.

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INTRODUCTION

The prevailing philosophy governing process development work in the chemical industry has been steadily changing over the last decade. Growing consciousness of ecological and social requirements has greatly influenced the engineer and has steered him towards a course which is not just profit oriented, but one that is tempered by the knowledge that the engineer has obligations toward his environment. Furthermore, the international events of the past year have introduced a new factor, i. e. decreased availability of many solvents, which makes recycling and recovery of this type of process solvent streams essential to ensure adequate supplies.

The processes developed were formulated holding both ecological factors, as well as economic concerns in mind. The term "process development" was used here to mean the establishment of the specific flow sequence and utilization of various unit operations. No attempt was made to size or cost the specific pieces of equipment used, but ample data has been provided for this. Recovery specifications were set based on available commercial and reagent grade solvents.

The process solvent streams under consideration originate at three different locations and will be identified as Streams #1, #2, and #3 and also referred to as the Heptane Stream, the Methylene Chloride Stream and the Butyl Acetate Stream, respectively. The approximate compositions of the liquid streams (as liquid volume %) are tabulated below.

TABLE 1
COMPOSITION OF SOLVENT STREAMS

Stream #1 1.5 MGPY		Stream #2 1.5 MGPY		Stream #3 1.0 MGPY	
Solvent	Vol %	Solvent	Vol %	Solvent	Vol %
Heptane	70-80	Methylene Chloride	45	Butyl Acetate	80-90
Chloroform	15-20	Isopropyl Alcohol	45	Heptane	7-10
n-Propyl Alcohol	0.5- 2	Heptane	0.5-2	-	-
Ethyl Chloride	0.1-0.5	-	-	-	-
Propyl Chloride	0.1-0.5	-	-	-	-
Water	1.0	Water	1.0	Water	1.0
Residues*	2-5	Residues*	2-5	Residues*	2-5

* High boiling acidic batch distillation residues.

The direction that the problem solving would follow rested upon whether the solvent streams would be kept separate or combined. If the three streams were to be combined, then a single storage tank rather than two or three separate storage facilities need be installed, and a single rather than separate solvent recovery processes would have to be found. Upon examination of the binary vapor-liquid equilibrium data of the "key pairs", it became evident that combining all three streams would make the recovery process exceedingly complicated and uneconomical. The presence of alcohols, mainly isopropyl alcohol, along with butyl acetate in the combined solvent stream would create a complex mixture of azeotropes which would severely hinder effective separation. Further difficulties would be caused by the high boiling acidic organic/inorganic impurities which upon heating to higher ($>140^{\circ}\text{C}$) temperatures decompose slowly giving up alkyl chlorides (ethyl and propyl) and partially decomposed butyl acetate. Due to the above-mentioned problems which would make the separation of a unified flow stream impractical, the choice was made to keep the solvent streams separate from one another, and recover the solvents in the three streams using the same process equipment. Batch, or semi-continuous blocked operation was selected because of the low total solvent mixture volume level of 3-5 million gallons per year (3-5 MGPY). Although the process lends itself to continuous operations in theory, it is uneconomical to do so at such low volumes.

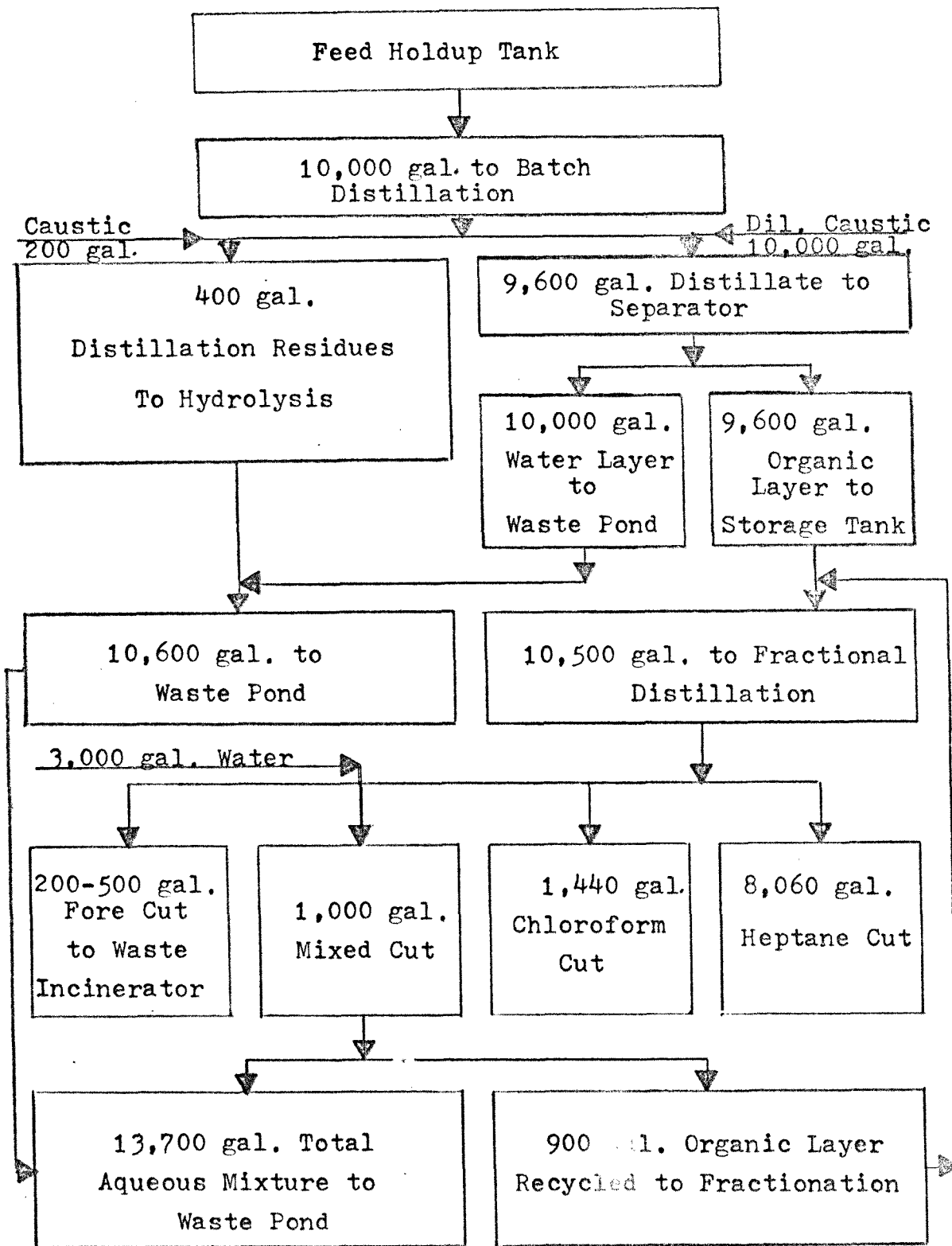
It is true that if all three streams were combined, the isopropyl alcohol and n-propyl alcohol could be removed via aqueous extraction. Isopropyl alcohol forms a constant boiling mixture with water at 80.37°C and 87.8 Wt. % isopropyl alcohol composition(1). Drying by dehydration with 50% caustic or organic salts(1), and azeotropic distillations would yield pure isopropyl alcohol. Incidentally, the combined stream was tried as a potential feedstock, but the degree of separation achieved was totally unsatisfactory and exhibited the aforementioned problems of azeotrope generation.

The overriding factor in the process selection was the consideration that there be a minimum of waste disposal, especially of the chlorinated solvents. All waste from the recommended process is either readily biodegradable and harmless to the environment or yields carbon dioxide and water via incineration.

Although, as illustrated above, maintaining separate solvent streams is preferred, the necessary data for processing a combined stream will also be given. For clarity and simplicity, the process is presented in flow sheet form on the following pages using a block type presentation.

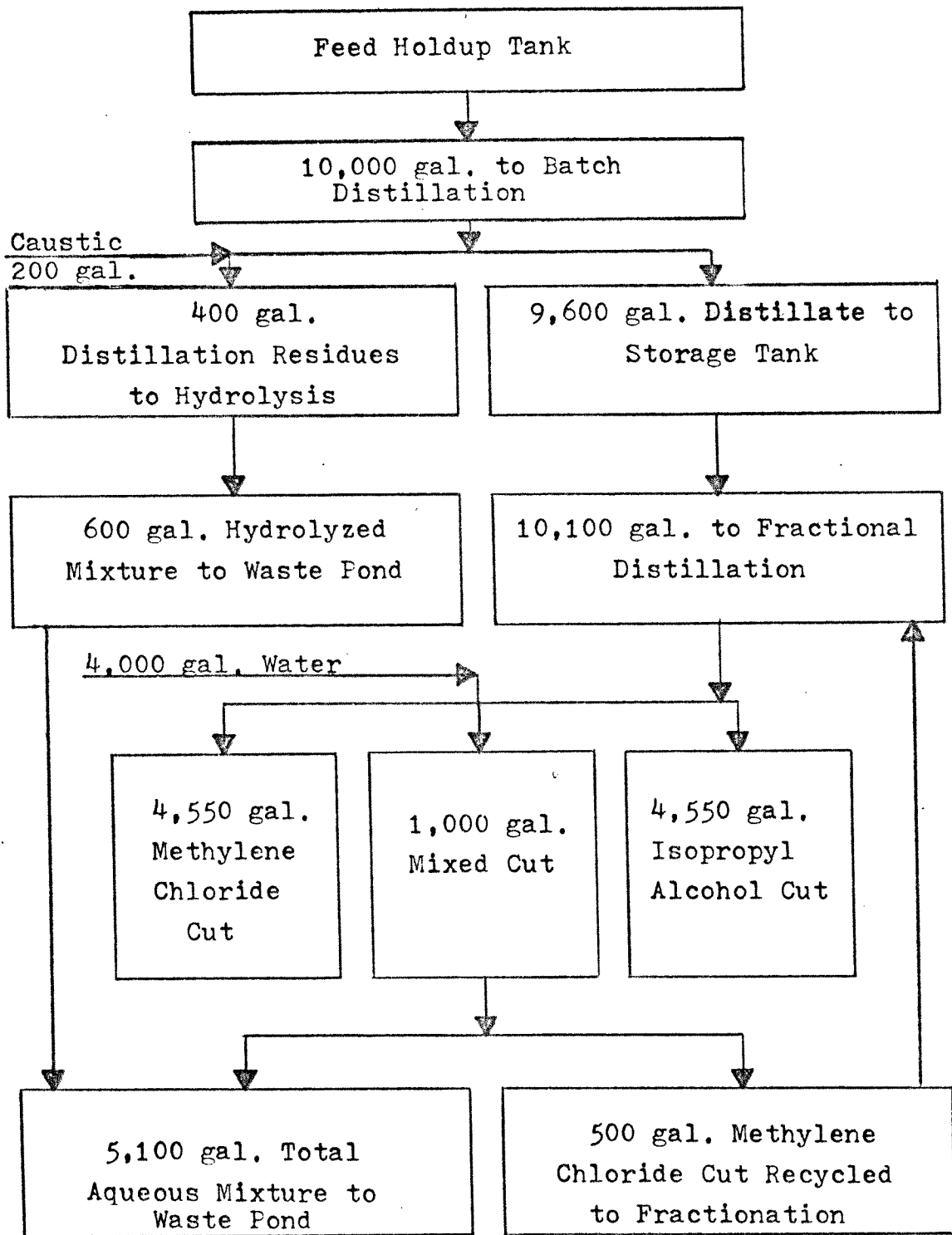
Heptane Stream (#1)

Volumetric Flow Rate: 1.5 MGPY or 10,000 gal./Batch



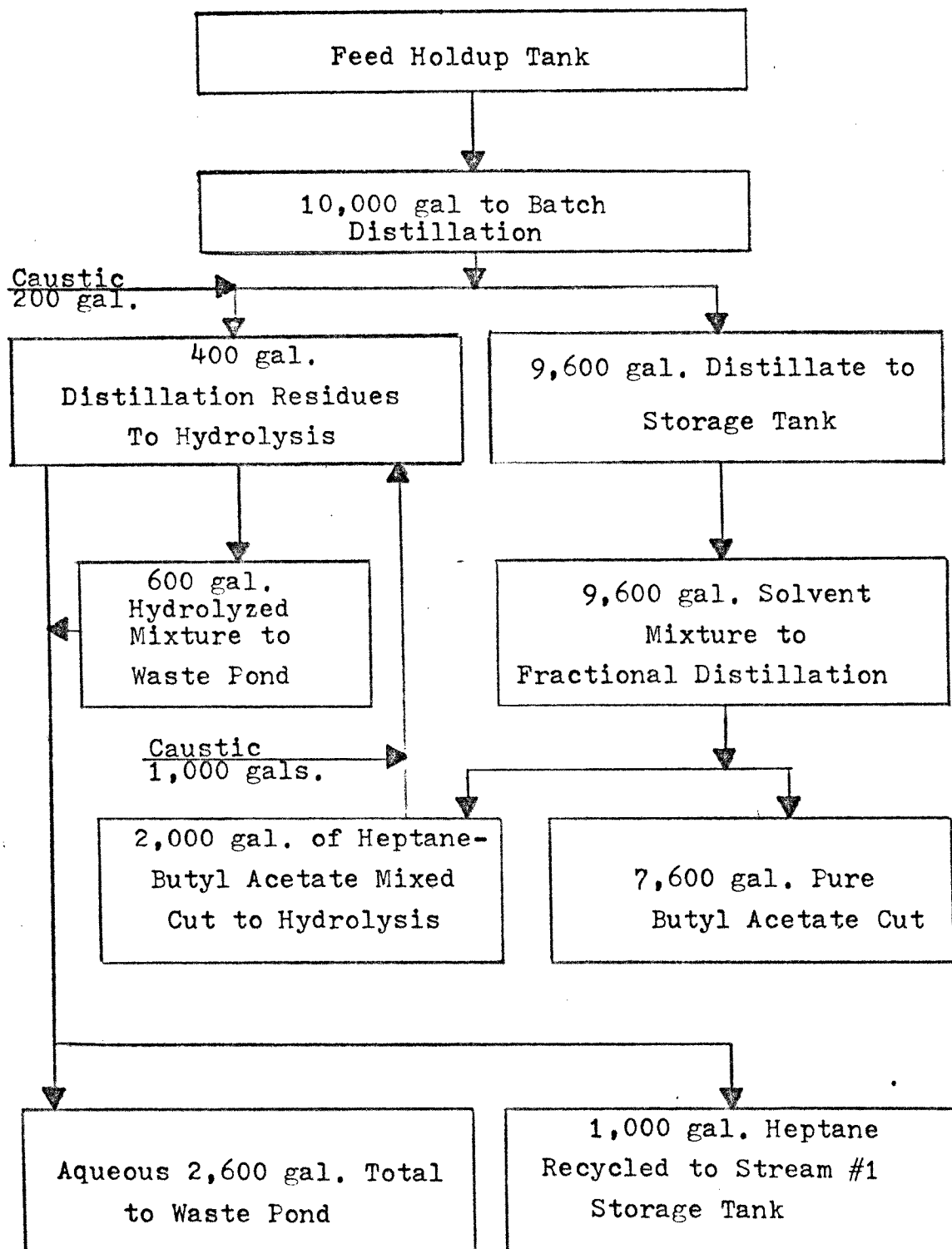
Methylene Chloride Stream (#2)

Volumetric Flow Rate: 1.5 MGPY or 10,000 gal./Batch



Butyl Acetate Stream (#3)

Volumetric Flow Rate: 1.0 MGPY or 10,000 gal./Batch



Notes to Recovery Process Schemes

The Heptane stream (#1) recovery process consists of simple atmospheric batch distillation followed by aqueous caustic neutralization/extraction in order to remove hydrochloric acid and n-propyl alcohol from the distillate. The batch pot residues are rendered harmless by hot caustic hydrolysis. Pure methylene chloride and heptane are recovered in good yields via fractional distillation.

In order to avoid heptane loss, at least five simple batch distillations are completed on top of the previous residue. The final distillation is carried on until a pot (liquid) temperature of 105°C is reached. If the above requirement is fulfilled, the hydrolysis results in a homogeneous aqueous phase since little heptane remains in the distillation residue. A "tight" fore-cut rich in alkyl chloride is forwarded to the incinerator. This cut could be used by the cleaning or solvent industry if such a market existed, rather than disposed of via incineration. n-Propyl alcohol from the mixed cut must be extracted with water to ensure efficient recovery.

The Methylene Chloride stream (#2) recovery process is similar to that of the Heptane stream, but omits the aqueous extraction. The distillate is neutralized by solid sodium carbonate in the distillate receiver because its addition as

an aqueous solution would result in azeotrope formation and thereby complicate the fractionation. The isopropyl alcohol from the aqueous layer of the mixed cut extraction could easily be recovered via azeotropic distillation. This is practical only if 97% purity (3% water) is satisfactory. Preparation of anhydrous isopropyl alcohol would be too costly at this volume level.

The Butyl Acetate stream (#3) recovery operation is similar to that for the Heptane and Methylene Chloride streams, with the following exceptions. Vacuum batch distillation is advantageous since the high boiling residues slowly decompose above 140°C. Consequently, efficient butyl acetate recovery would be cumbersome since the previous residues would be kept hot during the five subsequent distillations. (Five distillation residues to one caustic hydrolysis). Below five percent heptane level in the feedstock, a single mixed cut is collected. The butyl acetate content is hydrolyzed along with the pot residues and the heptane recycled to the Heptane stream (#1) storage tank (ST).



RECOVERY PROCESS

Based on generated thermodynamic and physical data, the final process developed is described below. The process has the following specific features:

- . Recovery of separate solvent streams.
- . Batch process via blocked operation chosen because of low total process solvent flow of 4.0 million gallons per year.
- . The solvents from all three streams are recovered using the same equipment.
- . The experimental data generated as part of this study was used as the basis for process oriented design.

It should be noted that no consideration was given to size, costs, and materials of construction for all storage and process equipment.

EXPLANATION OF FLOW CHART SYMBOLS

<u>Symbol</u>	<u>Description</u>
BST	Butyl Acetate Storage Tank
CST	Chloroform Storage Tank
Cond.-1	Brine Condenser for Batch Distillation Still
Cond.-2	Waste Reflux Condenser for Neutralizer Still
Cond.-3	Brine Condenser for Fractionation
CS	Caustic Scrubber for Vent Gases
CV	Check Valve
DC	Distillation Column
FHT	Feed Holdup Tank for Slop Stream
HST	Heptane Storage Tank
IST	Isopropyl Alcohol Storage Tank
L	Feed and Discharge Lines
LM-1	Line Mixer for Batch Distillate and Dilute Aqueous Caustic
LM-2	Line Mixer for Water and Mixed Cut
MST	Methylene Chloride Storage Tank
RD	Reflux Drum
RE	Jacketed, Baffled Stills with Agitator
RE-1	Batch Distillation Still
RE-2	Caustic Neutralizer/Hydrolysis Still
RE-3	Reboiler for Batch Fractionator
ST	Storage Tank for Batch Distillate
TA	Receivers for Fractional Distillation Cuts
TA-1	Batch Distillate Receiver-Aqueous/Organic Phase Separator
TA-2	Chloroform or Methylene Chloride or Butyl Acetate Receiver
TA-3	Heptane or Isopropyl Alcohol Receiver
TA-4	Fore-Cut Receiver
TA-5	Mixed Cut Receiver-Aqueous/Organic Phase Separator
V	Vent Lines
WT	Water Trap
	Valves
	Pumps

Description of Equipment Arrangement

The narrative is based on the Heptane stream (#1), the most complex, but the operations are similar in the cases of the Methylene Chloride (#2) and the Butyl Acetate (#3) streams.

The process stream from the feed holdup tank (FHT) is distilled in the batch still (RE-1) and the vapors are condensed via condenser #1 (Cond.-1). The condensed vapors are mixed with dilute aqueous caustic in order to neutralize the hydrochloric acid with the base and extract the n-propyl alcohol via the water content using the line mixer (LM-1). The water and organic layers are separated in the separator (TA-1). The water layer from the separator (TA-1) is forwarded to the waste disposal pond, and the organic solvent layer is pumped to the storage tank (ST). The storage tank is equipped with a water trap (WT) which is emptied periodically. After five batch distillations, the distillation residues from the batch still (RE-1) are charged to the caustic neutralizer still (RE-2) which contains 25% caustic. Here the residues are completely hydrolyzed. The hydrolyzed mixture is removed to the waste disposal pond. The distillate from the storage tank (ST) is pumped to the reboiler (RE-3) of the batch fractionated. During the fractional distillation the fore-cut is collected in receiver tank (TA-4) and forwarded to the

incinerator. The pure chloroform cut is collected in receiver tank (TA-2). The heptane cut is collected in receiver tank (TA-3). The mixed cut rich in n-propyl alcohol is extracted with water in the line mixer (LM-2) and the water-organic layers are separated in receiver tank (TA-5). The water layer is pumped to the waste disposal pond and because of blocked operation, the organic layer is recycled to the storage tank (ST). Since the recovery unit is alternately used for the recovery of streams #1, #2 and #3, it is more practical to recycle the mixed cut to the storage tank. Although only one feed holdup tank is drawn, there are actually three, one for each stream. In order to prevent noxious fumes from escaping to the atmosphere, the units are vented through caustic scrubber (SC-1).

Total Solvent Recovery Yields and Waste Disposal Loads

Combined recovery yields for all three solvent streams are presented in terms of liquid volume % of that originally present in the process solvent streams. Results are based on the laboratory fractionation data of the individual solvent streams. (See Appendix for summary of experimental data).

TABLE 2
SOLVENT RECOVERY YIELDS

Solvent	Stream #	Recovered Volume %		Maximum*
		One Pass	Total*	GPY*
Chloroform	1	90	97	196,500
Heptane	1	92	98	1,200,000
Isopropyl Alcohol	2	84	97	28,000
Methylene Chloride	2	91	97	28,000
Butyl Acetate	3	91	98	850,000

* Includes recovery yield increase due to recycling of mixed cuts. However, these are estimated since the recycle to purge (discard) ratio could not be established. No allowance was made for mechanical losses.

TABLE 3
TOTAL ANNUAL WASTE DISPOSAL LOAD

"Water" Waste		Organic (Incinerator) Waste	
Maximum	Minimum	Maximum	Minimum
4,500,000 gals.	4,000,000 gals.	282,500 gals.	187,500 gals.

Note: These amounts can vary significantly depending upon the optional process changes initiated.

DISCUSSION

The success of this project depended primarily upon the precise analysis of the solvent streams and the evaluation of the experimental results. Vapor phase chromatography (VPC) was utilized to determine solvent composition; acidity was determined via alkaline titration. Additional determinations such as density, total solid and water content via Karl Fisher titration were made. The solvent streams were characterized as to color, odor, composition, water solubility, and reaction with caustic. Vapor-liquid data were gathered for all of the key components. Fractional distillations were run for synthetic mixtures of reagent grade solvents simulating the authentic process streams. The actual process streams were treated using extraction procedures, simple batch distillation (continuous flash vaporization), and fractional distillations under varying conditions via 25 and 40 tray Oldershaw columns (10). The composition of the batch distillation pot residues was evaluated and carefully characterized. Distillation, thermo-degradations, as well as heat of mixing and hydrolysis studies were performed.

Characterization and Composition of the Solvent Streams.

The Heptane stream (#1) is a fuming, amber colored, acidic solution, with the acidic fumes due to the low solubility of hydrogen chloride in the mixture. About 95-96 volume % of this solution boils at 40-98°C; the remaining 4-5 volume % is a dark red, high boiling, foul smelling residue. An actual process sample was distilled at 1 atm. and T_{vapor} of 39° to 98°C, and T_{pot} of 40° to 125°C; and the crude solvent stream #1, the distillate and the residues were analyzed. It should be noted that the daily variation in composition can be as much as ±5 volume % for any given component, although the composition in the feed holdup tank (FHT) would be fairly consistent. Experimental work done here was done on stream samples due to availability.

TABLE 4
COMPOSITION OF HEPTANE STREAM (#1)

Composition		Stream #1	Distillate	Residues
Chloroform,	Volume %	13.5	13.5	-
Heptane,	"	83.0	83.0	20
n-Propyl Alcohol,	"	1.2	1.2	-
Ethyl Chloride,	"	0.05-0.1	0.05-0.1	-
Propyl Chloride	"	0.05-0.1	0.05-0.1	-
Acidity-1,	Normal	0.081	0.023	1.8
Acidity-2,	"	0.017	0.00	0.155
Acidity-3,	"	-	-	0.43
Acidity, Total,	"	0.098	0.023	2.38
Phosphor*	Wt. %	-	-	6.99
Water (K.F.)	mg/ml	2.2	2.4	3.3
Total Solid	"	-	-	200
Density	g/ml	0.790	0.78	0.990

* As mixture.

The Methylene Chloride stream (#2) is pale yellow to amber, unpleasant in odor, and has noticeable acid fumes. The color variation is due to the high boiling process residues. The main components of this stream are methylene chloride and isopropyl alcohol. Stream composition varied greatly, although, on the average, the two solvents were nearly equal in volume ratio.

TABLE 5

COMPOSITION OF METHYLENE CHLORIDE STREAM (#2)

Methylene Chloride	40-60	Volume %
Isopropyl Alcohol	40-60	"
n-Heptane	0.5-1.5	"
Water (K.F.)	8-11	mg/ml
Acidity-1*	0.052	Normal
Acidity-2*	0.070	"
pH	3.0	
Density	0.83 to 1.05	g/ml
Total Solid*	17	g/liter

* Due to dissolved organic residues from the process.

The Butyl Acetate stream (#3) is a reddish, foul smelling mixture. The main component of this stream is butyl acetate, along with some heptane and a high boiling acidic residue

similar to that in stream #1. The composition variation is also similar to that of stream #1.

TABLE 6
COMPOSITION OF BUTYL ACETATE STREAM (#3)

Butyl Acetate	87	Volume %
Heptane	8.0	"
Residues	3.0	"
Water (K.F.)	1	"
Acidity-1	0.47	Normal
Acidity-2	0.23	"
Acidity-3	0.39	"
Density	0.87	g/ml

The presence of each solvent was proven by the injection of reagent grade solvents alone and as mixtures, and by spiking actual process streams with pure solvents. Vapor phase chromatography was found to be unsatisfactory for water determination at low concentrations. Therefore, Karl-Fisher (K.F.) titration was employed instead. The vapor phase chromatography conditions presented here were the optimum ones for good separation and were found as a result of many trials.

RECOVERY PROCESS DETAILS

The process was developed based on laboratory generated data using the principle of separate solvent streams. Specific data is included in the Appendix.

Heptane Stream (#1)

The recovery process consists of a batch distillation followed by an aqueous caustic neutralization/extraction of the distillate via line mixing. Pure solvents are obtained via fractional distillation of the batch distillate. Pot residues of the batch distillation are hydrolyzed by caustic and the mixture is forwarded to the waste disposal pond.

The Heptane stream (#1) is fed to the batch distillation vessel and distilled at 1 atm. until the pot temperature reaches 100°C. Since the actual content of the high boiling residues varies between 2-4 volume %, the pot residue from the batch distillation is quite small. In order to increase the distillation efficiency and reduce batch down-time, several batches are distilled on top of the previous pot residue. Based on laboratory experiments, approximately five consecutive batch distillations can be completed before removing the accumulated residue. This results in a combined batch residue of 2000 - 2500 gals. out of a ca. 50,000 gal. feed, which was found to be a practical feed to residue volume to work with. During the last (fifth) distillation

the pot (liquid) temperature is allowed to reach 105°C in order to minimize the amount of heptane left behind.

The hot batch distillation residues are forwarded to the caustic neutralization still containing one half volume of 25% aqueous sodium hydroxide at reflux temperature (85-95°C, depending on composition). The rate of addition is controlled by the boil-up rate. This mode of hydrolysis was chosen for the built-in safeguard provided by the rapid hydrolysis at reflux temperature, and removal of heat of reaction (40 BTU/lb of mixture) by the reflux condenser. The cycle time depends on batch size, but is about 1-1.5 hours. The hydrolysis mixture is forwarded to the waste neutralizing pond for final disposal. Final pH must be above 7.0 in order to ensure complete hydrolysis. This operation is similar to the usual acid-base reaction and is perfectly safe as long as good mixing is assured.

The purpose of the extraction/neutralization of the batch still's distillate is two-fold, to remove dissolved hydrochloric acid and avoid a corrosion problem, and to eliminate alcohols to ensure efficient fractional distillation. One volume (per volume distillate) of dilute base removes 90-95% of the alcohols (n-propyl alcohol and ethyl alcohol) present in the distillate. Experimental results indicate that the extraction/neutralization achieves the desired alcohol reduction/removal. The n-propyl alcohol content of the Heptane

Stream (#1) is 1.35%. The batch distillate, neutralized with 1/10 volume 5% aqueous sodium bicarbonate contains 0.9 volume % n-propyl alcohol. Extraction of the batch distillate with 1 volume of water reduces the n-propyl alcohol to 0.08 volume %.

For a batch process two obvious alternatives are available. The first is a single extraction of each distillate with one volume of 1 % sodium bicarbonate. Here, large acid-resistant (glass-lined) receivers would be needed plus provision for good mixing. The second alternative would be the application of a line-mixer. The preferred choice would be the line-mixer, and the receiver is used as a semi-continuous separator. A four volume ratio of 0.5% aqueous sodium bicarbonate to one volume distillate is introduced into a line-mixer. The two phases are allowed to separate in a carbon steel receiver. Removal of the organic and aqueous phases starts after the volume is over the half-way mark. Semi-continuous removal is regulated by a density controller, or one based on dielectric constant. The organic phase is forwarded to a carbon steel storage tank (ST). Since perfect cut of layers cannot be made easily in a routine operation, some of the dilute base is left with the organic layer. This prevents the corrosion of the storage tank which can occur during storage of chlorinated solvents (3). The accumulated aqueous layer is removed periodically. The accumulated mixed solvent stream in the batch distillate

storage tank (ST) is processed via a fractional distillation column (DC) to obtain the pure solvents. The fractional distillation column design should be based on data presented in the Appendix.

During fractional distillation of the Heptane stream (#1) batch distillate a "tight" fore-cut is collected up to 59.5°C vapor temperature. This amounts to about 0.5-0.8 volume % and is discarded via the waste disposal. The second cut is collected from 59.5°C to 60.5°C vapor temperature and goes to the mixed cut receiver; this cut is about 3 volume %. The chloroform cut is collected from 60.5° to 62°C (99-99.5% purity), with an accumulation of about 15 volume %. The fourth fraction is a mixed cut collected from 62° to 96°C vapor temperature (depending upon the purity of the heptane) and amounts to about 5 volume %, which is sent to the mixed cut tank. The n-propyl alcohol content of the mixed cut is extracted with 1 to 4 volume % water in the receiver, or via a line-mixer similar to the one discussed above. The organic phase consisting of chloroform and heptane is recycled to the distillate storage tank for subsequent rerun. The heptane cut is collected from 96° to 98°C vapor temperature with an average purity of 99%. The pot residue is nearly pure heptane and is left as heel for the following fractionation.

As can be seen in Table 19, the vapor temperature change is very small during the pure chloroform fraction cut. For

example, at 60.4°C the chloroform purity is 97.5%; at 60.5°C, 99%. One tenth of a degree temperature change seems much too small to rely upon. It should be noted that this is within the effect of a barometric pressure change. Therefore, along with temperature recording, the use of a continuous vapor phase chromatography (VPC) analyzer is recommended. Fraction cuts are to be made based upon the chloroform and heptane content. A composition plot such as Table 19 would allow a perfectly reliable operation. The use of VPC also serves as a built-in in-process quality control. The often sounded disadvantage of VPC, namely, the relatively high maintenance cost, 4-5000 \$/year, could easily be offset by the labor saving factor of in-process quality control and the elimination of storage tank contamination caused by unchecked production mishaps. Instruments such as Temperature or Differential Vapor Pressure Controllers (5) would need backup analysis as a production safeguard.

Methylene Chloride Stream (#2)

The residues present in the methylene chloride, isopropyl alcohol and heptane mixture are all organic. Since acidity is due to dissolved hydrogen chloride only, and because of increased solvent polarity and lower fractionation temperatures, the recovery process is somewhat simpler than that of stream #1.

A simple atmospheric batch distillation is run up to a pot temperature of 85°C. The distillate is neutralized by the addition of solid sodium bicarbonate (addition of water would cause azeotropes) to the distillate receiver at a rate of 5 lbs. sodium bicarbonate per 1,000 gals. of distillate. The distillate is forwarded to a carbon steel storage tank ready for batch fractional distillation. After five batch distillations, the pot residue is hydrolyzed with 25% caustic. Pure methylene chloride and isopropyl alcohol are separated via fractional distillation.

A single methylene chloride fraction is collected at a vapor temperature of 39-41°C. The average purity of this cut is above 99.5%. Trace amounts of ethyl and n-propyl chlorides present are compatible with most cases of methylene chloride usage. In case of alkyl chlorides buildup, a small fore-cut purge is incorporated. The mixed cuts rich in methylene chloride are collected at 41° to 76°C vapor temperature. Cut-7 and cut-8 in Table 22 are recycled to the storage tank (ST). The heptane rich mixed cut, collected at 76° to 80°C (-9 and -10 in Table 22) is extracted twice with one volume of water which removes the isopropyl alcohol content. The heptane layer is then forwarded to stream #1 distillate storage tank (ST) and will be recovered as part of the Heptane stream (#1) process operation. The last cut is over 99% pure isopropyl alcohol contaminated with small amounts of heptane which can be tolerated due to its inertness.

Methylene Chloride stream (#2) can be fractionated directly without simple batch distillation. However, upon heating the residues decompose/polymerize and render an unpleasant sulfurous odor to the distillate, and generate impurities. Therefore, removing the residues ensures a neater fractionation and higher yields of methylene chloride and isopropyl alcohol. Aside from this, the recovery process is designed in such a way that the same recovery equipment is suitable for all three streams.

Butyl Acetate Stream (#3)

The recovery of this stream is similar to that of streams #1 and #2. A simple batch distillation is followed by neutralization of the distillate with solid sodium carbonate. The batch distillation pot residues are hydrolyzed with caustic. Separation of butyl acetate and heptane is made via fractional distillation which is maintained until the heptane content in the pot falls below two percent. The distillate is forwarded to waste disposal and the pot contents are sent to the butyl acetate storage tank. Note that the heptane is totally inert in the butyl acetate. The level tolerated should be determined by the particular effect heptane has upon the solubility, or other characteristics involved. In this specific application, a heptane level of up to 5% is acceptable.

CONCLUSION

The data accumulated for this solvent recovery process study clearly demonstrates that the principle of industrial recycling can be rewarding not only in terms of environmental benefits, but also as a highly profitable industrial proposition. The sole objective of this study has been to gather data for process design. Attention has not been given to such topics as sizing of equipment, the storage of process streams, the materials of construction, the timing of blocked operations etc., which were beyond the scope of this study.

APPENDIX

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Assays and Physical Data For Solvents.....	30
Vapor-Liquid Equilibrium Data.....	32
Solvent Recovery Laboratory Data Generation.....	48
Waste Disposal Load.....	67

ASSAYS AND PHYSICAL DATA FOR SOLVENTS

Assays for Solvents via Vapor Phase Chromatography (VPC)

Quality of solvents, as well as solvent composition were determined throughout the study using VPC. A brief description of the instrument and VPC data are given below.

Instrument

Varian Aerograph Model 200 with thermal conductivity detector, Speedomax H recorder and a Hewlett-Packard electronic integrator Model 3370A. Helium is the carrier gas.

Column

Good separation of most of the solvents was achieved on a 6' x $\frac{1}{4}$ " s.s. coil packed with SE-30 packing. The analysis of water, methylene chloride and isopropyl alcohol, however, required a 6' x $\frac{1}{4}$ " s.s. column packed with Porapak-N.

Tables 7 and 8 were prepared in order to present the pertinent physical and VPC data.

Notes to Tables 7 and 8

Purity refers to the commercially available "Reagent" or "Spectrograde" solvents.

a- Commercial chloroform usually contains about 0.75% alcohol as stabilizer. If not removed, even this small amount of alcohol lowers the recovery efficiency.

p- Pentene stabilized (150 ppm) chloroform, which is also available, is more desirable in a number of cases.

TABLE 7
PERTINENT PHYSICAL DATA FOR SOLVENTS

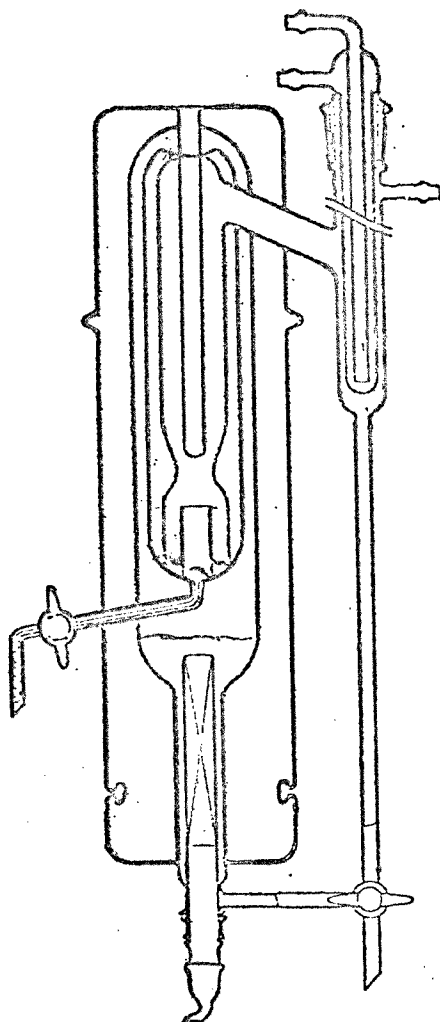
NAME	FORMULA	NW	BP °C	Density g/ml 20°	n_D^{20}	Purity of reagent grade (via VFC) %	Cost \$/gal. (11)
Methylene Chloride	CH ₂ Cl ₂	84.94	40-41	1.3255	1.4244	99.94	1.30
Chloroform [®] (11)	CHCl ₃	119.39	61-62	1.484	1.4476	99.30 99.93	1.73
n-Heptane	C ₇ H ₁₆	100.20	98.4	0.684	1.3855 ²⁵	99.80	0.20
n-Fropyl Alcohol	C ₃ H ₈ O	60.09	97-98	0.804	1.386	99.85	
Isopropyl Alcohol	C ₃ H ₈ O	60.09	82.5	0.78505	1.37723	99.8	
n-Butyl Acetate	C ₆ H ₁₂ O ₂	116.16	125-126	0.8826	1.3951	99.83	0.88
Ethyl Chloride	C ₂ H ₅ Cl	64.52	12.3	0.9214 ⁰	-	-	
Propyl Chloride	C ₃ H ₇ Cl	78.54	46-47	0.890	1.3886	--	
Water	H ₂ O	18.016	100	0.99998	1.33300	-	
Hydrogen Chloride	HCl	36.47	-85	1.268	1.256 _L	-	

TABLE 8
VAPOR PHASE CHROMATOGRAPHY DATA FOR SOLVENT ANALYSIS

Solvent	Retention Time Unit	Temperature °C			Purity by Area (%)	He	Injection ul	Column
		Column	Injection	Detection				
Air	68	85	250	250	-	18/60	-	SE-30
Methyl Alcohol	87	"	"	"	99.90	"	5	"
Water	103	"	"	"	"	"	"	"
Ethyl Alcohol	118	"	"	"	99.80	"	"	"
Isopropyl Alcohol	145	"	"	"	99.85	"	"	"
Methylene Chloride	170	"	"	"	99.96	"	"	"
n-Fropyl Alcohol	215	"	"	"	99.80	"	"	"
Chloroform	285	"	"	"	99.30	"	"	"
n-Heptane	545	"	"	"	99.88	"	"	"
n-Butyl Acetate	1150	"	"	"	99.64	"	"	"
Water	210	175	"	"		40/60	"	Porapak-N
Methylene Chloride	985	"	"	"		"	"	"
Isopropyl Alcohol	1500	"	"	"		"	"	"
Ethyl Chloride	200	200	"	"		"	"	"
Ethyl Alcohol	240	"	"	"		"	"	"
n-Propyl Chloride	380	"	"	"		"	"	"
n-Propyl Alcohol	465	"	"	"		"	"	"
Chloroform	550	"	"	"		"	"	"

VAPOR-LIQUID EQUILIBRIUM DATA

Laboratory vapor-liquid equilibrium determinations were



carried out using Equilibrium Still Model MES-100, designed by H.S. Myers of C.F. Braun & Co. of Whittier, California. The technique followed is described in detail in the operating instructions supplied by the manufacturer. Equilibration time of 2-3 hours was allowed and two points were collected a day. Whenever an azeotrope or "pinch" was observed, a number of points were measured repeatedly.

FIGURE 1

EQUILIBRIUM STILL-MODEL MES-100

Analysis Of Data

Measurements via refractive index and vapor phase chromatography (VPC) were tried. VPC was found to be more reliable and generally applicable for the solvent systems encountered here. Synthetic solvent mixtures were prepared,

VPC responses determined and the results plotted and used as standards. Mixtures of known composition were analyzed via the standard curves. This technique was compared with spiking with pure solvents and by the use of internal standards. Overall, the standard curve technique was found to be more satisfactory.

TABLE 9.

EXPERIMENTAL VAPOR-LIQUID EQUILIBRIUM DATA

<u>Binary Solvent Pairs</u>	<u>No. of Points Measured</u>	<u>Azeotrope</u>
Chloroform n-Propyl Alcohol	15	At both ends
Chloroform Heptane	18	-
n-Propyl Alcohol Heptane	8	Nearly 50% minimum
Isopropyl Alcohol Heptane	6	64% minimum
Methylene Chloride Heptane	12	Pinch at >98%
Methylene Chloride Isopropyl Alcohol	13	Slight pinch at >98%
Heptane Butyl Acetate	8	-
<u>Ternary</u>		
Isopropyl Alcohol Methylene Chloride Heptane	5	-

TABLE 10
BINARY AZEOTROPES: LITERATURE VALUES

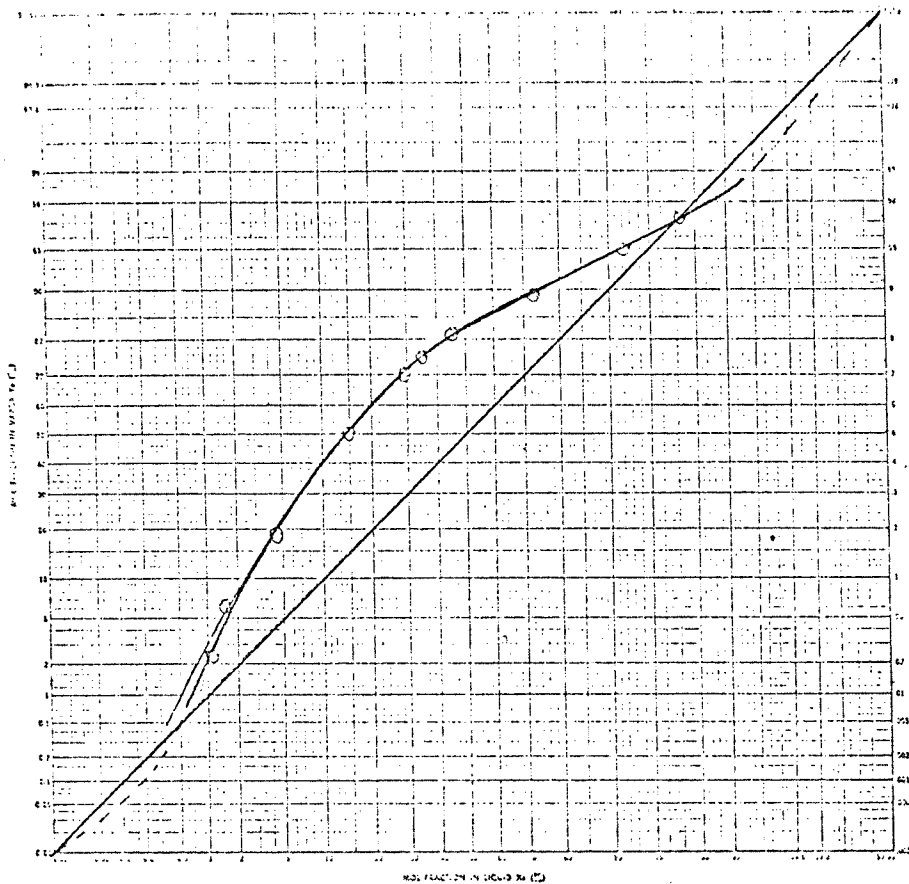
Solvents	B.P.	T °C	Azeotrope Composition %		Reference Number
			A	B	
<u>A Methylene Chloride</u>	<u>40.1</u>				
Water	100	38.8	99.0	1.0	4
Ethyl Alcohol	78.5	39.85	95	5	4
Isopropyl Alcohol	82.4	None	-	-	2-I
<u>A Chloroform</u>	<u>61.2</u>				
Water	100	56.3	97	3	4
Ethyl Alcohol	78.5	59.4	93	7	4
Isopropyl Alcohol	82.4	None	-	-	2-I
n-Propyl Alcohol	97.2	None	-	-	2-I
Butyl Acetate	126.2	None	-	-	2-III
<u>A Isopropyl Alcohol</u>	<u>82.4</u>				
Water	100	80.4	87.8	12.2	4
Heptane	98.4*	76.4	50.5	49.5	2-I & III
<u>A Propyl Alcohol</u>	<u>97.2</u>				
Heptane	98.45	87.5	36	64	2-III
<u>A Heptane</u>	<u>98.4</u>				
Water	100	79.2	87.1	12.9	4
Ethyl Alcohol	78.5	72	52	48	4
<u>A Butyl Acetate</u>	<u>126</u>				
Water	100	90.7	72.9	27.1	4
Heptane	98.4	None	-	-	9

* Error in reference

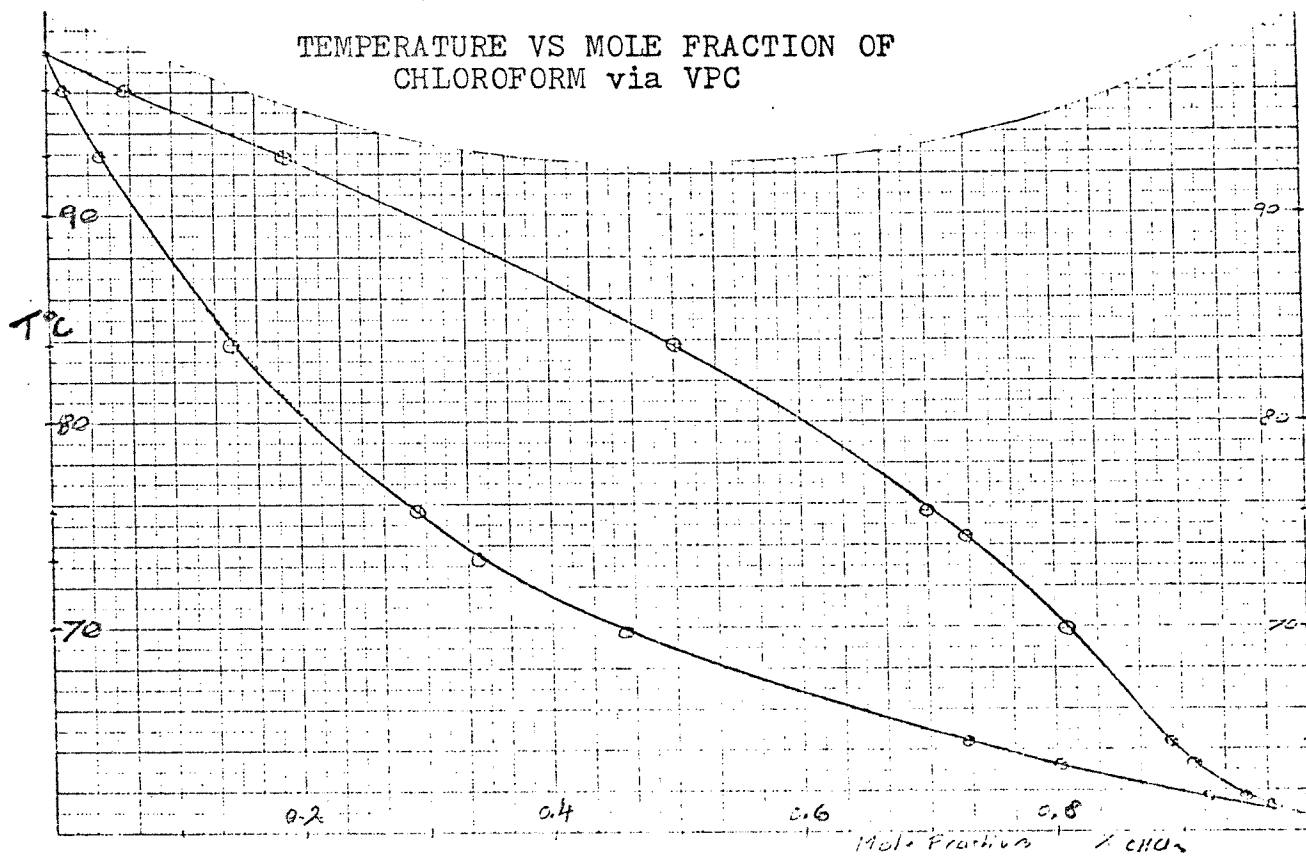
Graphical Presentation of Experimental Vapor-Liquid Equilibrium Data.

Mole fractions in vapor $Y(\%)$ vs. mole fractions in liquid $X(\%)$ are illustrated via the use of the "Diagram for McCabe-Thiele graphical method for determining theoretical in distillation columns." Temperature vs. mole fraction of the lower boiling components of the binary pairs were plotted on common graph papers. (See Figures 2 through 12).

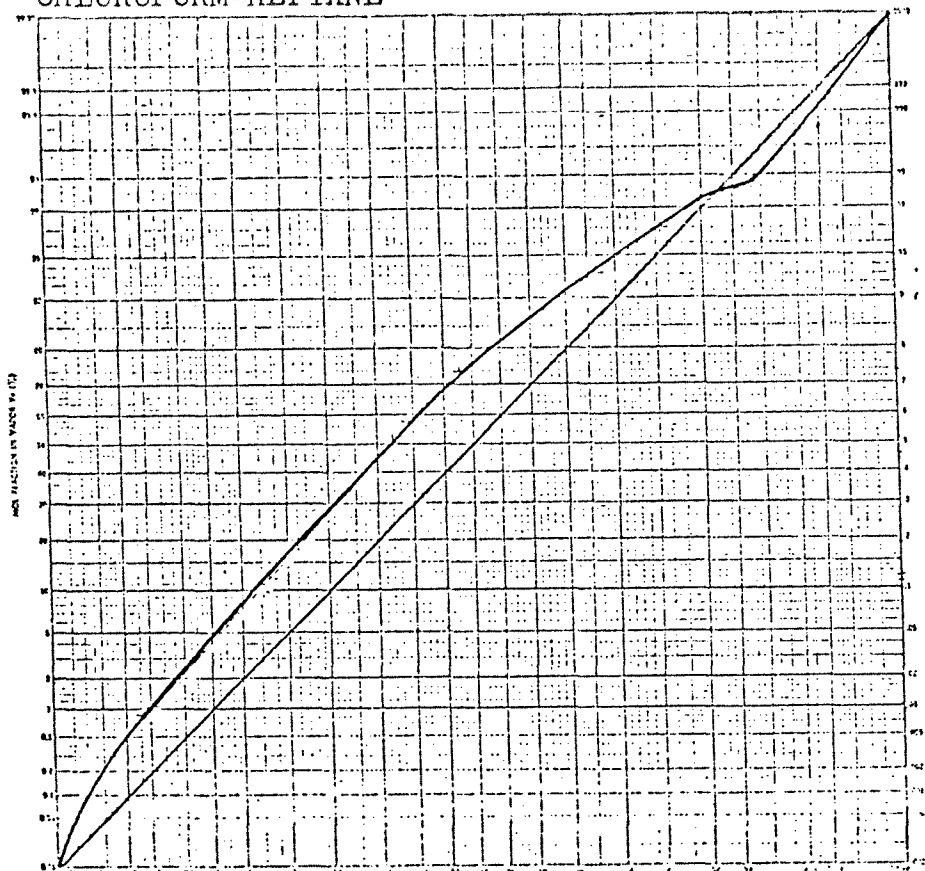
VAPOR-LIQUID EQUILIBRIUM (X-Y) DATA FOR
CHLOROFORM- n-PROPYL ALCOHOL



T C	Chloroform Mole Fraction	
	Liquid(X)	Vapor(Y)
60.8	0.990	0.9823
61.0	0.981	0.978
61.3	0.971	0.972
61.7	0.922	0.95
63.3	0.803	0.911
64.4	0.732	0.892
69.9	0.457	0.812
73.34	0.343	0.752
75.65	0.296	0.705
83.78	0.1476	0.506
92.92	0.0439	0.190
96.12	0.01564	0.0632
97.2	0.0117	0.0236
97.62	0.00864	0.0128
97.8	0.0084	0.0122



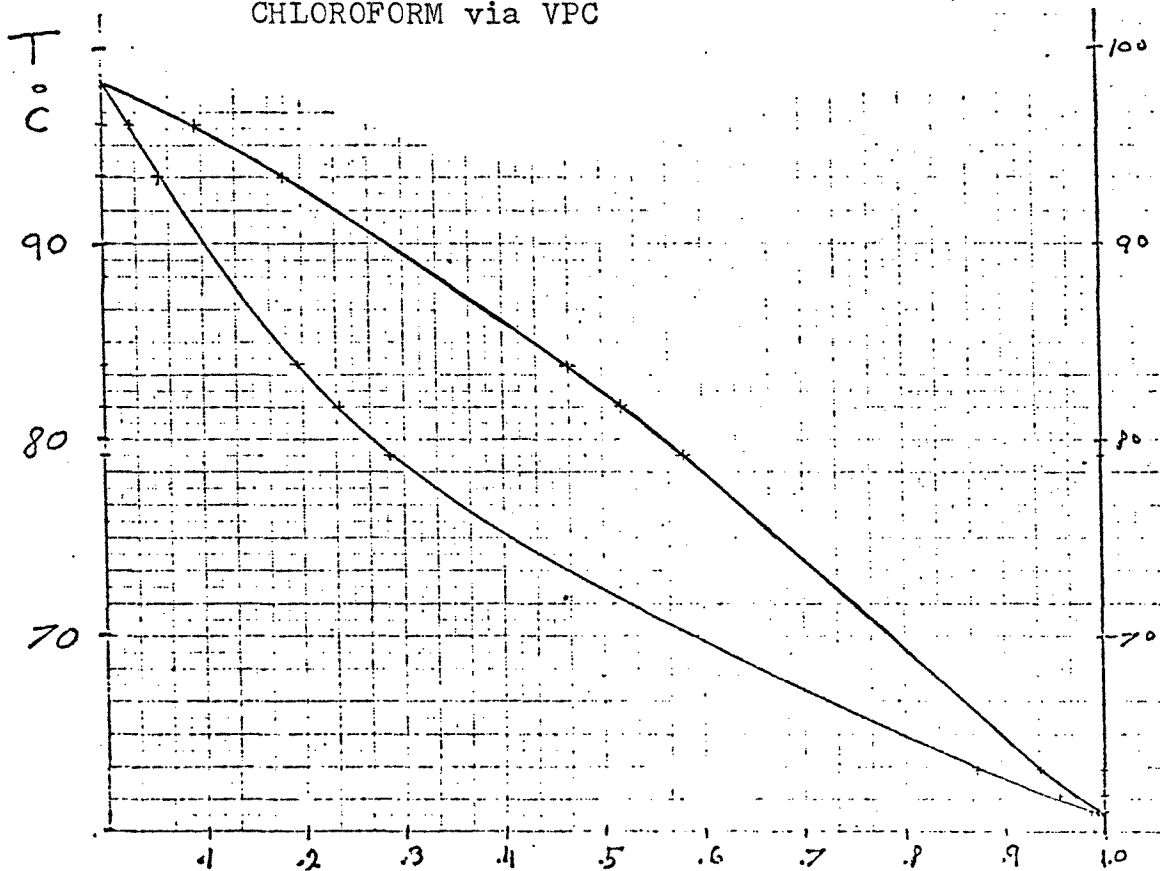
VAPOR-LIQUID EQUILIBRIUM (X-Y) DATA FOR CHLOROFORM-HEPTANE



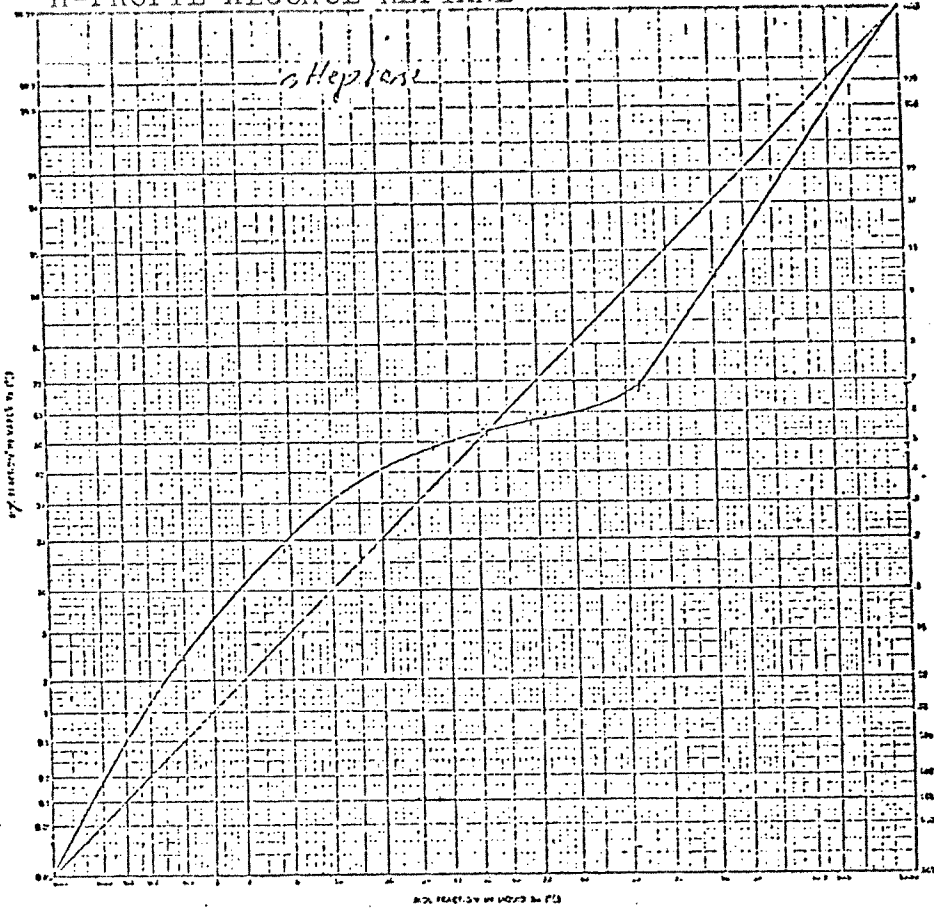
T C	Chloroform Mole Fractions	
	Liquid(X)	Vapor(Y)
61.0	0.991	0.987
61.0	0.994	0.989
61.0	0.978	0.982
61.1	0.994	0.998
61.2	0.9915	0.988
61.2	0.987	0.987
61.8	0.954	0.970
63.2	0.868	0.932
72.7	0.458	0.738
79.2	0.284	0.578
81.8	0.240	0.514
83.8	0.200	0.461
93.4	0.061	0.187
95.7	0.036	0.120
96.0	0.032	0.110
96.1	0.031	0.097
98.5	0.0022	0.0105
98.58	0.0016	0.0088

Aer. 200
SE-30 20%
T=#3.0 88 C

TEMPERATURE VS MOLE FRACTION OF CHLOROFORM via VPC

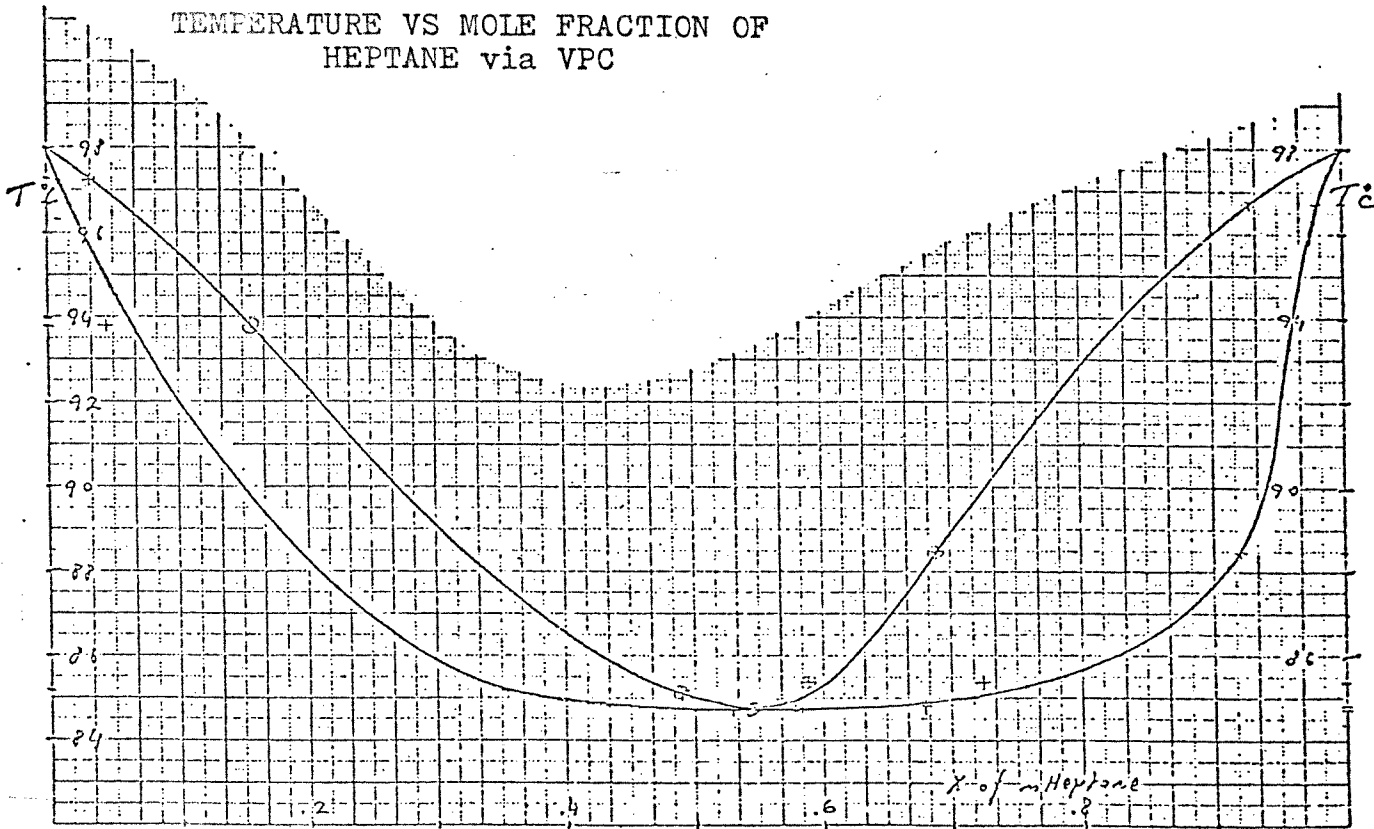


VAPOR-LIQUID EQUILIBRIUM (X-Y) DATA FOR
n-PROPYL ALCOHOL-HEPTANE

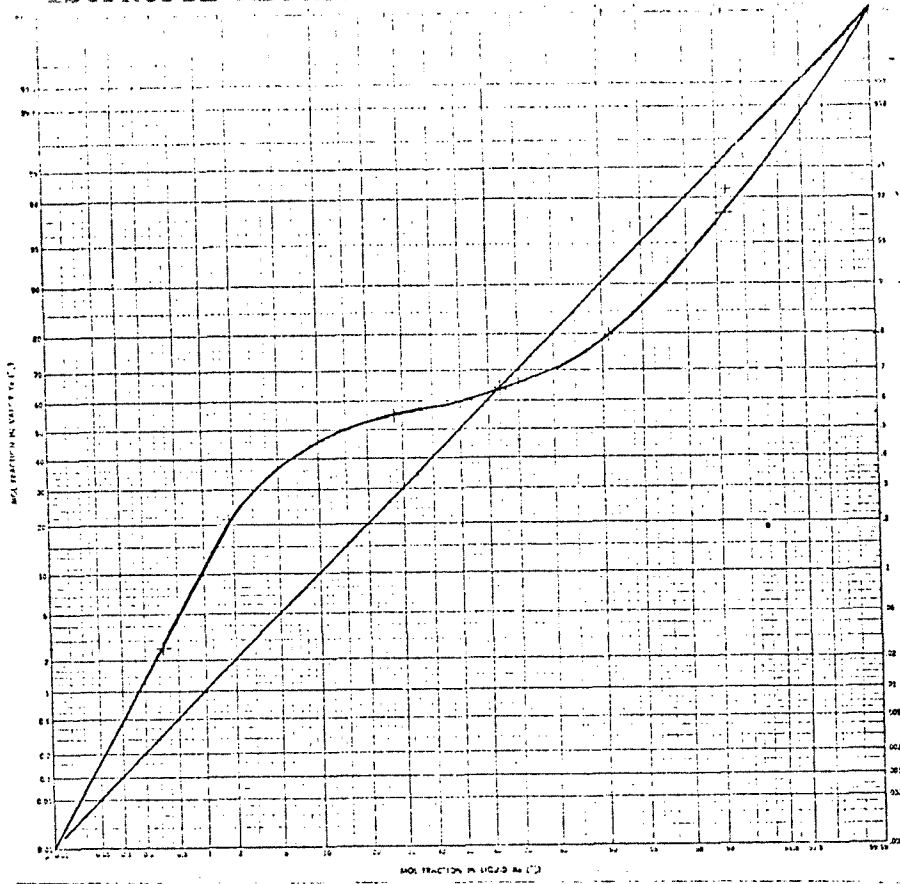


T C	Heptane Mole Fraction	
	Liquid (X)	Vapor (Y)
96.70	0.982	0.927
88.48	0.920	0.690
85.36	0.724	0.587
84.80	0.680	0.545
84.70	0.530	0.490
85.16	0.355	0.19
93.78	0.047	0.033

TEMPERATURE VS MOLE FRACTION OF
HEPTANE via VPC

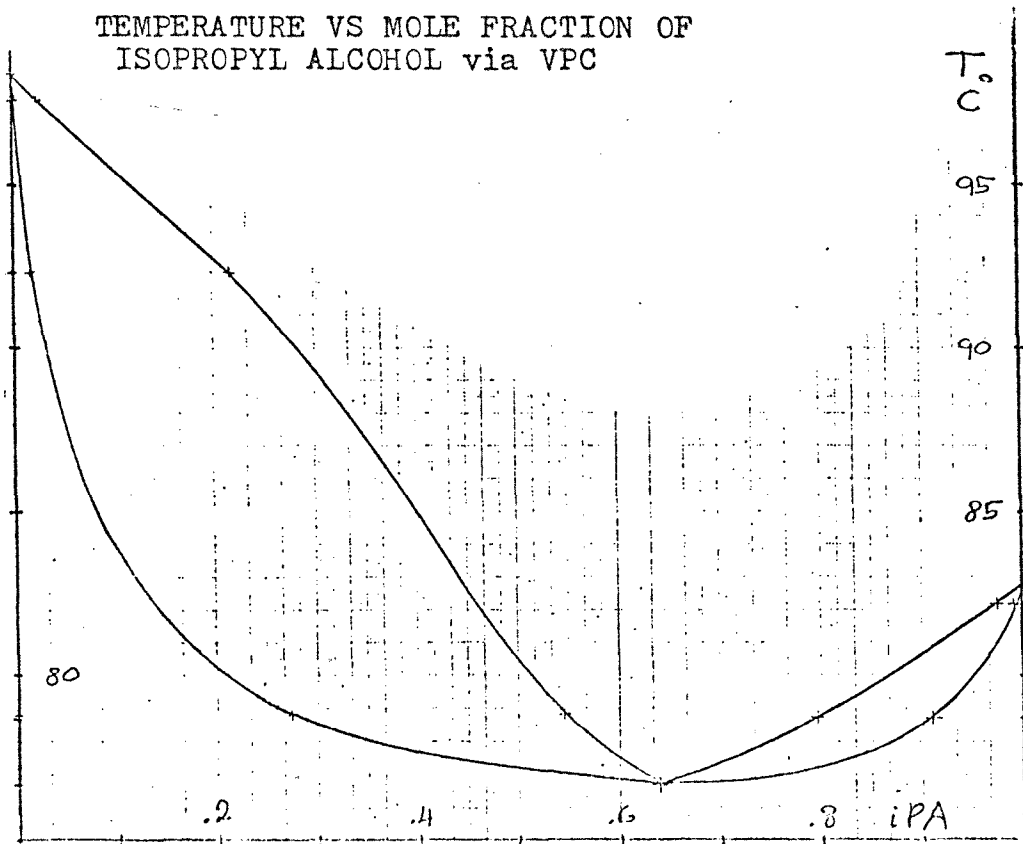


VAPOR-LIQUID EQUILIBRIUM (X-Y) DATA FOR ISOPROPYL ALCOHOL-HEPTANE



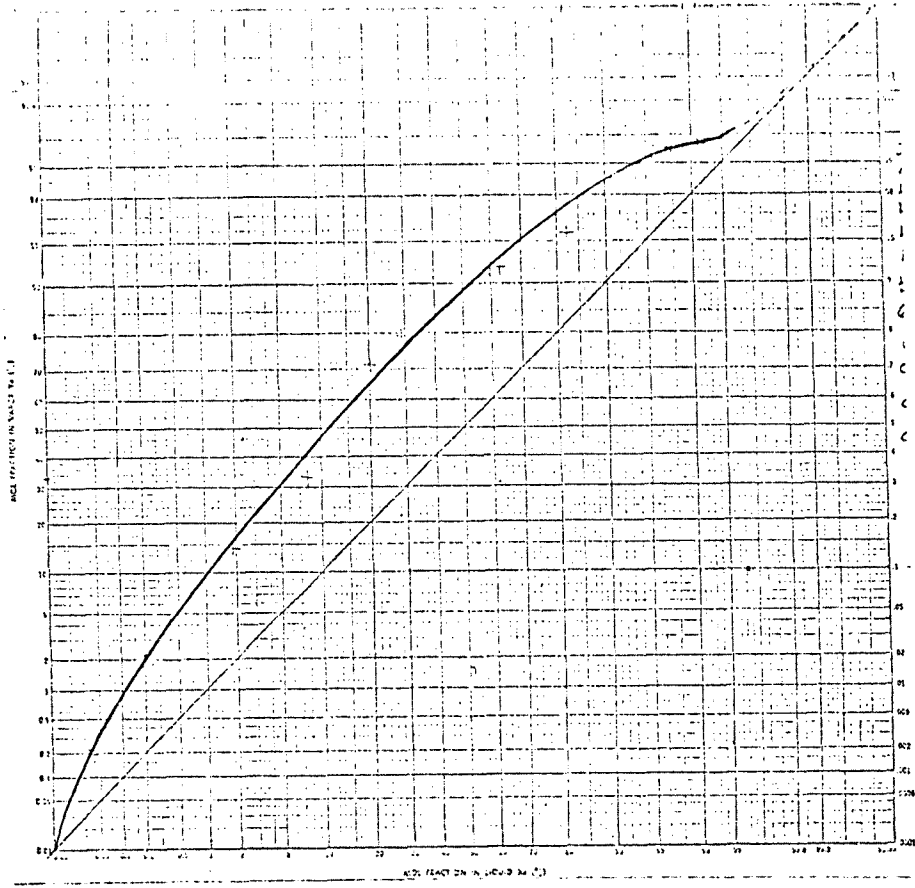
T C	Isopropyl Alcohol Mole fraction	
	Liquid (X)	Vapor (Y)
97.6	0.0033	0.0275
92.3	0.018	0.218
78.8	0.274	0.546
76.7	0.640	0.640
78.7	0.910	0.798
82.2	0.992	0.983
82.2	0.992	0.972

TEMPERATURE VS MOLE FRACTION OF ISOPROPYL ALCOHOL via VPC



T °C	X _{iPA}	Y _{iPA}
97.6	0.0033	0.0275
92.3	0.018	0.2176
78.8	0.274	0.546
76.7	0.640	0.640
78.7	0.910	0.7975
82.15	0.992	0.983
82.15	0.992	0.9715

VAPOR-LIQUID EQUILIBRIUM (X-Y) DATA FOR METHYLENE CHLORIDE-HEPTANE



T °C	Methylene Chloride Mole Fraction	
	Liquid (X)	Vapor (Y)
39.8	0.983	0.9933
40.3	0.982	0.9930
40.5	0.978	0.9915
40.5	0.970	0.9930
42.8	0.824	0.956
46.1	0.618	0.921
59.2	0.290	0.793
65.8	0.205	0.715
85.6	0.058	0.333
92.5	0.0185	0.142
97.8	0.00198	0.0222
98.58	0.000143	0.00214

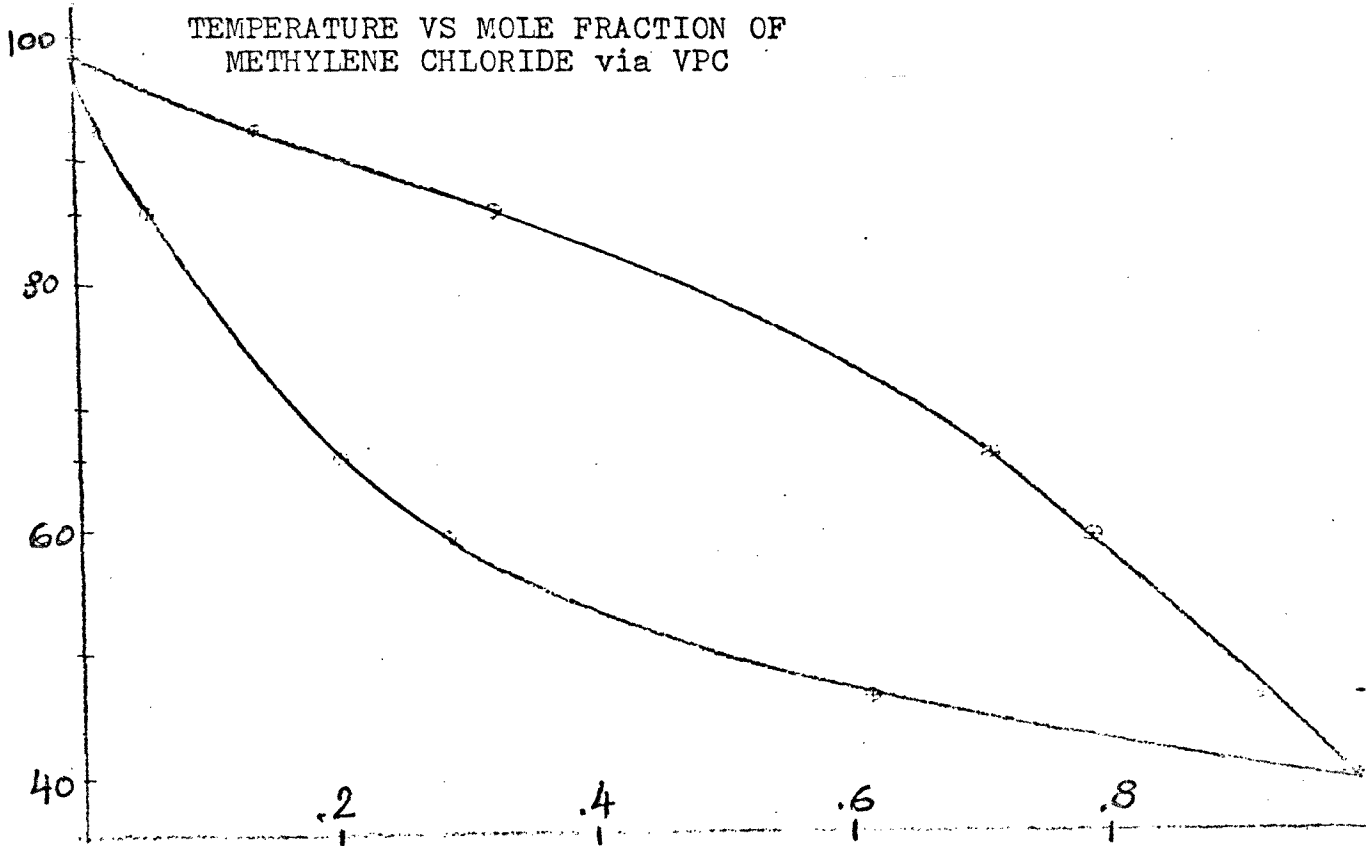
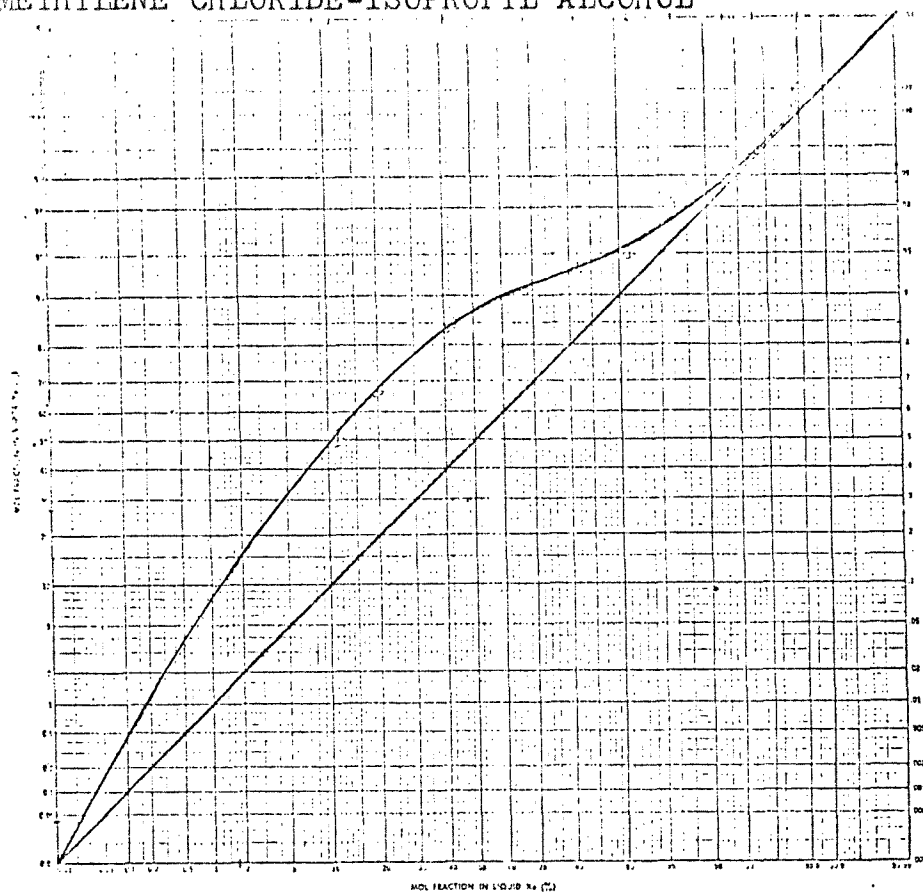


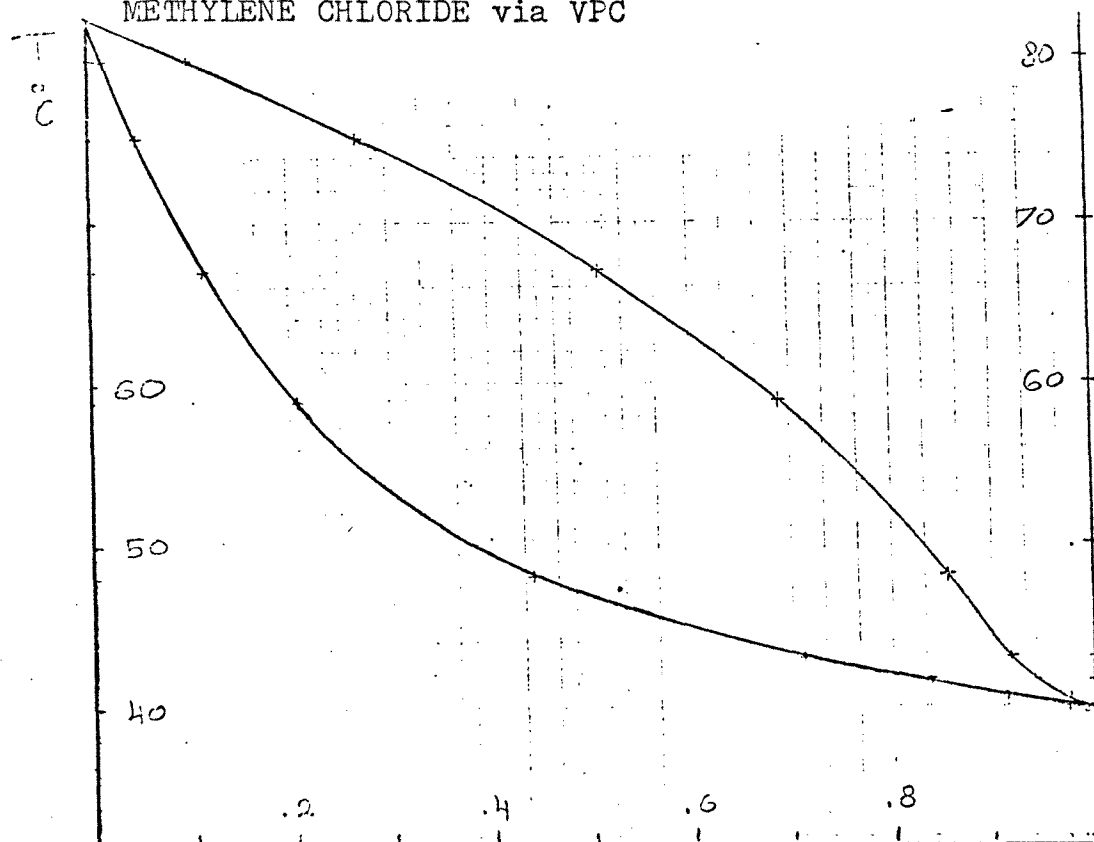
FIGURE 7

VAPOR-LIQUID EQUILIBRIUM (X-Y) DATA FOR
METHYLENE CHLORIDE-ISOPROPYL ALCOHOL

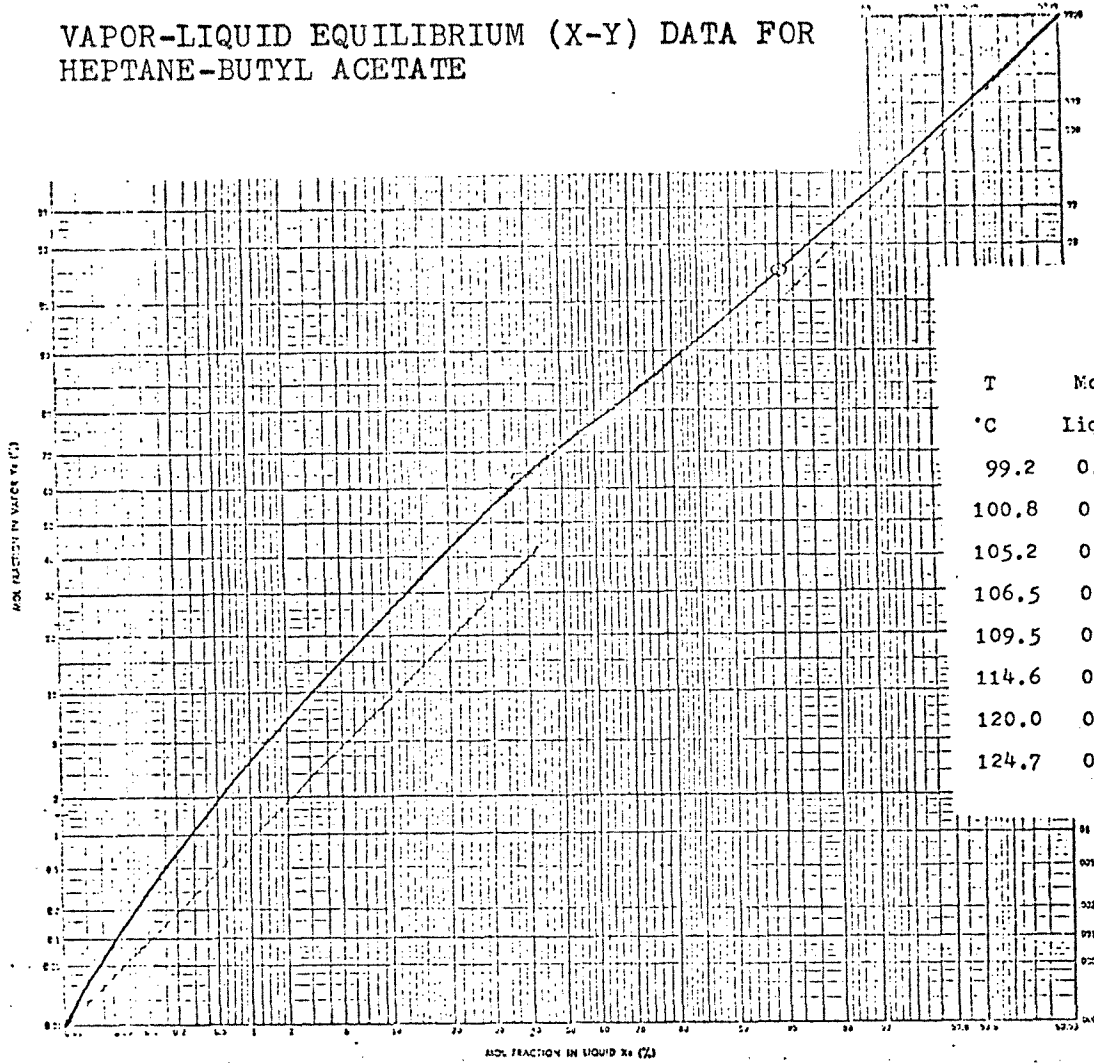


T °C	Methylene Chloride Mole Fraction	
	Liquid (X)	Vapor (Y)
39.8	0.989	0.992
40.0	0.962	0.982
40.25	0.998	0.999
40.3	0.9935	0.994
40.4	0.987	0.988
40.4	0.990	0.990
40.6	0.915	0.950
41.6	0.821	0.937
43.0	0.684	0.910
48.0	0.418	0.844
58.9	0.200	0.663
67.0	0.114	0.503
80.0	0.170	0.105

TEMPERATURE VS MOLE FRACTION OF
METHYLENE CHLORIDE via VPC



VAPOR-LIQUID EQUILIBRIUM (X-Y) DATA FOR
HEPTANE-BUTYL ACETATE



T °C	Heptane Mole Fraction	
	Liquid	Vapor
99.2	0.950	0.969
100.8	0.831	0.899
105.2	0.570	0.750
106.5	0.480	0.701
109.5	0.381	0.622
114.6	0.220	0.451
120.0	0.091	0.230
124.7	0.015	0.050

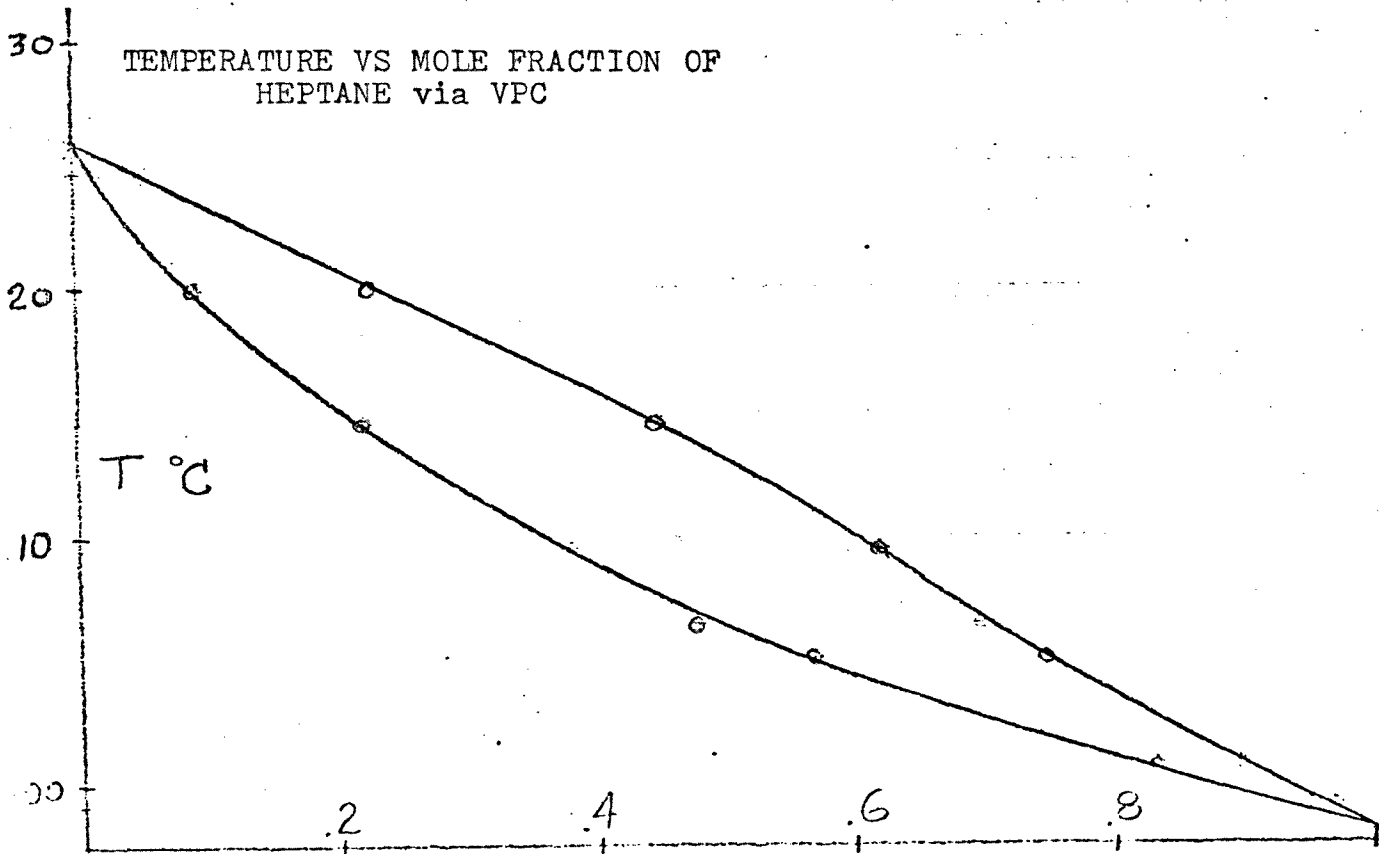
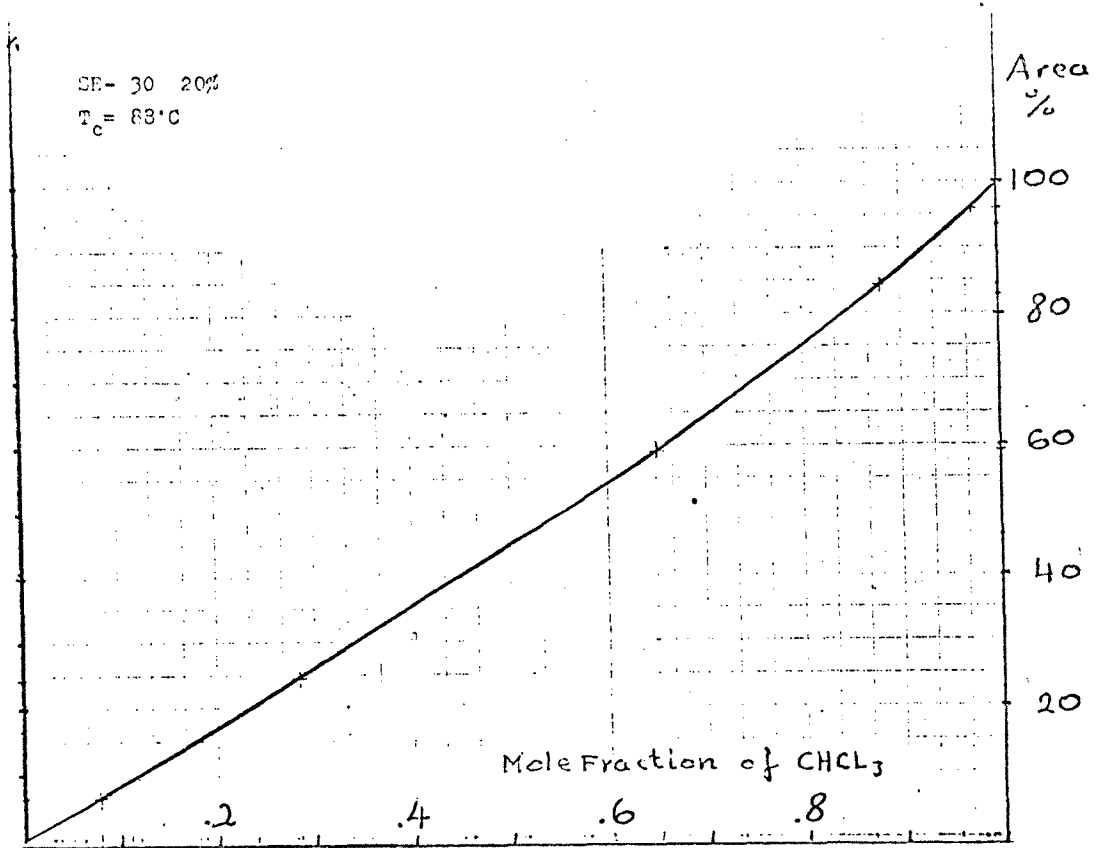


TABLE 11
VAPOR-LIQUID EQUILIBRIUM DATA FOR
ISOPROPYL ALCOHOL-METHYLENE CHLORIDE-HEPTANE

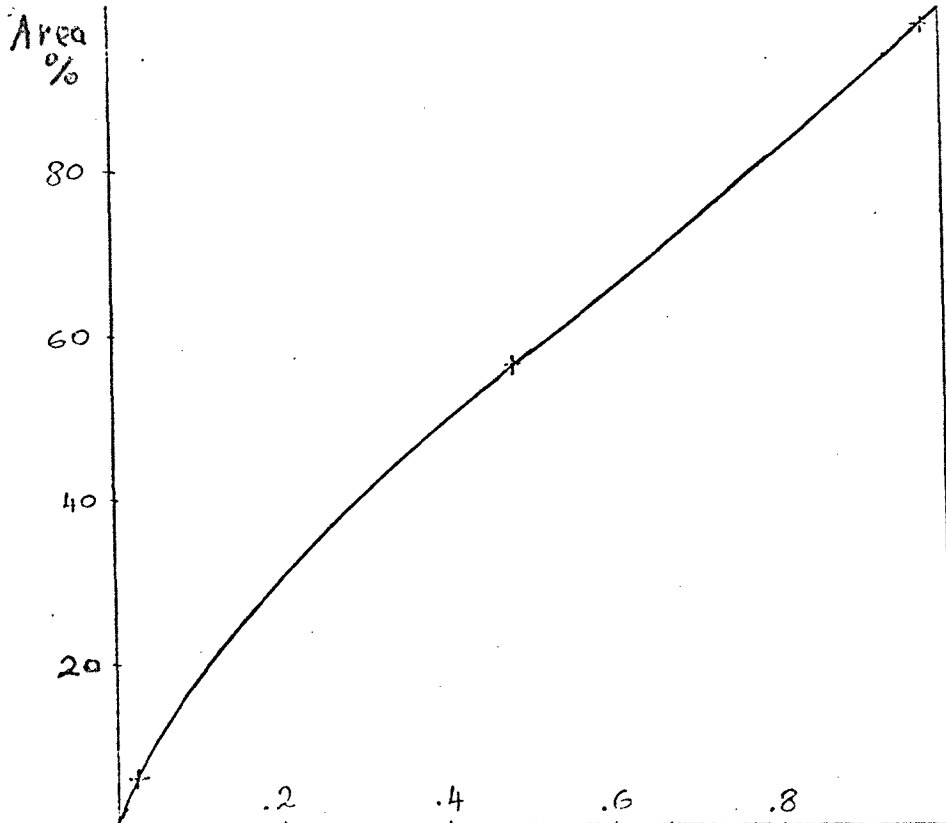
T C°	Liquid			Vapor		
	Isopropyl Alcohol	Methylene Chloride	Heptane	Isopropyl Alcohol	Methylene Chloride	Heptane
47.8	0.5244	0.4735	0.00206	0.1367	0.8621	0.00124
48.5	0.5207	0.4530	0.0261	0.1414	0.8417	0.01694
50.0	0.5413	0.4071	0.0516	0.1563	0.8100	0.03375
54.0	0.4715	0.3281	0.2003	0.18315	0.7136	0.0132
55.7	0.4288	0.2930	0.2781	0.1963	0.6726	0.13103

FIGURE 9

STANDARD VPC CURVE FOR SYNTHETIC MIXTURE OF
CHLOROFORM-HEPTANE



STANDARD VPC CURVE FOR SYNTHETIC MIXTURE OF
n-PROPYL ALCOHOL-CHLOROFORM

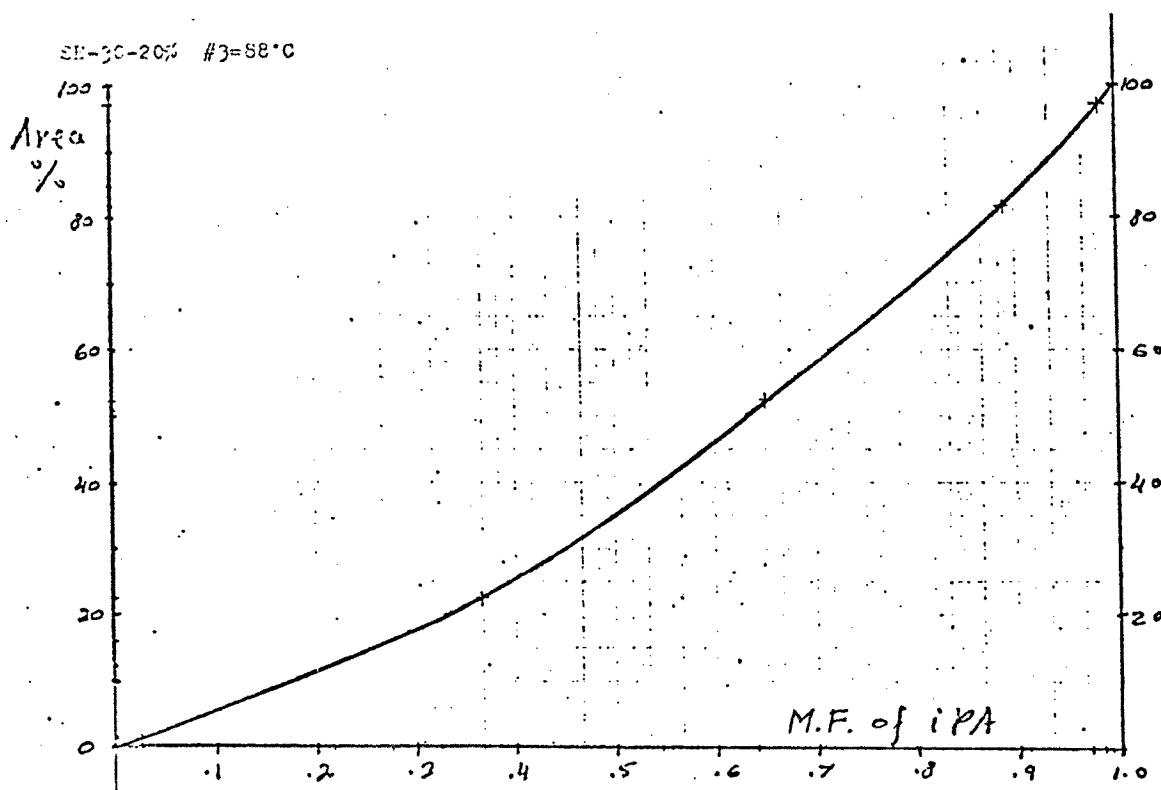


n-Propyl Alcohol		Chloroform	
A%	X	A%	X
93.923	0.9781	5.98	0.0219
43.444	0.5176	56.31	0.4824
2.00	0.0255	97.39	0.9745

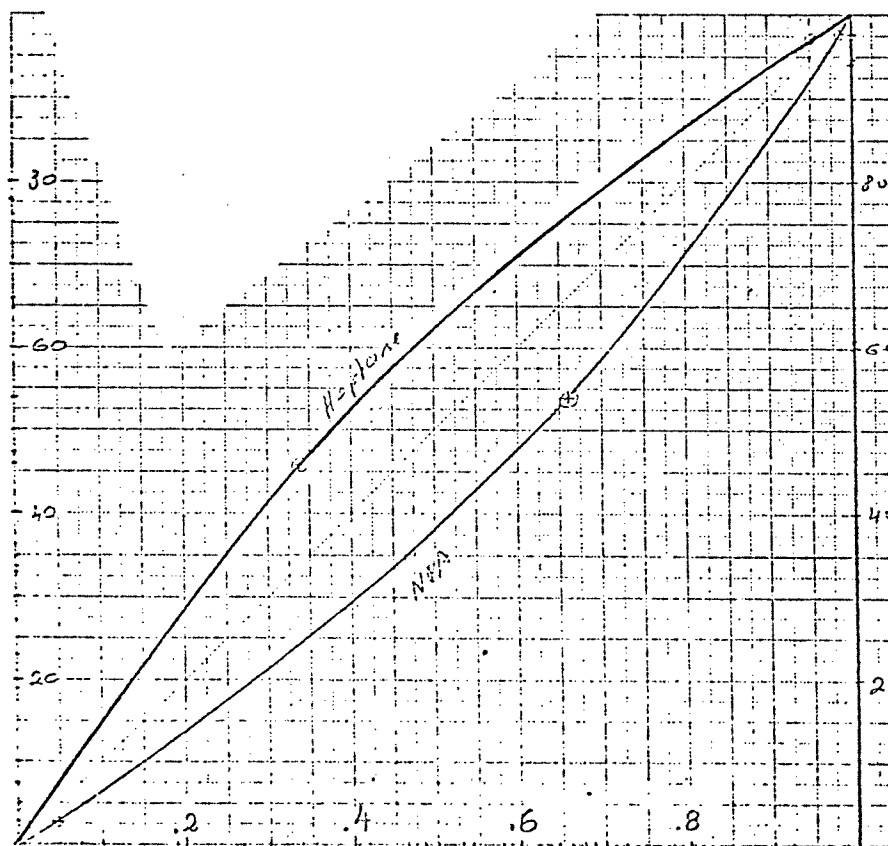
VPC: Aer 200
SE 30-20%
76°C
H.F. Integrator

FIGURE 10

STANDARD VPC CURVE FOR SYNTHETIC MIXTURE OF ISOPROPYL ALCOHOL-HEPTANE



STANDARD VPC CURVE FOR SYNTHETIC MIXTURE OF n-PROPYL ALCOHOL-HEPTANE



n-Propyl Alcohol		Heptane	
g	ml	g	ml
7.983	10	6.7906	10
0.4136	0.5	13.603	20
15.917	20	0.352	0.5
		0.9869	2.244
		0.9869	0.0131
		0.6622	0.3378
		0.0484	0.95166
		2.75	2.244
		54.02	0.0131
		45.87	0.3378
		97.106	0.95166
		2.244	0.0131

STANDARD REFRACTIVE INDEX (RI) CURVE FOR METHYLENE CHLORIDE-ISOPROPYL ALCOHOL

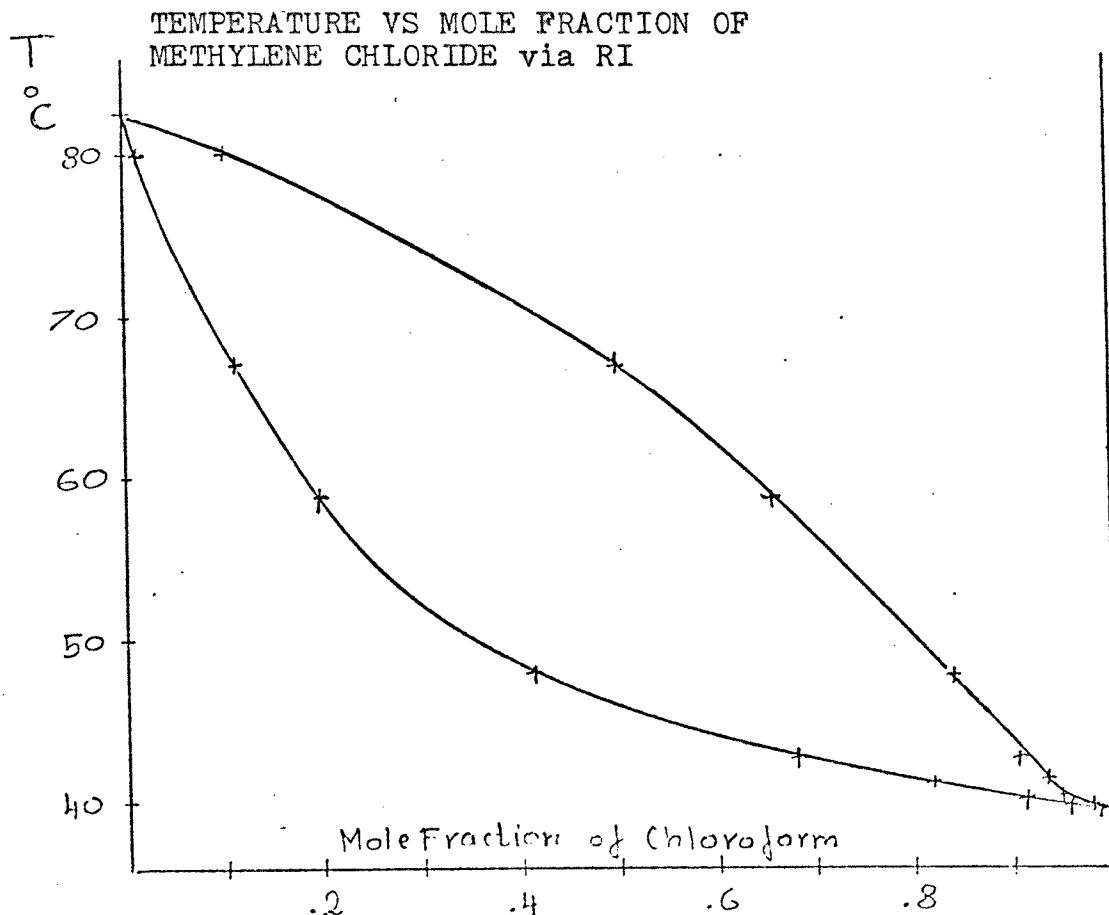
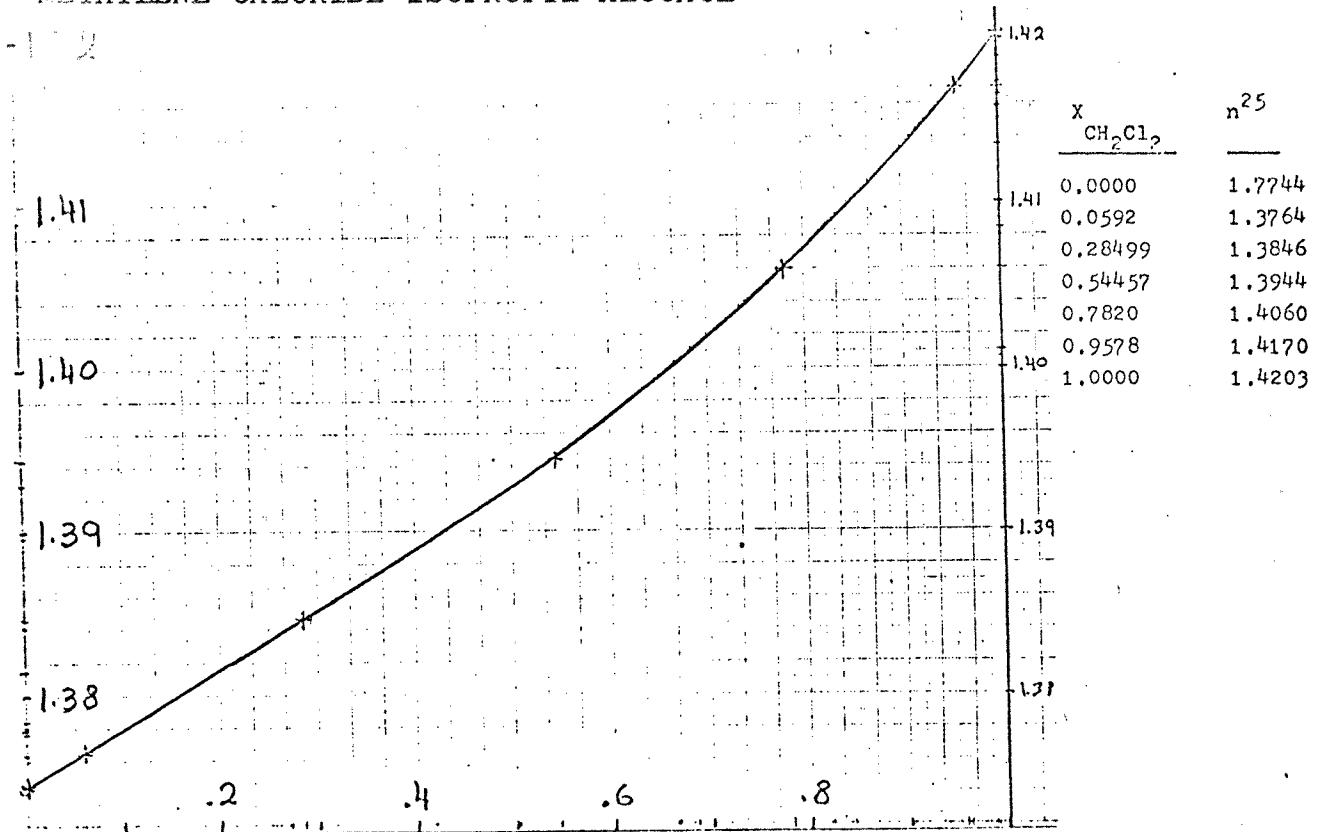
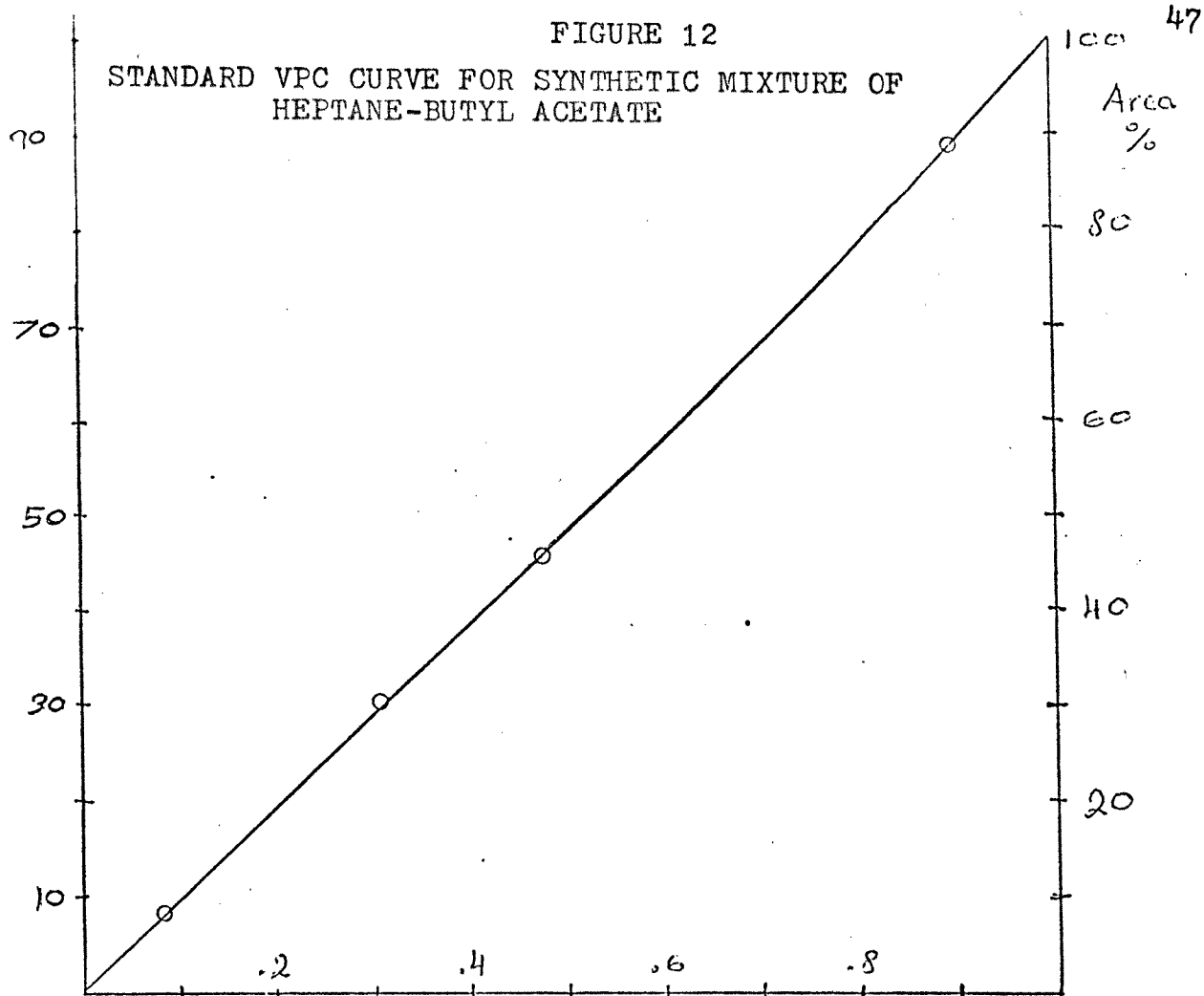
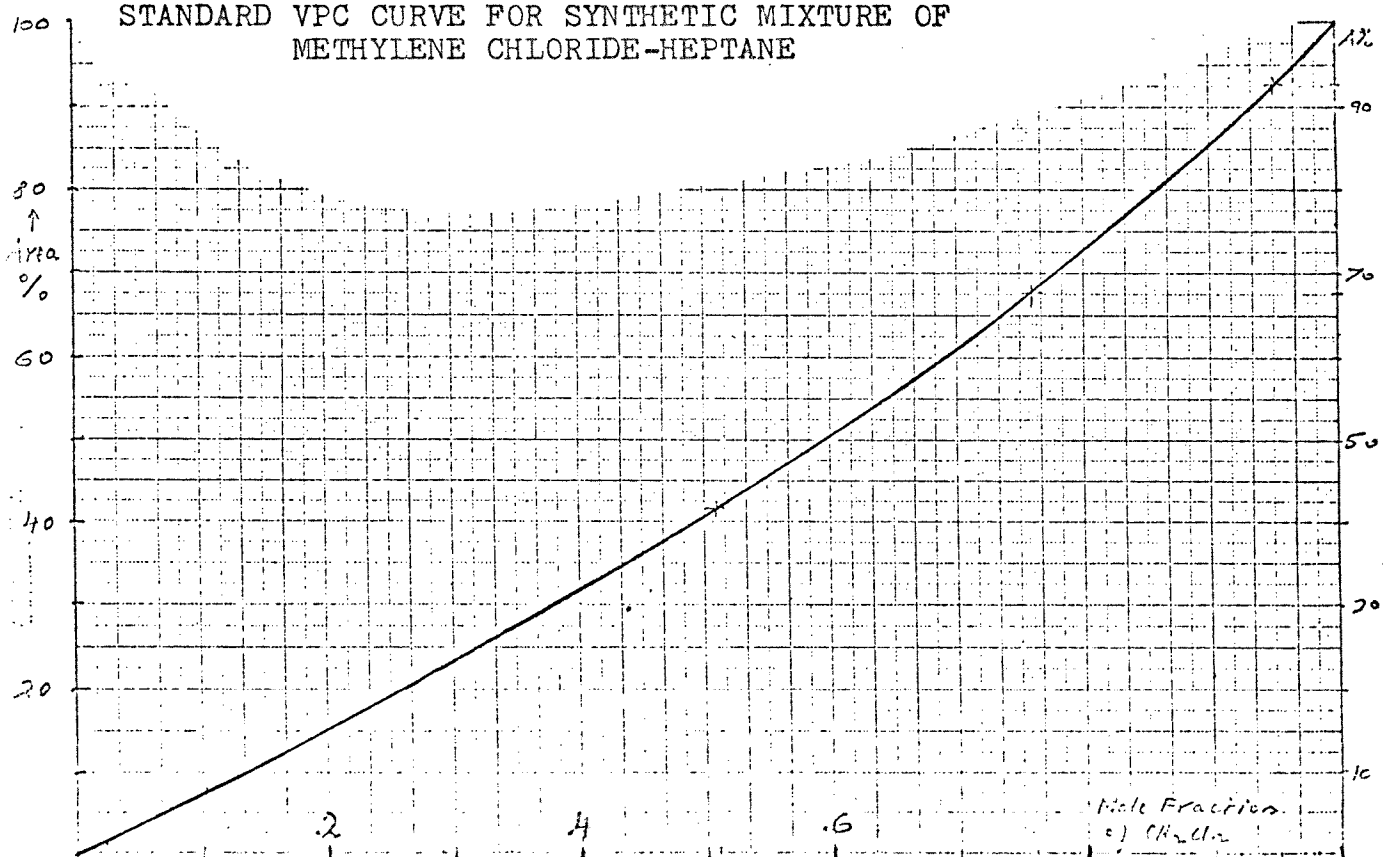


FIGURE 12

STANDARD VPC CURVE FOR SYNTHETIC MIXTURE OF
HEPTANE-BUTYL ACETATE



STANDARD VPC CURVE FOR SYNTHETIC MIXTURE OF
METHYLENE CHLORIDE-HEPTANE



SOLVENT RECOVERY LABORATORY DATA GENERATION

Heptane Stream (#1)

Simple Batch Distillation

During the simple batch distillation the distillate composition change was measured via vapor phase chromatography (VPC) as a function of pot temperature.

TABLE 12

COMPOSITION VS. TEMPERATURE CHANGE DURING BATCH DISTILLATION
OF STREAM #1

T °C	Liquid Volume % determined via VPC (Porapak-N T=197°C He=40/60)						
	Liquid	Heptane	Chloroform	n-Propyl Alcohol	RC1*	Water	
25		84.7	13.89	0.86	0.28	0.09	Pot Compo- sition
74		67.12	35.5	0.804	0.383	0.06	Stream sample of distillate
89		77.24	20.7	1.73	0.233	0.027	"
94		88.53	10.81	0.366	0.16	-	"
98		93.2	6.10	0.2	-	-	"

R=Alkyl

* Compared to that of a synthetic prep. sol'n.

Vent Gases From Simple Batch Distillation

During the simple batch distillation the vent gases must be absorbed by a caustic scrubber. The gases are both corrosive and have a noxious odor, therefore, they cannot be

allowed to escape into the atmosphere. The required caustic scrubber load is 355 ml 1 normal sodium hydroxide or 14.2 g/gal. of stream #1 mixture.

Simple Batch Distillate

Extraction/Neutralization With Aqueous Sodium Bicarbonate

A 1600 ml sample of Heptane stream (#1) sample batch distillate was treated with 500 ml (31 volume % of 3% sodium bicarbonate at 25°C over thirty minutes. The total n-propyl alcohol removed by the aqueous layer was 5.6 ml out of 13 ml, or 43% of the total.

TABLE 13.

n-PROPYL ALCOHOL REMOVAL VIA AQUEOUS SODIUM BICARBONATE EXTRACTION

Solvent	Liquid Volume % via VPC (Porapak-N, T=197°C, He=40/60)			
	Stream #1	Distillate	Organic Phase	Aqueous Phase
Water	-	0.07	0.28*	-
Alkyl Chlorides	0.15	0.162	0.112	-
n-Propyl Alcohol	1.10	0.807	0.473	1.13
Chloroform	1.84	18.5	16.94	-
Heptane	80.5	80.0	82.4	-

* In mg/ml by Karl-Fisher titration

Extraction With Water

The efficiency of n-propyl alcohol removal via aqueous extraction was checked by extracting a 300 ml sample of Heptane stream (#1) distillate with 300 ml deionized water at 25°C. The mixture was vigorously agitated for 0.5 hours in a one liter Morton flask, the layers were separated and the organic phase analyzed via VPC. As the data in Table 14 indicates, 91% of the isopropyl alcohol was removed via water, vs only 42% removed via sodium bicarbonate, due to salt effect.

Note: The stream #1 distillate is acidic due mainly to residual hydrochloric acid. Neutralization is necessary so that costly acid-resistant fractional distillation equipment will not have to be employed.

TABLE 14

SOLVENT STREAM (#1) ANALYSIS DURING AQUEOUS EXTRACTION

Solvent	Retention Time (min.)	Before Extraction (Volume %)	After Extraction (Volume %)
Air	0.40	0.07	0.07
Ethyl Alcohol*	0.54	0.03	0.01
Ethyl Chloride	2.04	0.07	0.05
Propyl Chloride	3.87	0.48	0.48
n-Propyl Alcohol	5.16	0.87	0.08
Chloroform	5.62	18.39	18.22
Heptane	7.45	80.08	81.08
		<u>99.99</u>	<u>99.99</u>

*The residual ethyl alcohol is from the commercial grade chloroform, used there as a stabilizer.

VPC Column: Porapak-N T= 200°C He= 40/60

Extraction As A Function of Temperature.

A sample of the crude process Heptane stream (#1) was extracted with 1/8 volume deionized water six consecutive times. The extractions were carried out in a three-necked round bottom flask with thirty minutes vigorous mixing simultaneously at 23°C and at 69°C (mild reflux). The layers were separated and analyzed.

It was concluded that the process was unsatisfactory since the organic residues were not removed by water. After six extractions, about 2 volume % high boiling residues remained in the organic layer. These residues become acidic upon standing, due to slow decomposition, and require treatment with 22-25% caustic for complete degradation. See Table 15 and Figure 13.

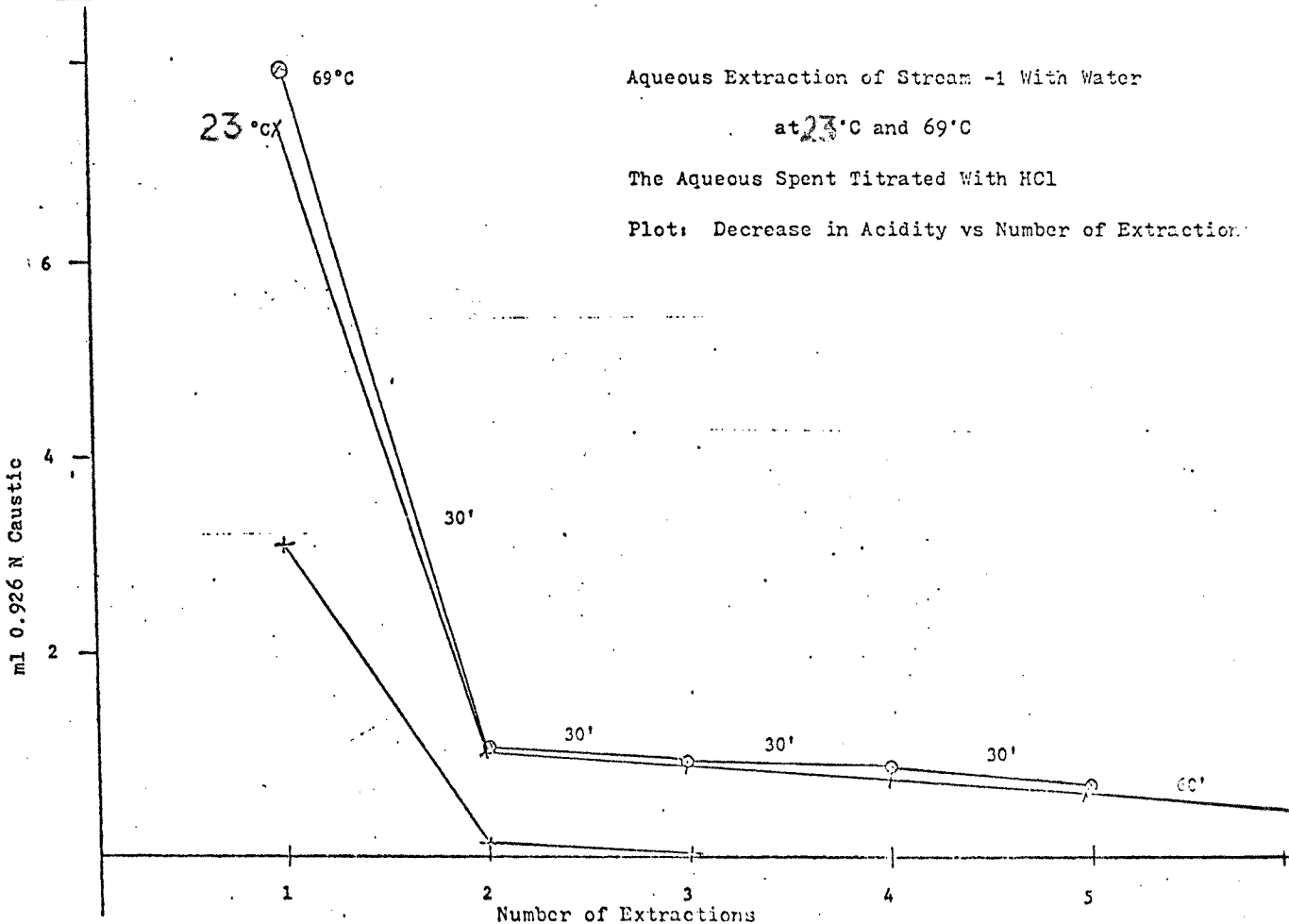
TABLE 15

AQUEOUS EXTRACTION OF PROCESS STREAM #1 AT 23° AND 69°C

Number of Extractions	T °C	Organic Layer(ml)		Aqueous Layer(ml)		Total Acidity(N)			n-Propanol in			VPC - Area % Farapak-N, 197°C He=40/60			
		IN	OUT	IN	OUT	Aqueous			Aqueous		Organic	RC1	NPA	CHCl ₃	Heptane (Total)
						H ₁ ⁺	H ₂ ⁺	H _T ⁺	Vol. %	% of Total	Vol. %				
1	23	2000	1955	250	263	0.667	0.051	0.718	3.22	38.4	0.777	0.156	0.69	24.23	74.7
	69	2000	1980	250	262	0.725	0.052	0.777	2.85	34.0	0.78	0.151	0.692	23.2	75.53
2	23	1894	1850	240	250	0.097	0.003	0.100	1.8	30.5	0.383	0.15	0.332	22.06	77.33
	69	1930	1900	240	242	0.089	0.003	0.092	2.10	33.7	0.415	0.184	0.363	24.93	74.32
3	23	1805	1785	230	235	0.084	0.001	0.085	1.13	38.2	0.214	0.144	0.187	23.75	75.7
	69	1853	1828	230	231	0.089	0.001	0.090	1.32	39.5	0.21	0.156	0.180	22.96	76.44
4	23	1722	1680	220	224	0.073	0.001	0.074	0.93	56.0	0.106	0.122	0.092	21.6	78.13
	69	1780	1760	220	224	0.082	0.001	0.083	1.0	59.0	0.103	0.14	0.089	23	76.6
5	23	1635	1600	210	213	0.057	0.001	0.058	0.338	46.5	0.10	0.121	0.087	21.72	77.36
	69	1710	1690	210	211	0.064	0.001	0.065	0.410	49.2	0.15	0.138	0.093	23.02	76.6
6	23	1556	1547	200	202	0.037	0.001	0.038				0.061	-	17	52.9

FIGURE 13

AQUEOUS EXTRACTION OF PROCESS STREAM #1 AT 23° AND 69°C



Batch Distillation Residues.

The purpose of this experiment was to determine whether contamination from degradation of residues would interfere with the fractional distillation in the event that the residues were not removed prior to fractionation. Only heptane distilled over up to 160°C, during one batch distillation. However, upon prolonged heating at temperatures above 140°C, the residue polymerized into a thick, foul-smelling mass. Noxious gases which were generated throughout the distillation were absorbed in a caustic scrubber.

Composition

A sample of typical pot residues from simple batch atmospheric laboratory distillation were analyzed and re-distilled in order to determine the boiling point range and composition of its components.

TABLE 16

ANALYSIS OF BATCH DISTILLATION RESIDUES

Acidity-1	1.06	m eq/ml
Acidity-2	0.06	m eq/ml
Acidity-3	0.05	m eq/ml
Karl-Fisher Titration*	1.2	mg/ml
Total Solids	200	mg/ml
Residue on Ignition	2.1	mg/ml
Heptane	20%	(vapor phase chromatography)
Specific Gravity	0.99	g/ml

* Water

Distillation

A 216 ml sample of the above residues was distilled at 1 atm. in order to determine the relative amounts of volatile/non-volatile compounds.

TABLE 17

BOILING POINT PROFILE OF BATCH DISTILLATION RESIDUES

Cut	ml	T _v °C	T _p °C	Water (K.F.)	Acid ₁ /Acid ₂	n-Propyl Alcohol	Heptane
1	68	97/115	102/160	0.79	0.001/.002	-	94.5
2	54	170/250	170/255	4.2	0.02 / .076	9	26
RR	48	-	-	2.2	3.36/.722	-	-

No other solvent was seen via vapor phase chromatography. In the pot residues (RR), nothing was seen by vapor phase chromatography. Cut #2 was spiked with n-propyl alcohol.

Heat of Mixing/Caustic Hydrolysis

Experiments

a. A 416 g sample of combined simple distillation residues was mixed with 253 g 25% caustic at 20°C in a one liter Dewar flask equipped with a resin kettle head, stirrer, thermometer and dry ice trap. Maximum temperature was reached in 15 seconds.

$$T_{\text{Max}} = 69.8^{\circ}\text{C} \quad \Delta T \sim 50^{\circ}\text{C}$$

b. Another sample of 456 g residues was mixed with 304 g 25% caustic at 26.5°C.

$$T_{\text{Max}} = 68.1^{\circ}\text{C} \quad \Delta T = 41.6^{\circ}\text{C}$$

$$\Delta H = C_p \Delta T \quad \Delta H_A = C_{pRes} \frac{416 \times 50}{669} + \frac{0.85 \times 253 \times 50}{669}$$

C_p of caustic ≈ 0.85 cal/g \cdot C

$$\Delta H_B = C_{pRes} \frac{456 \times 41.6}{760} + \frac{0.85 \times 304 \times 41.6}{760}$$

Assuming $\Delta H_A \approx \Delta H_B$, then

$$C_{pRes} \approx 0.31 \text{ cal/g } \cdot \text{C and}$$

$$\Delta H_{Max} \approx 25.3 \text{ cal/g or } \approx 46 \text{ BTU/lb}$$

The magnitude of heat evolved indicates no hazard.

Fractional Distillation

Heptane stream (#1) batch distillate was fractionated via a 25 tray Oldershaw column for the purpose of determining plate requirement for the fractionation column and also as an aid in determining the optimum reflux ratio. See Table 18.

TABLE 18
FRACTIONATION OF STREAM #1 VIA 25 TRAY OLDERSHAW COLUMN

Cut #	Reflux	T °C		Cut		H ₂ O mg/cc	VPC Volume %				
		Vap.	Pot	wt	%		RCl	NPA	CHCl ₃	Heptane	Y*
0	-	-	-	1300	100	0.28	0.112	0.473	16.94	82.4	
1	5	58-61	85-86	25	1.92	1.15	2.12	1.0	94.3	-	2.404
2	5	61	87	84	6.46	0.36	1.07	0.9	97.84	-	
3	10	61	87-95	52	4.0	0.59	-		99.9		
4	20	61-62	95-98	58	4.46	0.37			99.9		
5	20	62-95	100	65	5.0	0.43	0.49	9.1	54.2	36.06	
6	20	96-97	100	23	1.77	0.16		0.27	3.47	96.1	
7	5	97-98	100	76	5.85	0.09				99.8	
8	5	97-98	100	114	8.77	0.13				99.9	
9	5	97-98	100	104	8.0	0.09				"	
10	5	98	101	98	7.54	0.08				"	
11	1	98	101	290	22.3	0.08				"	
12	1	98	101	98	7.54	0.14				"	
R	-	-	-	98	7.54	0.25					

* Y is an unknown entity

The fractionation yielded an 8.38 volume % fore-cut, a 6.77 volume % center cut and a 15.25 volume % combined mixed cut. This represents about a 50% chloroform loss during the fractionation. The conclusion is that the column size is too small for efficient separation.

Comments: Total recovery from the fractionation was 99.7 volume %. The column retains about 100 ml. Mixed cuts to be recycled should be in the 8-10 volume % range. The presence of n-propyl alcohol is definitely the main source of the relatively large "mixed cut".

Fractionation via 40 Tray Oldershaw Column.

The purpose of this experiment was to determine fraction composition with narrow temperature ranges, as well as the maximum efficiency attainable depending upon the purity of cuts during the chloroform cut. Temperature recorder sensitive to ΔT 0.1-0.2°C is needed. Impurities of alkyl chlorides in the chloroform cut could be tolerated for most applications since they are chemically similar. Heptane-chloroform-n-propyl alcohol mixed cuts -11 through -18 could be recycled after removal of n-propyl alcohol via aqueous extraction. Data collected in this experiment is most suitable as a basis for process design. See Table 19.

TABLE 19

NARROW TEMPERATURE RANGE FRACTIONATION OF STREAM #1 BATCH

DISTILLATE

Cut			T °C					Area %							
#	cc	%	Liq	V>L	Mid-C	Vap	Reflux Ratio	Volt	EtOH	EtCl	PrCl	NFA	CHCl ₃	Heptane	
Feed	1700.0	100.0	-	-	-	-	-	-	-	0.094	0.443	0.67	19.53	79.0	
1	3.5	0.02	91	87	61	55.4-58	20	50	0.11	14.3	27.8	1.35	56.3	-	
2	6.6	0.04	"	"	"	58	"	"	-	1.91	19.41	1.0	77.6	-	
3	9.5	0.56	92	"	62	59.5	"	"	-	1.1	11.1	0.56	87.2	-	
4	13.1	0.77	93	87.5	"	60.1	"	55	-	0.3	5.7	0.3	93.6	-	
5	23.1	1.36	94.5	89.5	"	60.4	"	"	-	0.112	2.3	<0.3	97.5	-	
6	27	1.59	97	92.5	"	60.5	"	"	-	0.23	0.82	-	98.8	-	
7	169	9.93	98	95	"	"	"	"	-	-	0.31	-	99.5	-	
8	45	2.65	101	98	65	60.6	10	"	-	0.06	0.07	-	99.7	-	
9	2.7	0.015	"	99	98	61.2	20	57	-	-	-	-	99.8	-	
10	3.1	0.018	"	"	"	61.4	"	"	-	-	-	-	99.8	-	
11	8.9	0.52	"	"	"	62.4	"	"	-	-	-	0.92	97.2	1.9	
12	5.7	0.33	"	"	"	63.0	"	"	-	-	-	1.94	92.7	5.2	
13	8.2	0.48	"	"	"	67.5	"	"	-	-	-	3.83	85.0	11.02	
14	3	0.017	"	"	"	70.0	"	"	-	-	-	6.5	74.4	19.0	
15	8	0.47	"	"	"	77.0	"	"	-	-	-	10.9	57.0	31.9	
16	7.6	0.44	"	"	"	83.0	"	"	-	-	-	17.3	30.0	52.8	
17	6.8	0.40	"	"	"	94.5	"	"	-	-	-	14.0	14.1	71.8	
18	17.5	1.03	"	"	"	96.0	"	"	-	-	-	0.83	2.7	96.4	
19	19.0	1.11	"	"	"	96.7	"	"	-	-	-	-	0.62	99.3	
20	36.5	2.15	"	"	"	97.5	"	"	-	-	-	-	0.36	99.5	
21	1088.0	64.0	"	"	"	98.0	1	"	-	-	-	-	-	99.8	
P	165.0	9.7	"	"	"	-	-	-	-	-	-	-	-	99.8	

Liq= Liquid in pot V>L= Vapor over Liquid in pot
 Mid-C= Mid column Temp. (Between tray 20 & 21) Vap= vapor

Mixed Cuts

A combined sample of mixed cuts from various fractional distillations was refractionated via the 40 tray Oldershaw column. This fractionation was carried out for the purpose of assessing column capability for possible n-propyl alcohol recovery. Note the relatively high percentage of n-propyl alcohol (NPA) which would be removed by aqueous extraction. (See Table 20).

TABLE 20

STREAM #1 FRACTIONATION OF "MIXED CUTS" VIA 40 TRAY OLDERSHAW
COLUMN

Cut #	Reflux Ratio	T °C		Cut		VPC - Porapak-N, 198°C He=40/60						
		Vapor	Liquid	ml	%	H ₂ O	EtCl	EtCH	FrCl	NFA	CHCl ₃	Heptane
0	-	-	-	475	100	0.23	0.615	0.61	6.07	11.77	43.9	37.24
1	20	44-61	77-82	39	8.2	0.28	2.5	0.34	46.7	5.82	44.3	-
2	"	61-62	82-87	69	14.5	0.15	0.061	-	2.01	97.62	-	-
3	"	62-63	87	56	11.8	-	-	-	0.054	-	99.8	-
4	"	63-82	88	52	10.9	-	-	-	0.406	11.13	56.2	32.1
5	"	82-82.5	88	23	4.8	0.118	0.082	-	0.15	27.75	1.87	69.9
R	-	-	-	120	25.3	-	-	-	-	25.56	-	74.3
E _T *										2.7		97.14

The fractional distillation yields chloroform and n-propyl alcohol in acceptable purity. However, the recovery is inefficient. Therefore refractionation of mixed cuts is not recommended. Although no pure heptane cut was collected, two extractions of the pot residues with equal volumes of water removed most of the n-propyl alcohol. 5 ml pot residues extracted with 5 ml water:

Composition of Organic Layer	n-Propyl Alcohol	Heptane
After 1st extraction	2.7%	97.14%
After 2nd extraction	0.2%	99.7%

This experiment illustrates the desirability of removing n-propyl alcohol from the mixed cuts in order to ensure maximum chloroform and heptane recovery.

Methylene Chloride Stream (#2)

A synthetic mixture composed of 800 ml methylene chloride (45 volume %), 880 ml of isopropyl alcohol (49.5 volume %) and 100 ml heptane (5.5 volume %), similar to Methylene Chloride Stream (#2), was prepared from reagent grade solvents and fractionated via a 25 tray Oldershaw column. As the data in Table 21 indicates, the recovery of this stream is quite efficient.

TABLE 21

STREAM #2 SYNTHETIC MIXTURE FRACTIONATION VIA 25 TRAY OLDERSHAW COLUMN

800 ml Methylene Chloride + 880 ml Isopropyl Alcohol + 100 ml Heptane = Sample = 1780 ml
 (45.0 Vol.%) (49.5 Vol.%) (5.5 Vol.%)

CUT			Reflux Ratio	T of Liquid °C	T of Vapor above Liquid °C	T between trays 20/21 °C	T of Vapor °C	COMPOSITION %			
#	cc	%						CH ₂ Cl ₂	iPA	Heptane	H ₂ O
1	12	0.675	5	48	44	41	39.6-40	99.69	-	-	0.26
2	443	24.9	2	56	50	41	40.1	99.94	-	-	-
3	267	15.0	2	81	77	42	40.3	99.9	-	-	-
4	44	2.47	20	82	78	77	76.0	85.66	7.2	7.08	-
5	172	9.67	5	84	83	82	76.7	0.5	50.5	49.0	-
6	693	39.0	2	85	84	83	82.3	0.17	99.8	-	-
R	67.5	3.79	-					1.05	98.75	-	-

Residues are left as heel for the following batch and then purged every fifth batch. Solvent recovery via the general recovery unit (see flow sheet) gives excellent results.

Fractional Distillation Of An Authentic Methylene Chloride Stream (#2)

A 4,500 ml authentic Methylene Chloride stream (#2) sample with a composition of 57% methylene chloride, 38% isopropyl alcohol (via VPC) and 3.5% heptane was fractionated via a 25 tray Oldershaw column.

TABLE 22

STREAM #2 FRACTIONATION VIA A 25 TRAY OLDERSHAW COLUMN

Cut			Reflux Ratio	Temp ° C				Composition, % (VFC)					
#	ml	%		Liq.	Vapor Above Liq	Mid Col 20-21 Tray	Vapor	CH ₂ Cl ₂	iPrOH	Heptane	PrCl	EtCl	H ₂ O
1	30.5	0.68	5	44	42	40.0	38.5	98.4	-	-	1.14	0.12	-
2	43	0.95	"	"	"	"	38.7	99.9	-	-	-	-	-
3	224	4.98	"	"	"	40.5	39.2	99.95	-	-	-	-	-
4	304	6.76	"	"	"	41.0	39.7	"	-	-	-	-	-
5	1338	29.7	1	45	42.5	"	40.3	99.9	-	-	-	-	-
6	430	9.55	2	77	75	48.0	40.7	"	-	-	-	-	-
7	38	0.845	20	TC	78	77.0	73.1	70.7	8.9	20.9	-	-	-
8	36	0.80	"	"	"	"	76.1	4.61	41.4	52.85	-	-	-
9	48	1.06	"	"	"	"	76.4	0.35	48.2	51.0	-	-	-
10	244	5.42	10	"	"	"	76.6	-	50.0	49.7	-	-	0.116
11	76	1.69	5	"	82.5	81.0	79.9	-	92.9	6.7	-	-	0.17
12	390	8.67	2	"	"	82	81.5	-	98.9	0.35	-	-	0.20
13	1050	23.4	"	"	"	"	"	-	99.4	-	-	-	0.12
R	180	4.0	-	-	-	-	-	-	43.5	-	-	-	0.10

Recovery Yields:

Methylene Chloride 2339 ml 91%

Isopropyl Alcohol 1440 ml 84%

Fraction cuts 7 through 11 along with the residues go to waste disposal.

Treatment Of Combined Heptane Stream (#1) and Butyl
Acetate Stream (#3)

Aqueous Caustic Extraction and Fractional Distillation.

The purpose of this experiment was to check the loss of butyl acetate during the caustic treatment, which was negligible, and to check the effect of butyl acetate upon the fractional distillation.

A 1650 ml sample of the combined authentic streams #1 and #3 was analyzed via VPC. The layers were separated and the top organic layer was treated once more with 500 ml deionized water.

TABLE 23

AQUEOUS EXTRACTION OF COMBINED STREAMS #1 AND #3

Organic Layer	Volume ml	Volume %			
		n-Propyl Alcohol	Chloroform	Heptane	Butyl Acetate
Before Treatment	1650	0.89	18.60	61.7	15.74
After Treatment	1592	0.06	17.50	61.5	15.30
Loss During Treatment (%)	3.5	93.3	6.0	0.4	2.8

Fractional Distillation

1,533 ml of the above organic mixture was fractionated via a 25 tray Oldershaw column. As can be seen from a comparison

of the fractionation data obtained from this experiment with that from subsequent experiments, the 25 tray column is grossly inefficient. Only an 8.8% recovery (99.2% pure) was realized.

On the basis of similar fractionations, a 40 tray column would have yielded about 11-14% pure chloroform cut. (See Table 24).

TABLE 24

FRACTIONATION DATA OF COMBINED STREAMS #1 AND #3

CUT			Reflux Ratio	Temperature °C		Composition % via VPC					
#	ml	% of Feed		Liquid	Vapor	H ₂ O	R-Cl	n-PrCH ₃	CHCl ₃	Heptane	Butyl Acetate
1	16	1.04	10/1	92	60	6.1	0.3	6.7	86.9	-	-
2	134	11.43	15/1	99	61	-	0.1	0.66	98.7	-	-
3	39	2.54	"	101	64	-	-	-	92.4	3.24	-
4	55	3.58	"	102	86	-	-	-	57.5	39	-
5	35	2.28	"	103	94	-	-	-	-	65.2	-
6	157	10.4	"	103	95	-	-	-	16.3	78.3	-
7	153	9.96	10/1	104	98	-	-	-	-	97.22	-
8	112	7.3	"	105	98	-	-	-	-	97.8	-
9	142	9.25	"	107	98	-	-	-	-	98.2	0.42
10	395	25.8	15/1	132	99	-	-	-	-	98.64	0.346
11	46	3.0	20/1	133	126	-	-	-	-	46.6	46.2
12	127	8.27	5/1	138	126	-	-	-	-	0.37	99.1
Pot*	114	7.43									77.1*

* Contains unhydrolyzed residues

Butyl Acetate Stream (#3)

The composition of an authentic stream #3 sample was determined via VPC and found to be 8.7 volume % heptane,

88.2 volume % butyl acetate and 3.1 volume % residues.

Batch Distillation

A 2000 ml Butyl Acetate stream (#3) sample was distilled from a three liter three-necked flask and samples were analyzed for composition as a function of temperature.

TABLE 25

STREAM #3 COMPOSITION OF THE DISTILLATE VS TEMPERATURE DURING BATCH DISTILLATION

T° C		Sample #	Composition %	
Pot	Vapor		Heptane	Butyl Acetate
116	102	1	82.2	17.7
127	116	2	49.0	49.6
131	123	3	9.2	90.0
139	123	4	7.4	92.0
142	126	5	0.7	98.2

The above simple distillation along with the XY data clearly indicates the ease of separation of heptane and butyl acetate.

Batch Distillate Volume: 1822 ml

Composition: Heptane 9.1% Butyl Acetate 90.7% (via VPC)

Pot Residue: 172 ml

Composition: Heptane 0.87% Butyl Acetate 63%

The remainder is high boiling organic residues.

Above 140°C pot temperature, degradation takes place resulting in foul smelling products (decomposition of the high boiling organic residues). Therefore, a considerable pot residue had to be left behind.

Another sample of stream #3 was distilled under vacuum up to a pot temperature of 85°C. The pot residue contained only 3.8% butyl acetate. However, it nearly solidified upon cooling to 25°C. Therefore, the residue would have to be mixed with caustic before sending it to the hydrolysis tank. On a plant scale, vacuum distillation would be recommended, if feasible. The batch distillate (1822 ml) was neutralized with 25 g solid sodium bicarbonate. (The distillate stayed above the base). 1700 ml of the organic solution was fractionated via a one inch 40 tray Oldershaw column.

TABLE 26

FRACTIONAL DISTILLATION DATA OF BUTYL ACETATE STREAM (#3) VIA
A 40 TRAY OLDERSHAW COLUMN

Cut			Reflux	Temp. °C		Composition %	
#	ml	% of Feed	Ratio	Liquid	Vapor	Heptane	Butyl Acetate
1	14	8.24	20/1	111	98	98.0	1.13
2	290	17	20/1	134	126	36.2	63.4
3	81	4.77	20/1	139	126	21.7	78.1
Pot	1310	77.1	-	-	-	0.66	99.2

Recovery yield for the fractionation was 77.1 volume % butyl acetate, 0.824 volume % heptane and 21.8 volume % mixed cut to recycle, giving a material balance of 99.724%.

Experimental Equipment Results

The equipment used in the experiments are of laboratory scale and thus are readily available in chemical engineering laboratories.

1. Extraction/Neutralization Studies.

One liter three necked Morton flask equipped with thermometer, condenser, teflon/glass stirrer, cooling bath and heating mantle. The flask had a bottom outlet and thus served as a separatory funnel.

2. Simple Distillation

Three liter three necked flasks equipped with stirrer, condenser, adaptor, dry ice trap, receiver, thermometer and oil bath.

3. Caustic Hydrolysis

The same as used for simple distillation.

4. Fractional Distillation

For all the fractional distillation experiments Oldershaw columns were used consisting of the following components:

One 20 tray unit, 32 mm ID x 30"

One 15 tray unit, 32 mm ID x 30"

One 5 tray unit, 32 mm ID x 30"

One automatic reflux head adaptor and a condenser

Three thermo well adaptors

One three liter three necked flask and heating mantle

One three point Speedomax H recorder

Three thermocouples; one thermometer

The fractionation column performed quite well. Tray to

tray visual observation along the whole column was convenient in all cases.

5. Adiabatic Reactor for Heat of Reaction Determination.

A one quart Dewar flask equipped with a resin kettle head, stirrer, thermometer and dry ice condenser/receiver.

WASTE DISPOSAL LOADA. From Heptane Stream (#1)

1. Simple Distillation

Dilute aqueous caustic from extraction/neutralization of distillate is about 1,500,000 GPY. There is also another 1,500,000 GPY from the same step, which contains trace amounts of n-propyl alcohol.

2. Caustic Hydrolysis

About 4 volume % of stream #1 is hydrolyzed with 2 volume % of 25% caustic. About 80,000 gals. aqueous caustic goes to waste per year. About 10,000 gals. organic goes to the incinerator per year.

3. Fractional Distillation

Mixed cut purge to the incinerator is about 4.5 volume % or 67,500 GPY. Water containing trace amounts of n-propyl alcohol (from extractions of mixed cuts) is about 4 x 15 volume % or 90,000 GPY.

B. From Methylene Chloride Stream (#2)

1. Hydrolyzed Residues

Same as under Stream #1.

2. Mixed Cuts From Fractionation

The amount of organic mixed cuts going to the incinerator is about 7 volume % or 105,000 GPY. This can be reduced to

about 10,000 GPY by the removal of isopropyl alcohol via the aqueous extraction of the mixed cuts.

C. From Butyl Acetate Stream (#3)

1. Caustic Hydrolysis Residues

Same as previous.

2. Mixed Cuts to Incinerator

About 100,000 GPY.

Total Annual Waste Disposal Load

"Water" Waste		Organic (Incinerator) Waste	
<u>Maximum</u>	<u>Minimum</u>	<u>Maximum</u>	<u>Minimum</u>
4,500,000 gals.	4,000,000 gals.	282,500 gals.	187,500 gals.

Note: These amounts can vary significantly depending upon the optional process changes initiated.

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