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Study of Feasibility of Herbicide Orange Chlorinolysis

Office of Research and Development
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STUDY OF FEASIBILITY OF HERBICIDE ORANGE CHLORINOLYSIS

by

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ABSTRACT

A process termed chlorinolysis (exhaustive chlorination) was applied to samples of USAF herbicide ORANGE, a discontinued military defoliant. The herbicide (a 50/50 mixture of the n-butyl esters of 2,4-D and 2,4,5-T) contained a production impurity, 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD or dioxin) - a powerful teratogen.

The research objective was to demonstrate the feasibility of chlorinolysis as a resource saving method to convert such herbicides into useful and marketable products, namely, carbon tetrachloride (CCl_4), carbonyl chloride ($COCl_2$), and hydrogen chloride (HCl), while destroying/converting any dioxin present therein.

Bench scale (100 g/hr) chlorinolysis of herbicide ORANGE was evaluated over a range of conditions. The critical reaction parameters were found to be: chlorine to carbon ratio (4.4-7.2), temperature (600-800°C), pressure (225-300 psig), and retention time (0.5-1.0 minute).

Thermodynamic analysis had indicated that CCl_4, hexachlorobenzene (HCB), and chlorine (Cl_2) would exist in equilibrium at the reaction conditions utilized. Because of the balance required between reaction rate (reactor size) and HCB content of the effluent, recycle of unconverted HCB from the product recovery system was found to be necessary. Recycle tests demonstrated that single pass HCB conversion rates of greater than 80% could be realized.

Destruction of dioxin was complete to below the detectable limit of 10 parts per trillion (ppt) in a single pass operation of the reactor system. Preliminary toxicological tests of the recovered CCl_4 on rabbits and rats showed no evidence of dioxin contamination.

Recovery of the 2,4-D ester component via fractional distillation was shown to be feasible in an Oldershaw column operated under vacuum. Data indicated that about 80% of the 2,4-D ester could be recovered as a distillate free of detectable dioxin. Economics of a combined fractionation/conversion process for herbicide ORANGE disposition appears to be superior to chlorinolysis alone.

This successful study opens the path to an effective method for conversion of environmentally unacceptable materials into useful products of commerce. Investigation of the application of the process for the disposal of other materials, such as DDT, lindane, dieldrin, PCBs, waste chlorocarbons, and certain military chemicals, is recommended.

ACKNOWLEDGEMENTS

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I - CONCLUSIONS

A. High temperature chlorinolysis under the proper conditions effectively converts Herbicide ORANGE and the contained tetrachlorodibenzo-p-dioxin to carbon tetrachloride, carbonyl chloride, and hydrogen chloride (gas).

B. Destruction of tetrachlorodibenzo-p-dioxin is complete to the detectable limit of <10 parts per trillion (ppt) in a single pass through the reaction-refining system.

C. Single pass operation of the reactor results in the production of some hexachlorobenzene and chlorinated polybenzene residue.

D. A residue-free process is feasible because residues from single pass operation when mixed with fresh feed and passed through the reactor were converted to carbon tetrachloride.

E. Preliminary toxicology tests of the recovered carbon tetrachloride on rabbits and rats showed no evidence of tetrachlorodibenzo-p-dioxin contamination.

F. The chlorinolysis process as outlined offers an environmentally safe method of disposing of Herbicide ORANGE.

G. The chlorinolysis process offers an opportunity to convert many environmentally unacceptable materials to useful industrial chemicals and to conserve resources.

II - RECOMMENDATIONS

Chlorinolysis is recommended as a resource saving method of converting Herbicide ORANGE and the contained tetrachlorodibenzo-p-dioxin to useful industrial chemicals, carbon tetrachloride, hydrogen chloride, and carbonyl chloride.

Investigation of the applicability of the chlorinolysis process for the disposal of other materials, such as DDT, Lindane, Dieldrin, PCBs, and certain military chemical agents is also recommended.

III - INTRODUCTION

Herbicide ORANGE, a military defoliant, was withdrawn from use in Vietnam in 1970 because of potential teratogenic effects. About 2.3 million gallons of this materiel was on hand when further use was banned. Since this time, the U. S. Air Force (USAF) has been attempting to dispose of this materiel inventory.

Herbicide ORANGE is a 50:50 mixture of the n-butyl 2,4-dichloro- and 2,4,5-trichlorophenoxyacetates. A small concentration of tetrachlorodibenzo-p-dioxin (dioxin), an artifact in the preparation of 2,4,5-trichlorophenoxyacetic acid, is present in ORANGE. Because unrestricted use of 2,4,5-T herbicides was banned by EPA and dioxin is a highly toxic teratogen, the method for disposing of ORANGE must be environmentally acceptable.

Environmental acceptability precludes the normal use for control of vegetation on rangeland, pastures, and rights-of-way because the dioxin content of ORANGE exceeds the 0.5 ppm limit tentatively recommended by EPA. Thus, the methods of disposal available are reduced to incineration and chemical conversion.

Presently known incineration processes are not completely acceptable when assessed against the zero pollutant discharge concept of environmental statutes, particularly with respect to potentially hazardous materials.

Prior to 1972, the only known chemical conversion process, base hydrolysis, e.g., treatment with caustic or an organic base, was equally

unacceptable because of the large volumes of aqueous wastes that are produced. In 1972, a new process was developed in the laboratories of Diamond Shamrock Corporation for the conversion of refractory chlorocarbon wastes to useful industrial chemicals. This process is completely closed, that is, no vapor, solid or liquid discharges are generated other than conversion products. Through the auspices of EPA and with support by the Air Force, a research program was developed to evaluate the applicability of this process to the disposal of ORANGE.

Inherent in this program were requirements to define suitable conditions, to delineate a process to recover the products, and to demonstrate that the recovered products were free of dioxin. Evaluation of quality and safety of the recovered carbon tetrachloride would be accomplished by instrumental analysis and toxicology effects found in test rabbits and rats exposed to the product. Because of the diverse and complex nature of the various evaluations, the program was conducted in cooperation with the Bioeffects Branch of EPA in Chamblee, Georgia, and the Pesticide Degradation Laboratory of the USDA in Beltsville, Maryland. The project was coordinated by the Office of Research and Development of EPA through its Industrial Pollution Control Division, Washington, D. C. and the Southeast Environmental Research Laboratory, Athens, Georgia.

The overall objective was to demonstrate that the chlorinolysis process would convert ORANGE and the contained dioxin to carbon tetrachloride, carbonyl chloride, and hydrogen chloride. The allowable residual dioxin content in the refined carbon tetrachloride was set at

10 ppt maximum (the proven limit of detectability). Instrumental analysis of the refined carbon tetrachloride was performed in the USDA laboratory by Dr. E. A. Woolson under the direction of Dr. P. C. Kearney. Toxicological evaluation of the refined carbon tetrachloride was performed by Dr. R. D. Kimbrough, Acting Chief of the Bioeffects Branch of EPA.

IV - THEORETICAL CONSIDERATIONS

The overall chemical reactions projected to occur in the chlorinolysis of ORANGE are shown in Figure 1. However, several intermediate reactions may be expected to occur with their products also being destroyed under the reaction conditions. Mechanistic analysis of the reactions indicates that hexachlorobenzene will be formed as an intermediate and because of its inherent stability can be expected to be present in the product mix from a reactor of a finite size.

Analysis of the thermodynamic data available indicates that carbon tetrachloride (CCl_4), hexachlorobenzene (HCB), and chlorine (Cl_2) exist in equilibrium at the reaction conditions proposed for chlorinolysis:

$$HCB + 9\ Cl_2 \rightleftharpoons 6\ CCl_4 \qquad (1)$$

$$K = \frac{(P_{CCl_4})^6}{P_{HCB}(P_{Cl_2})^9}, \text{ in atm}^{-4} \qquad (2)$$

$$\text{where } K = \exp\left(-78.6 + \frac{74500}{T}\right) \qquad (3)$$

and K = equilibrium constant

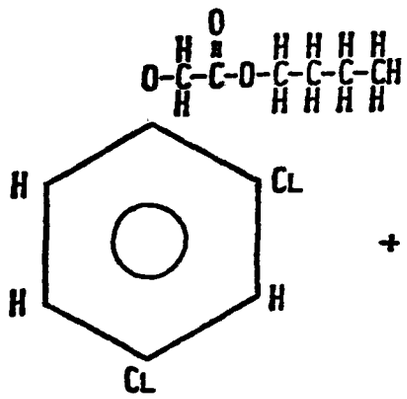
P = Partial pressure, atm

T = Absolute temperature in °K

This relation is of concern because, in any practical operation,

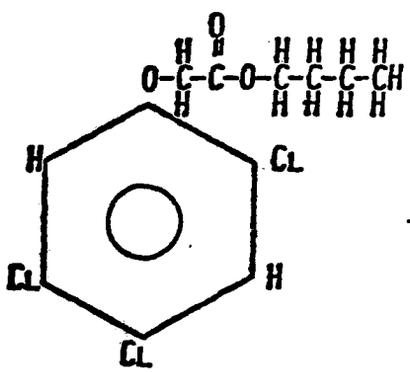
FIGURE 1

THEORETICAL REACTIONS FOR
HERBICIDE ORANGE CHLORINOLYSIS



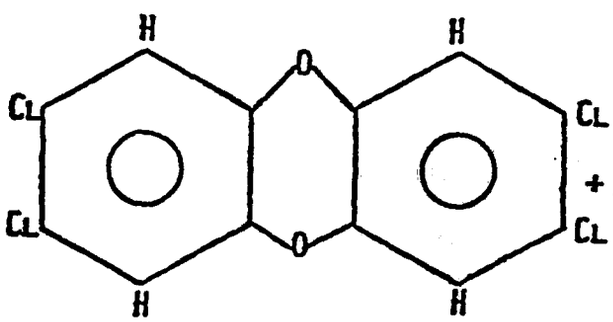
$$+ 27\ Cl_2 \longrightarrow 9\ CCl_4 + 14\ HCl + 3\ COCl_2$$

N BUTYL - 2,4-DICHLOROPHENOXYACETATE



$$+ 26\ Cl_2 \longrightarrow 9\ CCl_4 + 13\ HCl + 3\ COCl_2$$

N BUTYL - 2,4,5-TRICHLOROPHENOXYACETATE



$$+ 22\ Cl_2 \longrightarrow 10\ CCl_4 + 4\ HCl + 2\ COCl_2$$

DIOXIN (2,3,7,8 TETRACHLORODIBENZO-P-DIOXIN)

HCB will be found in the product from the reactor. Examination of the equilibrium expression as shown in Equation 4 gives clues to reaction conditions necessary to minimize the HCB content in the reactor effluent.

$$x_{HCB} = \frac{(x_{CCl_4})^6}{K(x_{Cl_2})^9 \pi^4} \qquad (4)$$

where:

x = mole fraction

π = total pressure, atm.

Favorable effects will obviously be realized by operating at high chlorine concentration and elevated total pressure. High carbon tetrachloride concentrations and elevated temperature will tend to produce unfavorable equilibrium effects. However, elevated temperatures were found to be desirable from a process standpoint because they promote high rates of reaction, i.e., highly favorable kinetics at the expense of equilibrium conversion.

Because of the necessary balance between rates of reaction (reactor size) and HCB content of the effluent, it is obvious that some recycle of unconverted HCB from the product recovery system back through the reactor may be necessary to ensure that no buildup of this environmentally unacceptable chemical will occur. The trade-off will essentially be between reactor size and recycle stream size or possibly allowable HCB concentration in the feed mixture.

V - DISCUSSION OF RESULTS

A. Feed

ORANGE containing 14 ppm of 2,3,7,8 tetrachlorodibenzo-p-dioxin supplied by the USAF was used throughout this study. Analyses of three replicate samples of the material supplied (single container) performed by the USDA, showed an average dioxin content of 14.8 ppm (actual values were 15.8, 13.6, 14.9 (see Appendix A)). Commercial grade carbon tetrachloride was used to dilute the herbicide as needed to moderate the reaction temperature.

B. Experimental Results

Several attempts to feed ORANGE on an "as received" basis were unsuccessful because prereaction and carbonization occurred at the inlet end of the reactor. Dilution of ORANGE with carbon tetrachloride to reduce the reactivity of the feed resulted in satisfactory performance of the system. All subsequent test work was done with ORANGE diluted on a 1:1 by volume basis.

Reactor performance was studied over a range of conditions. Critical factors in this feasibility test were chlorine-to-carbon feed ratio, temperature, pressure, and retention time. The ranges of these variables studied are summarized in Table 1.

TABLE 1 - REACTOR CONDITIONS DURING FEASIBILITY STUDIES

Chlorine to Carbon Ratio, Cl_2/C	4.4 - 7.2
Temperature, °C	600 - 800
Pressure, psig	225 - 300
Retention Time, minute	0.5 - 1.0

Single pass tests were made to establish comparisons of reactor performance prior to attempting recycle operation. A summary of pertinent experimental results is shown in Table 2. Several trends can be observed in these results. As predicted by the CCl_4-HCB equilibrium relationship, an increase in system pressure, while holding all other conditions constant, produces an increase in CCl_4 yield and a reduction in HCB yield (see tests 46 and 52). The reduction in HCB yield is desirable as it reduces the volume of recycle required to convert the hexachlorobenzene by-product make.

The effect of increased Cl_2/C ratio upon selectivity to carbon tetrachloride is also favorable as evidenced by the results of tests 46 and 54.

Adjusting reaction temperature may be expected to have two effects in this reaction. The first effect postulated is that increasing temperature will increase the concentration of HCB at equilibrium. Estimates of these concentrations from equations 3 and 4, shown in Table 3, indicate that this effect will be inconsequential in a reactor of finite size.

Table 2

Summary of Selected Chlorinolysis Runs

Run No.	Duration Hrs	Organic Feed Rate gms/hr	Temp °C	Press psig	Ret. Time min	Cl_2/C	Orange Conv. %	Orange Selectivity to CCl_4	Orange Selectivity to HCB	Orange Selectivity to $COCl_2$	Carbon Accountability %
Single Pass Operation											
46[A]	13.5	69.3	700	300	1.0	6.8	100	63	8	-	100
52[A]	9.0	54.9	700	225	1.0	7.0	100	52	12	-	94
54[A]	16.0	101.0	700	300	1.0	4.6	100	53	16	-	101
58[A]	15.5	202.3	700	300	0.5	4.4	100	46	26	-	100
68[A]	12.0	46.2	700	300	1.4	5.7	100	58	9	-	99
72[A]	5.0	63.5	800	300	1.0	8.0	100	69	4	25	104
74[A]	5.5	78.0	600	300	1.0	6.7	100	41	17	-	90
Simulated Recycle Operation											
100[B]	10.0	78.0	800	300	1.0	7.2	100 80	75 100	0 0	25 0 } *	97
102[B]	5.0	58.6	800	300	1.0	9.0	100 81	75 100	0 0	25 0 } *	89

A. 50:50 by volume mixture of Orange and CCl_4.

B. Mixture of Orange-residues and CCl_4 (See analysis in Table 3 for simulated recycle operation.) Residues are essentially HCB in CCl_4.

* The upper figures represent the conversion and selectivity of Orange to products. The lower figures represent the conversion and selectivity of residues (HCB) to products.

TABLE 3

EFFECT OF TEMPERATURE ON

EQUILIBRIUM HCB CONCENTRATIONS

TEMP °C	PRESS. psig	Cl_2/C	WT% HCB IN PRODUCT*
700	300	5	0.5×10^{-7}
700	300	6	0.15×10^{-7}
700	300	7	0.05×10^{-7}
800	300	5	0.4×10^{-4}
800	300	6	0.11×10^{-4}
800	300	7	0.04×10^{-4}

*Product excludes HCl, excess Cl_2, and $COCl_2$

The second effect, which is the most significant, is the increased rate at which the reaction proceeds as the temperature is increased. Thus, with all other conditions being fixed, an increase in temperature should permit a closer approach to equilibrium conditions. This effect is shown by the results of tests 46 and 74 in which operation at 700°C results in a lower HCB concentration than operation at 600°C.

The effect of contact time when the feed is completely converted is similar to that of temperature. Increased contact time permits a closer approach to equilibrium in a finite size reactor. The selectivity to

HCB is reduced as contact time is increased. The results of tests 54 and 58 demonstrate this effect.

These results all indicate that maximum selectivity to CCl_4 will be achieved at the higher end of the range of conditions studied. To demonstrate this effect in single pass operation, test 72 was made. The results show the highest selectivity to carbon tetrachloride and lowest selectivity to hexachlorobenzene of all the single pass tests.

Recycle operation to demonstrate that residues from the carbon tetrachloride recovery distillation could be processed effectively was also examined. The feed for these tests was made up by blending two volumes of CCl_4, with one volume of ORANGE plus residue. This feed had the composition and density as shown in Table 4. The high percentage of CCl_4 was necessary to ensure complete solubility of the HCB.

TABLE 4

SIMULATED RECYCLE OPERATION - RESIDUE CONVERSION

Percent By Weight

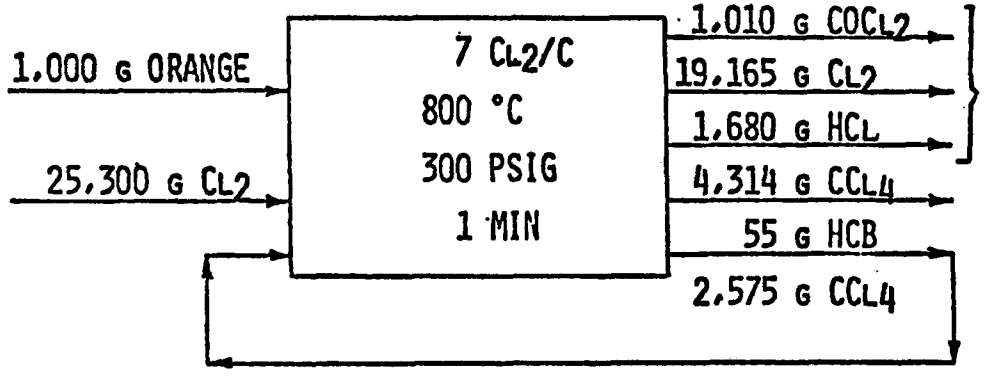
Run No.	HCB	CCl_4	ORANGE	Specific Gravity at 20°C
100	7.5	66.3	26.2	1.550
102	7.2	59.0	33.7	1.524

Operating conditions for these two tests are shown in Table 2. Several one hour off-gas samples were collected by total condensation for each of these runs. The HCB balance was then examined to determine what portion of the HCB in the feed was converted. The results for tests 100 and 102 show HCB conversions of 80 and 81 percent, respectively.

An overall material balance for recycle operation based upon the results of test 100 is shown in Figure 2. Ninety-four percent of the carbon fed to the reaction system as ORANGE was recovered in the reactor effluent. The 6 percent of carbon unaccounted for in the material balance is attributed to metering erros, work-up of samples, and weighing errors.

FIGURE 2

MATERIAL BALANCE FOR
HERBICIDE ORANGE CHLORINOLYSIS
WITH HCB RECYCLE



GAS ANALYSIS (VOL)
3.1%
82.8%
14.1%

CARBON BALANCE

IN	OUT
ORANGE - 490 G	$COCL_2$ - 123 G
	CCL_4 - 336 G
	459 G = 94%

C. Carbon Tetrachloride Product

1. Dioxin Content

Six 2 liter samples of carbon tetrachloride were recovered from the various runs made. Five of these samples represent the results attainable with single pass operation of the reaction system and the sixth sample represents the results of the recycle operation, in which distillation residues from the preceding single pass runs were incorporated in the feed to the reactor. These samples were analyzed for dioxin content by the USDA laboratory.

Their final report, which is appended (See Appendix A), shows that the chlorinolysis process effectively converts dioxin and ORANGE to carbon tetrachloride. The analytical results and run conditions are summarized in Table 5. It should be noted that each of the samples of carbon tetrachloride are composites of several runs. It should also be noted that during the early phase of the analytical program the method of analysis was capable of detecting 10 parts per trillion of dioxin in pesticide quality carbon tetrachloride. The first three samples, AD-1, -2, and -3, of carbon tetrachloride recovered from the chlorinolysis were contaminated with silicone grease from the distillation apparatus. The presence of the grease interfered with the dioxin analysis and the sensitivity of the analytical procedure was limited to 0.1 - 1.0 parts per billion dioxin. Evaluation of samples of AD-2 and -3 using combined gas chromatograph/mass spectrometry indicated no detectable dioxin.

The carbon tetrachloride recovery system was refined to eliminate

silicone grease contamination. Samples AD-4, -5, and -6 were then prepared. Gas chromatographic analysis of these samples showed "no detectable" dioxin at a sensitivity of <10 parts per trillion. The analytical results are summarized in Table 5.

Analysis for dioxin in the residues from the carbon tetrachloride distillation was complicated by the presence of hexachlorobenzene and chlorinated polybenzenes. Thus, the level of detectability of dioxin in the residues was in the parts per billion range. Analysis of the two samples of residue submitted, RD-1 and RD-4, showed dioxin levels less than 100 parts per billion. These materials would normally be recycled through the reactor. The analytical results are summarized in Table 6.

2. Toxicology

Preliminary toxicology tests of the carbon tetrachloride samples AD-5 and -6 were made on rabbits and rats. The results of these tests indicated no ill effects attributable to dioxin. A report summarizing the results of these tests is appended (See Appendix B). Further work in this area using larger animal populations is necessary to confirm these results.

TABLE 5 - DIOXIN CONTENT OF RECOVERED CCl_4

SAMPLE NO.	TEST NO.	TEMP °C	PRESS. psig	Cl_2/C	DIOXIN CONTENT, ppt GC	GC-MS
AD-1	1- 8	800	150-225	3/1-10/1	< 100	N.D.
AD-2	9-15	600-700	300	7/1-30/1	<1000	N.D.
AD-3	16-21	700	225-300	4/1-13/1	< 100	N.D.
AD-4	22-30	600-800	300	5/1- 8/1	N.D.	-
AD-5	31-37	700	300	5/1- 7/1	N.D.	-
AD-6	38-43	700-800	300	4/1- 9/1	N.D.	-

N.D. - None Detected

TABLE 6 - DIOXIN CONTENT OF RESIDUES

SAMPLE NO.	TEST NO.	TEMP °C	PRESS. psig	Cl_2/C	DIOXIN CONTENT ppm
RD-1	1-8	800	150 - 225	3/1 - 10/1	N.D.
RD-4	22-30	600-800	300	5/1 - 8/1	< 0.1

N. D. - None Detected

VI - PROCESS ECONOMICS

The 2.3 MM gallons of Herbicide ORANGE can be converted into the following products:

Carbon Tetrachloride	125.3 MM lbs
Carbonyl Chloride	26.9 MM lbs
Hydrogen Chloride	44.6 MM lbs

The gross economics were examined on the basis of a price range for each of the products and raw materials involved (See Table 7). The values used were chosen to reflect optimistic, pessimistic, and most probable prices necessary to market the products in a competitive situation, recognizing that these materials would be available only over an assumed two year period for ORANGE processing.

A plant capacity of 25 tons of herbicide per day was chosen to prepare a capital estimate. The flow scheme of this plant is shown in Figure 3. The investment for this plant was estimated to be $6.0 MM. The sales and cost of sales for each case are shown in Table 8. Also shown is the total cost for conversion of Herbicide ORANGE assuming that the plant is written off . These figures show that the total cost will be about $11 MM in the worst case, about $8 MM in the most probable case, and about $4 MM in the best case. These costs can be mitigated to some degree by erecting a plant dedicated as a regional disposal unit to be operated over a 10-year period. This would reduce the annual depreciation charges and provide the opportunity to establish a more favorable marketing position.

TABLE 7 - HERBICIDE DISPOSAL PRICING ASSUMPTIONS

PRODUCT AND RAW MATERIAL PRICES

CHLORINE	50-	55-	60	$/TON
CARBON TETRACHLORIDE	60-	75-	90	$/TON
CARBONYL CHLORIDE	0-	100-	200	$/TON
HYDROGEN CHLORIDE	(30)-*	0-	30	$/TON

*( ) Denotes negative value, i.e., cost for disposal.

FIGURE 3

HERBICIDE ORANGE DISPOSAL

TOTAL CHLORINOLYSIS

FLOW SHEET

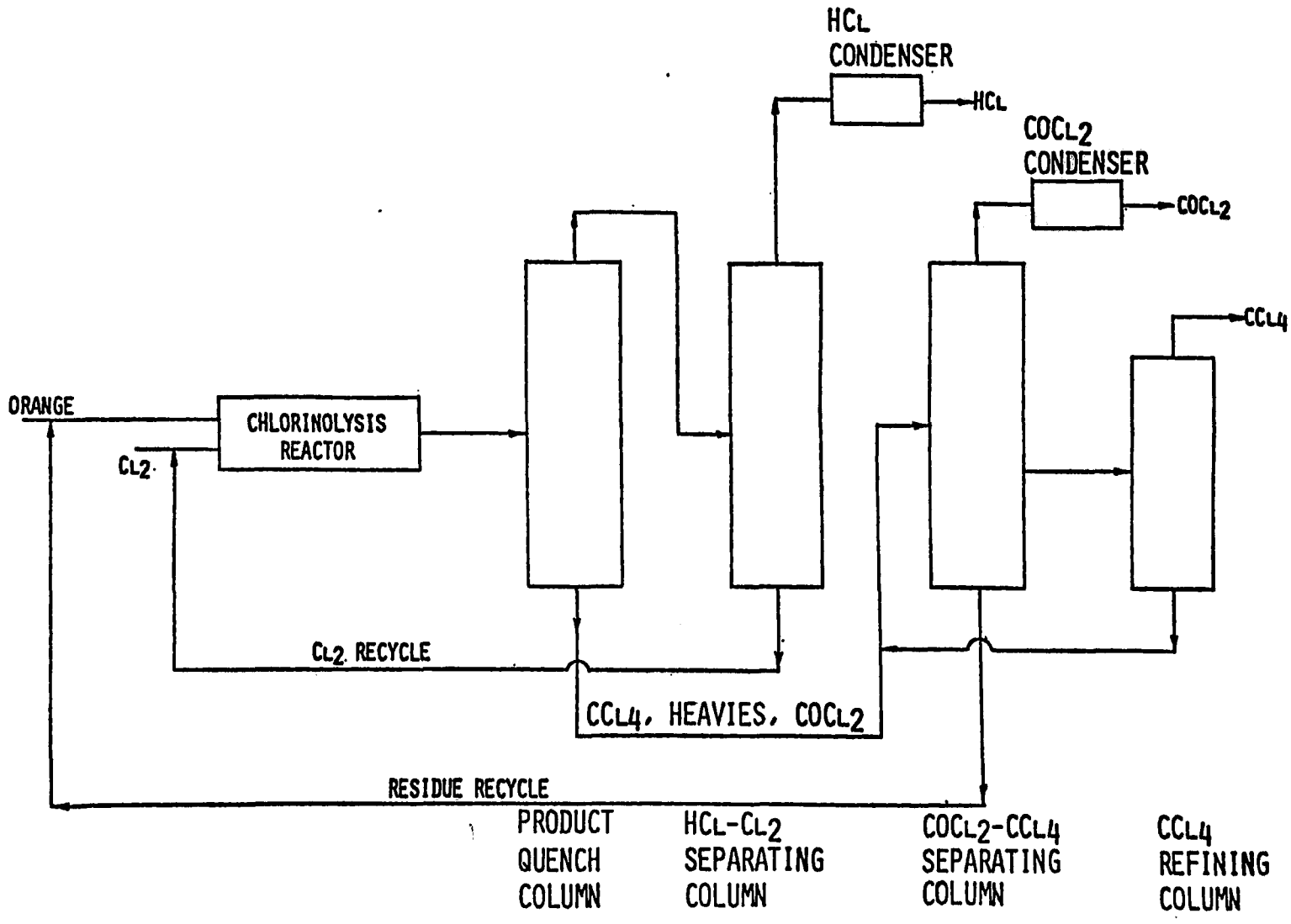


TABLE 8 - HERBICIDE ORANGE DISPOSAL

GROSS ECONOMICS TOTAL CHLORINOLYSIS ($MM)

SALES	WORST CASE	PROBABLE CASE	BEST CASE
CCl_4	3.759	4.698	5.638
$COCl_2$	0	1.245	2.690
HCl	(.669)	0	0.669
TOTAL	3.090	6.043	8.997
COST OF SALES (EXCLUDES DEPRECIATION)			
CCl_4	7.800	7.317	6.834
$COCl_2$	0.094	0.094	0.094
HCl	0.0	0.139	0.139
TOTAL	7.894	7.550	7.067
REVENUE*	(4.804)	(1.507)	1.930
CAPITAL	6.0	6.0	6.0
NET TOTAL COST	~11.	~8.	~4.

*( ) means expense, i.e., negative revenue.

Further refinement of the technology is necessary to establish a firmer estimate of the plant investment and potential usefulness as a regional disposal facility. In addition, an extensive marketing and raw material (suitable chlorocarbon waste) survey must be made before any technical decision to construct a full scale facility for ultimate write-off as a regional disposal unit can be justified.

VII - EXPERIMENTAL EQUIPMENT AND OPERATING PROCEDURE

A. Chlorinolysis Reaction System

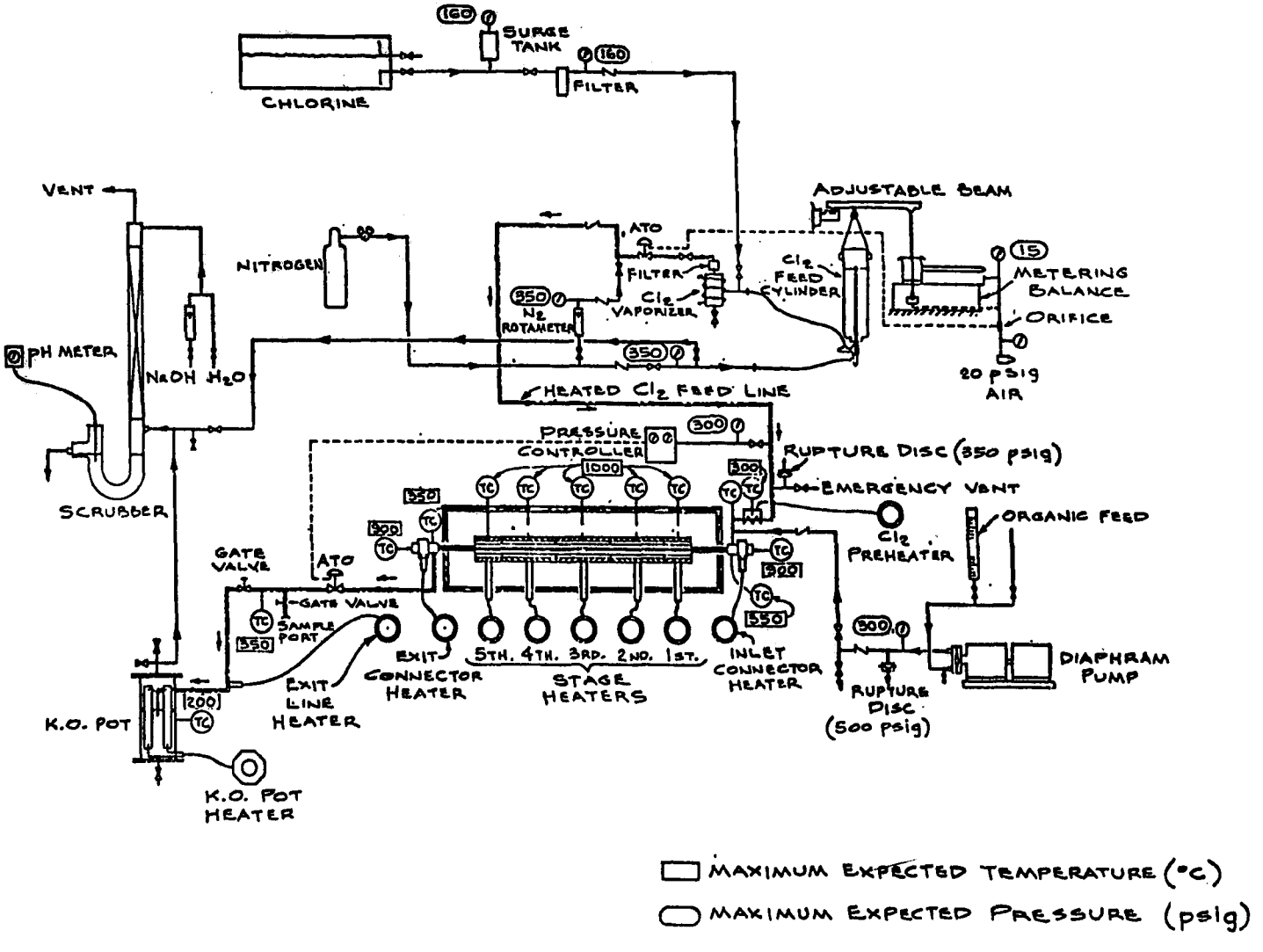
1. Equipment

The equipment for bench-scale chlorinolysis of Herbicide ORANGE, shown schematically in Figure 4, consisted of a quartz tube 1-inch in diameter by 48-inches long. Nickel stuffing boxes were used on the ends of the reactor. The entire reactor and stuffing box assembly was mounted on a Unistrut frame using standard Unistrut pipe clamps to restrain the stuffing boxes. This Unistrut frame was positioned external to an electrically powered oven used to heat the quartz reactor. Sectionalized, individually controllable, clamshell heaters were used to heat the reactor tube. Heater temperatures were monitored by thermocouples inserted through the heater walls. Two additional thermocouples were provided in a clear quartz thermowell mounted axially in the reactor to measure the reaction temperature profile.

A metering balance and air operated motor valve were used to control the chlorine flow to the reactor. Chlorine from a pressurized cylinder was vaporized, filtered and then passed through the control valve. The chlorine was then preheated to its feed temperature in an electrically heated nickel tube prior to mixing with the organic feed stream.

FIGURE 4

Bench-Scale Chloronolysis Unit



The organic materials were fed to the reactor at a controlled rate by a Whitey diaphragm metering pump with a steam heated pumping head. The flow rate of organics to the reactor was monitored by pumping out of a burette. Readings were taken over specified time intervals. When the organic feed was not normally liquid at room temperature, as in the case when hexachlorobenzene was present in the mixture, the feed vessel was changed to a heated, pressurized, calibrated glass pipe. In all cases, the feed lines were heated with electrical heaters.

The feed lines for the organics and chlorine were 1/8-inch and 1/4-inch diameter tubing, respectively. (Nickel was used for the chlorine and stainless steel for the organics.)

Products from the reactor passed through a monel control valve which maintained the reactor pressure at the desired level. The pressure sensing tap for the pressure control system was located on the chlorine feed line. The products after the control valve were either totally condensed, for samples, or sent to a caustic scrubber for disposal. When the products were sent to the scrubber, they were first passed through a nickel knockout vessel where solids, such as hexachlorobenzene, which would plug the scrubber, were removed. The knockout pot was charged with hexachlorobutadiene or carbon tetrachloride to dissolve the solids. This material was replaced periodically with fresh solvent. The spent solvent was treated with caustic. All the vent lines from the reactor were heated with electrical heaters to minimize plugging.

2. Operating Procedure

Chlorinolysis was carried out by feeding a mixture of chlorine and the organic to be investigated directly into the quartz reactor tube. The system was started up by establishing an approximate temperature profile in the reactor using the external electric heating mantles. The chlorine flow was then initiated at the desired rate and the reactor temperature readjusted. The organic flow was then established at a predetermined rate to meet a specified chlorine to carbon ratio.

An axial temperature profile was then determined using the two moveable thermocouples in the reactor centerwell. Reaction conditions and feed rates were gradually fine-tuned to the final specified conditions. Sampling was initiated following lineout at the final settings.

Sampling of the reactor effluent was accomplished by complete condensation of all components except HCl using a dry ice-isopropanol cooled condenser, as shown in Figure 5. Chlorine was refluxed into the packed stripping column to ensure recovery of all organic components. To accomplish sample collection, the sampling system was connected to the reactor outlet piping downstream from the pressure control valve. The condenser was vented back to a caustic scrubber during sampling (See Figure 4). A sample was started by simultaneously closing the valve in the knockout pot line and opening the valve to the sample port, thereby forcing all vapors into the sample collection unit. Samples were collected for a specified time, usually 15, 30, or 60 minutes, according to the organic feed rate. The longest sample period were used at the lower flow rates. After completing the collection of a sample, the

valving sequence was reversed and the reactor effluent redirected to the knockout pot. The sampling system (Figure 5) was then disconnected from the reactor vent line. The collection flask was then removed from the sampling apparatus and weighed. After weighing, the sample flask was connected to the distillation apparatus (Figure 6) and a distillation performed to remove residual hydrogen chloride, chlorine, and carbonyl chloride. All glassware used in the sample collection and distillation was taped with electrician's tape to prevent the occurence of ultraviolet initiated chlorination during sample collection and preparation.

Figure 5

Collection System

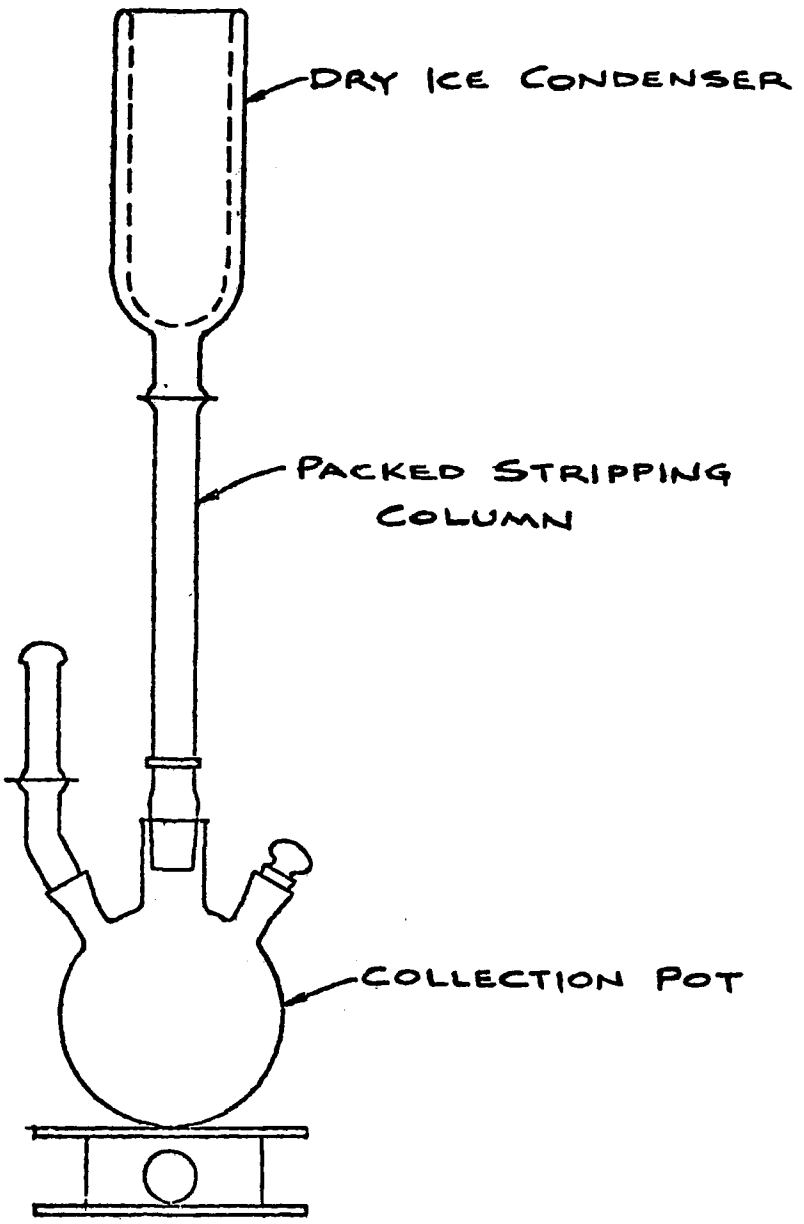
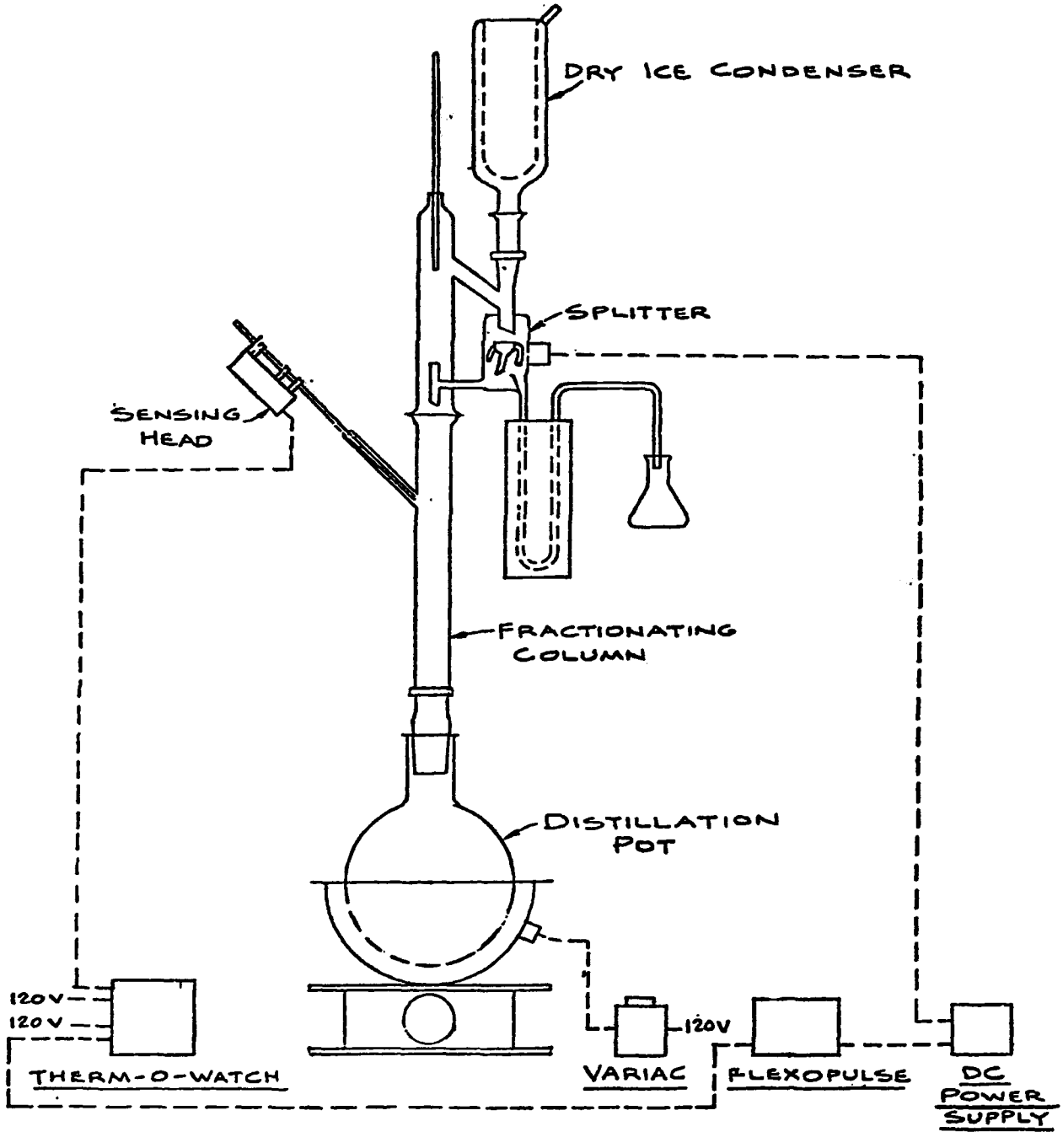


Figure 6

Chlorine Distillation System



B. Carbon Tetrachloride Recovery

1. Equipment

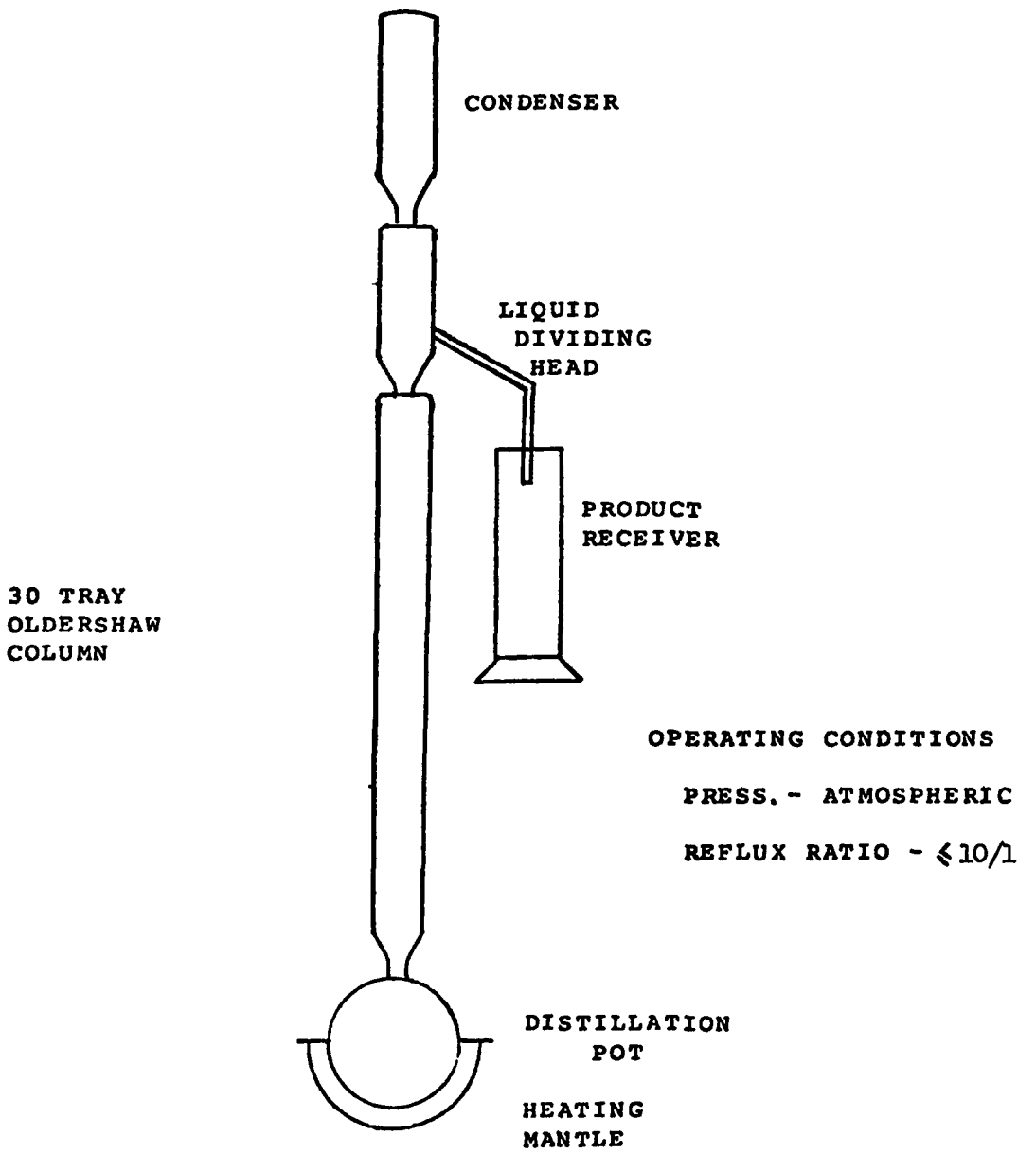
A standard 2-inch diameter by 30-tray perforated-plate Oldershaw distillation column was used for recovery of carbon tetrachloride. The column was equipped with a liquid dividing head, a 5-liter kettle, product receiver, and thermometers in both the kettle and the head. The kettle was provided with a Glas-Cal mantle for heating purposes (See Figure 7).

2. Procedure

The kettle was charged with 3 to 4 liters of degassed crude product, i.e., the pot residue from the chlorine distillation (Figure 6). Heating was initiated and cooling water applied to the condenser. The system was allowed to both come up to temperature and load the column while on total reflux. When stable conditions were established, the reflux setting was adjusted to give a reflux to make ratio of 10:1. The initial cut removed was methylene chloride which had been added as part of the product collection procedure. Following the removal of the methylene chloride, as indicated when the vapor temperature at the head had attained the boiling part of CCl_4, collection of carbon tetrachloride was initiated and continued until 2 liters of product had been accumulated. The system was then shut down and the contents of the kettle allowed to cool.

Figure 7

Carbon Tetrachloride Recovery Still



VIII - ANALYTICAL METHODS

A. General Procedure and Equipment

The liquid portion of the reaction product after degassing to remove hydrogen chloride, chlorine, and carbonyl chloride, generally consisted of carbon tetrachloride and dissolved and undissolved hexachlorobenzene in methylene chloride solvent. This necessitated a multiple step treatment of the sample to obtain an analysis. Vapor phase chromatography (VPC) was used to determine the CCl_4 and dissolved HCB content of the liquid portion of the sample. The undissolved HCB was recovered by filtration, washed with methylene chloride, air dried and weighed.

All VPC analyses were performed on a Model 5720 Hewlett-Packard gas chromatograph equipped with a 1/4-inch diameter by 10-foot long column packed with 8-percent OV210 on "Gas Chrom Q" support. The carrier gas was helium, and a thermal conductivity cell detected the components. Details of the procedure follow.

The gaseous portion of the reaction product consisted of hydrogen chloride, chlorine, and carbonyl chloride. This mixture was analyzed by the wet chemistry procedure outlined.

B. Detailed Sample Analysis

1. Analysis of Chlorinolysis Samples - Non-Gaseous Components

   Standards

   Three sets of standards were required as follows:

   a. Carbon Tetrachloride - CCl_4

(1) A standard containing 25.00 g CCl_4 diluted to 100 ml with methylene chloride.

(2) A standard containing 50.00 g CCl_4 diluted to 100 ml with methylene chloride.

b. Hexachloroethane - HCA

(1) A standard containing 6.00 g HCA diluted to 100 ml with perchloroethylene.

(2) A standard containing 12.00 g HCA diluted to 100 ml with perchloroethylene.

c. Hexachlorobenzene - HCB

(1) A standard containing 0.50 g HCB diluted to 100 ml with perchloroethylene.

(2) A standard containing 1.00 g HCB diluted to 100 ml with perchloroethylene.

No standard was used after it was three weeks old. Loss of solvent by evaporation and the possibility of contamination made standards suspect when they were used beyond this length of time.

VPC

The analysis was carried out on a 5720 dual column Hewlett-Packard gas chromatograph equipped with a 10 ft. x 0.25 in. column packed with 8-percent OV210 on "Gas Chrom Q." The carrier gas was helium, and a thermal conductivity cell detected components as they eluted.

Sample Preparation

Samples of unusual color or solid content were noted. The sample was diluted exactly to the mark with methylene chloride and well mixed

by inverting the volumetric flask ten times immediately prior to analysis. The total volume was recorded.

Sample Preparation

Samples of unusual color or solid content were noted. The sample was diluted exactly to the mark with methylene chloride and well mixed by inverting the volumetric flask ten times immediately prior to analysis. The total volume was recorded.

Analysis Procedure

a. Carbon Tetrachloride

(1) The VPC column temperature was adjusted to 80°C

Recorder - on 1/4 in/min

Filament Current - 165 ma

Helium Flow - 30 ml/min

Attenuator - 128

(2) Duplicate 10 µl shots of the 25.0 g CCl_4 standard were run. If the peak heights of CCl_4 did not agree within ± 2 chart divisions, shots were repeated until the agreement was satisfactory.

(3) Duplicate 10 µl shots of the 50.0 g CCl_4 standard were run. Again, agreement between the shots had to be ± 2 chart divisions for CCl_4.

(4) A 10 µl shot of unknown was run. If the peak remained on scale, a duplicate shot was made. If the peak went

off scale, the shot size was reduced sufficiently to keep the peak on scale. Duplicate shots were required to agree within ±3 chart divisions for CCl_4.

b. Hexachloroethane

(1) The column temperature was raised to 180°C. The attenuator was lowered to 64.

(2) The duplicate HCA standards were shot in the same manner as used in the CCl_4 analysis. Peak heights had to agree within ±1 chart division.

(3) The unknowns were run in the same manner as for the CCl_4 analysis above. Peak heights for duplicate shots were required to agree within ±2 chart divisions.

c. Insoluble Hexachlorobenzene

(1) If no insoluble HCB was present, we went directly to Step d.

(2) The insoluble HCB was filtered through a tared filter paper. The solids were rinsed with 20 ml of methylene chloride.

(3) The filtrate and washings were retained for Step d.

(4) The solids were air dried to constant weight. The solids plus paper were weighed. The difference between total weight and weight of filter paper was the weight of insoluble HCB.

d. Soluble Hexachlorobenzene

(1) The filtrate from Step c was transferred to an

appropriate sized volumetric flask and diluted to the mark. The total volume was noted.

(2) The VPC column temperature was raised to 240°C, and the attenuator lowered to 4.

(3) Duplicate shots of the 0.50 and 1.00 g HCB standards were made. Peak heights were required to agree within ± 2 chart divisions.

e. Data Treatment

Peak heights were measured by drawing the most suitable base line and dropping a perpendicular from the highest point on the peak to the base line. This perpendicular was taken as the peak height. Calculations were carried out on a Wang Calculator equipped with an 80-step card programmer. The data were entered manually on the keyboard, and the programmer carried out the manipulation of the data. Basically, the programmer automatically carried out the computation of the constants, a and b, for the equation $y = ax + b$ using the data from the standard shots. In the linear equation, y was taken to be grams of component per 100 ml of sample, while x was the observed peak height. The constants were stored and automatically recalled during the calculation of an unknown. This technique virtually eliminated computational errors, in addition to dramatically decreasing the time required. Appropriate corrections to the calculated answer were carried out manually if the standard and unknowns were in different sized volumetric flasks or if standard and unknown shot sizes were not equal.

2. Analysis of Chlorinolysis Samples - Gaseous Components

The following procedure presupposes that no interferences are present. Hexachlorobenzene and carbon tetrachloride do not interfere, but CO_2 does.

Principle

When a mixture of chlorine, carbonyl chloride, and HCl is reacted with an excess of NaOH, the following reactions will take place:

$$Cl_2 + 2\ NaOH \rightarrow NaCl + NaOCl + H_2O \quad (5)$$

$$Cl_2CO + 4\ NaOH \rightarrow 2\ NaCl + Na_2CO_3 + 2\ H_2O \quad (6)$$

$$HCl + NaOH \rightarrow H_2O + NaCl \quad (7)$$

The NaOCl is determined by an iodometric titration and calculated back to chlorine according to (5) above.

The Na_2CO_3 is determined by precipitation with $BaCl_2$, filtered off, titrated with standard HCl, and calculated as carbonyl chloride according to (6) above. Finally, total chlorine is determined with $AgNO_3$, the chlorine from carbonyl chloride and chlorine substracted, and the difference calculated as HCl.

Reagents and Materials

a. ~1N NaOH

b. 0.1N HCl

c. Phenolphthalein

d. KI

e. (1 + 1) Sulfuric acid, at room temperature

f. 0.1N Sodium thiosulfate

g. Starch solution, ~0.3%

h. 0.1 N silver nitrate

i. 0.1N thiocyanate

j. Ferric alum., 40%

k. Nitrobenzene

l. 30% Hydrogen peroxide

m. 250 ml volumetric flasks

n. Pipets (50, 100 ml)

o. Glass funnel (about 50-100 ml capacity)

p. 500 ml Erlenmeyer Flasks

q. 10% Barium chloride solution

r. Centrifuge (250 ml tubes)

Procedure

a. Make sure that the volume, pressure, and temperature of the gas mixture are known. For convenience in the equations (8-10), we have assumed 30°C and 760 mm of mercury.

b. Absorb all the gases in an excess of 1N NaOH. This is done by cooling the gas bulb with ice for 5-10 minutes, attaching a funnel with rubber tubing to one of the stopcocks, pouring the excess of NaOH on the funnel, and carefully opening the stopcock to let the NaOH into the bulb. Do not allow air into the bulb. Close the stopcock. Shake well to absorb all the mixture.

c. Transfer all the NaOH to a 250 ml flask, wash the gas bulb and add the washings to the flask. Make up to 250 ml and mix well.

d. Place 100-150 ml of water in an Erlenmeyer flask, add 4-5 g

of KI, dissolve, add an aliquot of the NaOH solution from Step c above, (50 ml suggested) mix well, add about 5 ml of (1 + 1) sulfuric acid (an excess), and titrate the liberated iodine with thiosulfate and starch. (Vol. of thiosulfate = V_1, normality = N_1, aliquot factor = f_1).

e. Transfer another aliquot of the NaOH solution from Step c (150 ml suggested) to a 250 ml centrifuge tube, add a slight excess of $BaCl_2$ solution, stopper, mix well, and centrifuge off the precipitate of barium carbonate. Carefully, pour out the liquid, add some $BaCl_2$ solution to wash the precipitate and centrifuge again. Discard the liquid.

f. Add a slight, measured excess of 0.1N HCl to the precipitate in the centrifuge tube and dissolve. Transfer all to a beaker, wash the tube, boil to expel CO_2, cool, and backtitrate the excess of HCl with 0.1N NaOH and phenolphthalein. (Volume of HCl = V_2, normality = N_2, volume of 0.1N NaOH = V_3, normality = N_3, aliquot factor = f_2, from Step e above.)

g. Transfer another aliquot of the NaOH solution from Step c above (25 ml suggested) to a 500 ml Erlenmeyer, carefully add 30% hydrogen peroxide dropwise with stirring to decompose all the hypochlorites until no more effervescence occurs where the drop falls. Then add 2-3 more drops. Mix well.

h. Add 100 ml of water, mix, and boil for 10 minutes.

i. Cool to room temperature or below, acidify with a slight excess of (1 + 1) sulfuric acid, and titrate the chlorides with silver nitrate and thiocyanate by the Volhard procedure (Volume of silver

nitrate = V_4, normality = N_4, volume of thiocyanate = V_5, normality = N_5, aliquot factor = f_3, Step g above.)

j. Calculate the milliliters of chlorine, carbonyl chloride, and hydrogen chloride in the whole sample by the following equations (30°C, 760 mm mercury):

$$\text{ml of chlorine} = 12.4 \; f_1 \; V_1 \; N_1 \text{ (See Step d)} \tag{8}$$

$$\text{ml of carbonyl chloride} = 12.4 \; f_2 \; (V_2N_2 - V_3N_3) \text{ (See Step f)} \tag{9}$$

$$\text{ml of hydrogen chloride} = 24.8 \; f_3 \; (V_4N_4 - V_5N_5) - 2 \text{ (ml of } Cl_2 + \text{ml of } Cl_2CO\text{) (See Step i)} \tag{10}$$

k. Once the above results have been calculated, determine the percentage of each component in the mixture.

Notes

a. The above equations give the milliliters of each gas in the whole gas bulb taken for analysis, at 30°C and 760 mm of mercury.

b. Results for chlorine and carbonyl chloride are considered to be reasonably accurate. Since HCl is reported by difference, it might be in error as happens in all indirect procedures.

c. The ideal gas law was assumed to be applicable to each component of the mixture.

IX - DISTILLATION RECOVERY OF n-BUTYL 2,4-DICHLOROPHENOXYACETATE

During the chlorinolysis study it occurred to the author that recovery of the n-butyl 2,4-dichlorophenoxyacetate portion of ORANGE might be achieved by distillation. Although this approach to treatment of the problem was not part of the contract, some work was done to determine if this approach was feasible.

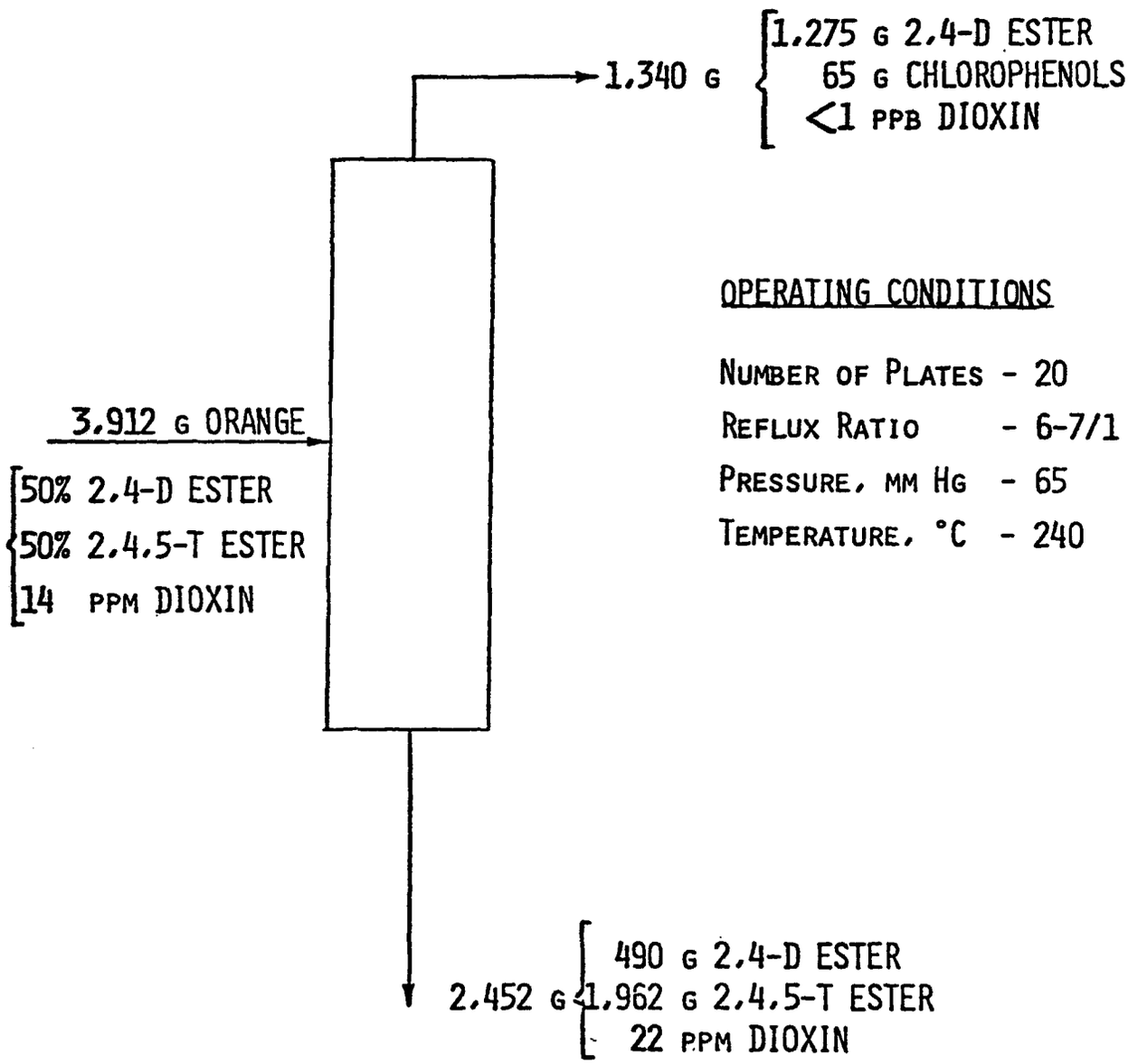
Investigation of the literature indicated that there was sufficient difference between the boiling points of the major components in ORANGE to permit a separation to be made.

Such a distillation was actually performed using an Oldershaw perforated plate column operated under vacuum. This distillation demonstrated that about 80-percent of the n-butyl 2,4-dichlorophenoxyacetate contained in ORANGE could indeed be recovered as a distillate. The tetrachlorodibenzo-p-dioxin content of the distillate was demonstrated by USDA analysis to be less than 1 part per billion. An overall material balance and operating conditions for this distillation are shown in Figure 8.

The use of a distillation procedure to pretreat ORANGE could materially reduce the volume of material to be processed by chlorinolysis and provide directly a useful and valuable herbicide in addition to the carbon tetrachloride, hydrogen chloride, and carbonyl chloride products. Economics of such a combined process for ORANGE disposal appear to be superior to those of chlorinolysis alone.

FIGURE 8

DISTILLATION OF HERBICIDE ORANGE



APPENDIX A

ANALYSIS OF CARBON TETRACHLORIDE FOR TCDD

A cooperative project with the Diamond Shamrock Company, Environmental Protection Agency and the United States Department of Agriculture.

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May 8, 1973

Final Report on Conversion of TCDD to Carbon Tetrachloride

On October 10, 1972, the Pesticide Degradation Laboratory, Agricultural Environmental Quality Institute, Agricultural Research Service, United States Department of Agriculture entered into a Reimbursable Agreement for Services between Federal Agencies (under WRU 308-1125-14761) with the Industrial Pollution Control Division, Environmental Protection Agency, to analyze a number of samples of carbon tetrachloride for dioxin content. Specifically, the agreement was to determine the quantity of 2,3,7,8-tetrachloro-dibenzo-p-dioxin (TCDD) in samples of carbon tetrachloride produced experimentally by chlorinolysis of Herbicide Orange. Chlorinolysis was conducted by the Diamond Shamrock Company of Painesville, Ohio, as part of an overall study being conducted for the U.S. Air Force for the disposal of approximately 26.5 million pounds of surplus Herbicide Orange.

This pilot study was conducted in a small chlorinolysis apparatus which causes the destruction of Herbicide Orange by reaction with chlorine gas at high temperature under moderate pressure (300 psig). If economically and chemically feasible, a large scale operation would be constructed for the conversion of 26.5 million pounds of Herbicide Orange into 125.3 million pounds of carbon tetrachloride, 26.9 million pounds of phosgene and 45.6 million pounds of hydrogen chloride.

This report covers the analysis of experimentally produced carbon tetrachloride from samples of Herbicide Orange containing approximately 14 ppm TCDD, specifically to determine the concentrations of TCDD in the carbon tetrachloride at a level of sensitivity of 10 ppt by electron capture gas chromatography.

Methods and Materials

Method for TCDD in Carbon Tetrachloride - Condense CCl_4 (0.1 - 0.5 liters) by using a 3-ball Snyder column on a 1 liter erlenmeyer flask. Gently remove final traces of CCl_4 with a N_2 stream. Take up residue in pesticide quality hexane. Transfer onto a 15 g activated alumina column (19 mm. id., prewash with 100 ml hexane, Fisher's A-540) and wash with 100 ml hexane. Elute with 100 ml 1:1 diethyl ether:hexane and condense for GLC analysis using a Kuderna-Danish concentrator. Gas chromatographic columns and conditions are described by Woolson *et al*. (1972). Recovery at 0.4 ppb ranged from 80-110% from CCl_4.

2,4-D, 2,4,5- T - Transfer an aliquot to a 1 liter separatory funnel. Add 100 ml hexane, 100 ml 5N NaOH and shake. Draw off and discard the aqueous phase and repeat the NaOH wash. Rinse with water, followed by 100 ml H_2SO_4. Shake vigorously and allow to settle. Remove H_2SO_4 and repeat treatment until H_2SO_4 is clear and colorless after sitting overnight. Wash with water, dry with anhydrous Na_2SO_4 and proceed with the alumina column as before.

Results

Sample	Composition	TCDD Content
AD-1	CCl_4	< 0.1 ppb
AD-2	CCl_4	< 1 ppb
AD-3	CCl_4	< 0.1 ppb
AD-4	CCl_4	< 10 ppt
AD-5	CCl_4	< 10 ppt
AD-6	CCl_4	< 10 ppt
AD-1	residue	None detected
AD-4	residue	< 0.1 ppm

Herbicide Orange - 1	2,4-D/2,4,5-T	15.8 ppm
Herbicide Orange - 2	2,4-D/2,4,5-T	13.6 ppm
Herbicide Orange - 3	2,4-D/2,4,5-T	14.9 ppm
2,4-D	Distilled	< 1 ppb
2,4-D	Distillation residue	22 ppm
tech. CCl_4	CCl_4	< .1 ppb
pest. quality	CCl_4	<10 ppt

Summary

The chlorinolysis of Herbicide Orange to CCl_4 appears to be a feasible means of chemical disposal. At no time were we able to detect TCDD in any sample of Herbicide Orange subjected to chlorinolysis. Fractional distillation of 2,4-D from Herbicide Orange likewise appears to be a means of recovering part of a useful mixture. No TCDD (<1 ppb) was found in the 2,4-D. Grease, apparently from joints in the distillation apparatography failed to reveal the presence of dioxins. Impurities were generally not chlorinated, but were similar in nature to silicone oils.

In conclusion, TCDD present in Herbicide Orange at a concentration of about 14 ppm was converted by the pilot chlorinolysis procedure used by Diamond Shamrock to a concentration of <10 ppt in CCl_4. Additional safety evaluations will have to be conducted by toxicologists to assess any human health hazards associated with carbon tetrachloride produced from Herbicide Orange.

Reference

Woolson, E. A., R. F. Thomas, and P. D. J. Ensor, J. Agric. Fd. Chem. 20:351, 1972.

APPENDIX B

TOXICOLOGICAL TESTS ON CARBON TETRACHLORIDE RESIDUES

by

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April 5, 1973

INTRODUCTION

Two separate toxicological studies were conducted on three CCl_4 samples received from the Pesticide Degradation Laboratory, Agricultural Environmental Quality Institute, Northeastern Region Agricultural Research Center. A study in white rabbits was designed to investigate the acnegenic activity of the test materials due to possible dioxin contamination. A post implantation exposure study in rats was designed to provide data on the prepartal, perinatal, and postpartum toxicity of the test materials.

METHODS

The samples of CCl_4 were described as follows:

Sample A - The residue from 1000 ml AD-4, 1000 ml AD-5, and 1000 ml AD-6 CCl_4 from Diamond Shamrock.

Sample B - The residue from 3000 ml technical CCl_4-MCBCX425 (this sample replaced a sample received originally that was improperly sealed).

Sample C - The residue from 3000 ml Baker Analyzed Reagent CCl_4-1512.

The actual weights of the samples received were 4.06, 2.34 and 3.42 g for Samples A, B, and C, respectively. Each residue was adjusted to a weight of 6 g by the addition of A.C.S. Spectroanalyzed CCl_4 from Fisher. All subsequent references to dosage and formulations in this report will indicate quantities of this "adjusted residue." These adjusted residues were formulated as 30% W/V solutions in acetone for

the rabbit study, and as 2% W/V solutions in peanut oil for the rat study. Sample A contained a grayish sediment that imparted an opaque appearance to the peanut oil formulation.

The 2,3,7,8 tetrachlorodibenzo-p-dioxin (Dow Chemical) was formulated to final concentrations of 2.51 ug/ml in acetone and 2.51 ug/ml in 30% CCl_4 in acetone solution. Originally the experimental design called for a 3 ug/ml solution, but we were unable to dissolve this amount in acetone. The CCl_4 used in the control treatments was A.C.S. Spectroanalyzed CCl_4 (Fisher) from our laboratory.

Twelve weanling male white rabbits about 5 weeks old and weighing 633-830 g were divided into 4 groups of 3 rabbits each. Each ear that was treated with test or control material received a total volume of 1 ml of formulation (0.333 ml/day for 3 consecutive days). Each rabbit received a total dose of 300 mg adjusted residue of samples A, B or C on the left ear. Control treatments of CCl_4/acetone and acetone only were applied to the right ear of Groups 1 and 2, respectively. The right ear of Group 3 received no treatment. Group 4 received dioxin/acetone on the left ear and dioxin/acetone/CCl_4 on the right ear for a total dose of 5.02 ug (See Table 1 for details of dosage). Before the first dose each ear was swabbed with 70% alcohol. The materials were applied with a hypodermic needle and syringe as uniformly as possible to the inner surface of the ear. The rabbits were observed daily for any response to the treatments. Eighteen days after the last dose the rabbits were weighed and sacrificed. Organs were examined grossly and the livers weighed, fixed in formalin and studied microscopically.

In the rat study Sherman strain SPF female rats 90-100 days old were pair-mated with young adult males. When a copulatory plug was observed insemination was verified by microscopic inspection of a vaginal smear. When 32 females had been inseminated they were distributed into 4 groups of 8 rats each. Counting the day of insemination as day 0 the rats were dosed daily by stomach tube on days 7 through 15 of pregnancy. Each rat received 100 mg/kg/day of adjusted residue of Samples A, B, or C for a total of 900 mg/kg. Control rats received peanut oil only. Records of offspring were maintained through weaning (21 days). Offspring from several litters in each group were autopsied at weaning and examined grossly. Fourteen days after her litter was weaned each dam was sacrificed, examined grossly, implantation sites counted and liver weighed and fixed in formalin for further study.

RESULTS

One rabbit in Group 2 (Sample B) developed faint reddish areas on the left ear about 1 week after the last dose. One rabbit in Group 4 (dioxin) developed similar areas on both ears. The condition persisted for about 4 days and then was no longer noticeable. One rabbit in Group 1 (Sample A) and one rabbit in Group 3 (Sample C) developed diarrhea and died after 2 and 1 applications, respectively. Diarrhea and post weaning mortality is not uncommon in young rabbits and the deaths were probably not dose related. All of the rabbits in Group 4 (dioxin) exhibited noticeably depressed growth rates.

Jones and Krizek (1962) reported grossly visible acneform responses

in 5/7 adult rabbits treated with 3 ug of 2,3,7,8 tetrachlorodibenzo-p-dioxin on the inner surface of the ear, but found no systemic toxicity.

No well defined topical response was seen in ears of rabbits in any group in our study. However, the liver proved to be a sensitive indicator of dioxin toxicity. Compared to the other groups the livers from rabbits in Group 4 (dioxin) were markedly enlarged. Two livers had grossly visible lesions and all 3 livers had histological changes when examined microscopically. The liver weights and pathology are presented in Table 2. All livers of animals dosed with Samples A, B, and C were normal grossly and microscopically.

Microscopic examination of the livers of rabbit dosed with dioxin showed anisocytosis and hypertrophy of the liver cells throughout the sections. The cytoplasm of the hepatocytes was vacuolated or had a foamy appearance. Some liver cells contained a light brown pigment and inclusions. Many multinucleated cells were also seen. Slight interstitial fibrosis was also present. Two of three livers examined showed also foci of necrosis surrounded by fibrosis and multinucleated giant cells. Organisms were not demonstrated within the necrotic lesions by microscopic examination.

The reproduction and survival of pups in the rat study are summarized in Table 3. No significant difference in the number, size, or condition of pups was observed. The overall survival rate (89%) was

slightly reduced in rats dosed with Sample A, however, this falls within the lower range of normal for our rats. Most mortality in this group occured before the fourth day.

The liver weights of the dams are presented in Table 4. No difference in weight or gross appearance was observed. The livers of these rats were also normal on microscopic examination.

CONCLUSION

The mean total dose of 2,3,7,8 tetrachlorodibenzo-p-dioxin which caused changes in the rabbit liver was 7.05 ug/kg body weight. The mean total doses of Samples A, B, and C were 434, 444, and 464 mg/kg body weight, respectively. If the dioxin is present in the material from which Sample A was derived our studies indicate a concentration of less than 0.029 ug/g or less than 0.047 ug/ml of original material.

It is emphasized that the rabbit test is specific for the presence of 2,3,7,8 tetrachlorodibenzo-p-dioxin or less toxic materials that elicit the same response. Because of limited quantities of test material both the rabbit and rat tests utilized small numbers of animals. Detailed characterization of the toxicity of the test material would require additional tests and larger numbers of animals.

REFERENCES

E. Linn Jones, M.D. and Helen Krizek, Ph.D., "A Technique for Testing Acnegenic Potency in Rabbits, Applied to the Potent Acnegen, 2,3,7,8

Tetrachlorodibenzo-p-Dioxin," Journal of Investigative Dermatology, 39, pp. 511-517 (1962).

ACKNOWLEDGMENTS

The following individuals contributed significantly to the test project: Mr. Ralph Linder of RTP was responsible for the animal dosing and Dr. Robert Moseman, also of RTP, was instrumental in the preparation of some of the solutions.

Table 1. Dosage rates for rabbits dosed with CCl_4 samples and 2,3,7,8 tetrachlorodibenzo-p-dioxin (3 rabbits per group).

Group	Test material	Treatment***		Dose	
		Left ear	Right ear	Daily	Total
1	A	30% Sample A in acetone	30% CCl_4 in acetone**	100 mg*	300 mg*
2	B	30% Sample B in acetone	Acetone	100 mg*	300 mg*
3	C	30% Sample C in acetone	No treatment	100 mg*	300 mg*
4	Dioxin	2.51 ug/ml in acetone	2.51 ug/ml in CCl_4/ acetone**	1.67 ug	5.02 ug

* Adjusted residue.

** A.C.S. Spectroanalyzed CCl_4 (Fisher).

*** 0.333 ml/day for 3 consecutive days to inner surface of ear.

Table 2. Body Weight, liver weight, and autopsy findings of rabbits sacrificed 18 days after last dose.

Test material	Rabbit No.	Body Weight Original (gm)	Body Weight Final (gm)	Liver Weight (gm)	Liver Weight (% of body wt.)	Liver Wt. (mean) (gm)	Liver Wt. (mean) (% of body wt.)	Gross appearance at autopsy	Microscopic examination
Sample A*	1942	686	1390	50.0	3.60				
	1943	830	Died	-	-	53.8	3.74	Normal	Normal liver
	1944	698	1484	57.6	3.88				
Sample B*	1945	679	1423	52.0	3.65				
	1946	662	1312	38.6	2.94	47.3	3.34	Normal	Normal liver
	1947	688	1496	51.3	3.43				
Sample C*	1948	662	1649	65.7	3.98				
	1949	633	1491	54.9	3.68	60.3	3.83	Normal	Normal liver
	1950	692	Died	-	-				
Dioxin**	1951	711	1161	79.5	6.85			2 livers had whitish lesions up to 3 cm. in diameter.	3/3 enlarged hepatocytes, some multinucleated. Foamy or vacuolated cytoplasm. Light brown pigment, in some liver cells inclusions, slight interstitial fibrosis 2/3 foci of necrosis surrounded by fibrosis.
	1952	672	1200	66.8	5.57	71.9	6.08		
	1953	757	1194	69.5	5.82				

* 100 mg adjusted residue/rabbit/day on left ear for 3 days.
** 0.837 ug 2,3,7,8 tetrachlorodibenzo-p-dioxin/rabbit/day on each ear for 3 days.

Table 3. Reproduction and survival of pups from dams dosed orally on days 7-15 of pregnancy.

Test Material	Females dosed	Mean Implantation Sites	No. of litters		Average litter size		Total pups per group Born(found)		Alive at		Survival (%)	Average body wt. Birth (gm)	Weaning (gm)
			Born	Weaned	Birth	Weaning	Dead	Alive	4 days	weaning			
Peanut Oil (control)	7**	14.3	7	7	12.7	12.6	2	89	88	88	98.9	6.0	32.7
Sample A*	8	12.8	8	8	11.4	10.1	1	91	82	81	89.0	5.9	33.2
Sample B*	8	14.0	8	8	12.0	11.0	1	96	88	88	91.7	5.7	34.2
Sample C*	8	13.1	8	8	12.1	11.6	1	97	94	93	95.9	5.8	33.5

*100 mg/kg/day of adjusted residue.
**One rat died from dosing injury, not used in calculations.

Table 4. Liver weights from dams dosed orally on days 7-15 of pregnancy.**

Test material	No. of rats	Liver Wt. (gm) Mean ± S.E.	Liver wt. (% of body wt.) Mean ± S.E.
Peanut oil (control)	7	10.66 ± 0.217	3.66 ± 0.036
Sample A*	8	10.51 ± 0.518	3.57 ± 0.152
Sample B*	8	10.86 ± 0.313	3.65 ± 0.049
Sample C*	8	10.63 ± 0.465	3.49 ± 0.090

* 100 mg of adjusted residue/kg/day
** Rats sacrificed 14 days after weaning.

APPENDIX C

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

MEMORANDUM OF AGREEMENT

between

ENVIRONMENTAL PROTECTION AGENCY

and

U.S. AIR FORCE LOGISTICS COMMAND,
WRIGHT PATTERSON AIR FORCE BASE
DAYTON, OHIO

for a project covering the Research Program:

DETOXIFICATION AND DISPOSAL OF AGENT "ORANGE"

1. Purpose

The objective of this agreement is the development of a laboratory program to evaluate the practicality of the application of chlorinolysis for the disposal of Agent ORANGE. The investigation will also include a verification of the destruction of the teratogenic impurity "dioxin" present in the 2,4,5-T ester component. Information and data obtained in this research will be utilized by the EPA to ascertain whether the proposed concept (1) can be applied and used as a viable means of disposal of stockpiles of this defoliant and (2) can contribute significantly towards solving the dilema of disposal of biorefractory chlorinated hydrocarbon residues that exists in the Petrochemical Industry today.

2. Services to be provided

The Industrial Pollution Control Section (IPCS), Applied Science and Technology Branch, Technology Division, Office of Research and Monitoring, Environmental Protection Agency will manage the research

program for the U.S. Air Force. The Diamond Shamrock Corporation, Painesville, Ohio, will conduct on their premises, the laboratory evaluation of the chlorinolysis concept for destruction of Agent ORANGE and detoxification of the dioxin impurity present therein. It is understood that the USAF will supply at least one 55 gallon drum of Agent ORANGE for this investigation. This program to demonstrate the feasibility of the chlorinolysis concept will entail 9 man-months of effort for completion (2 calendar months) and will cost $35,000. Verification of the fate of dioxin during the chlorination process will be conducted by the U.S. Department of Agriculture (USDA) team (Dr. Philip Kearney, Leader) at Beltsville, Md. at a nominal charge of $100 per sample. It is envisioned that 50 to 100 samples will be provided to the USDA by the Diamond Shamrock Corporation, thus requiring an additional $5,000 - $10,000.

The EPA-IPCS will prepare a final report containing all data collected, together with conclusions and recommendations. It is understood that proprietary information is to be disclosed, and as such, is considered FOR OFFICIAL USE ONLY.

3. Period of agreement.

This agreement is effective for a three (3) months from date of acceptance of both parties.

4. Names, titles, addresses of respective project officers:

Mr. Paul E. Des Rosiers
Staff Engineer
Industrial Pollution Control (RD-679)
Environmental Protection Agency
Washington, D.C. 20460
(202) 426-4171

Mr. Carlton W. Carter
HqUSAF (LGSKE)
Washington, D.C. 20330
(202) 697-8635

Dr. Philip C. Kearney
Pesticide Degradation Laboratory
Agricultural Environmental Quality Institute
Agricultural Research Service
Agricultural Research Center
Beltsville, MD 20705
(301) 344-3082

5. Funding arrangement

The USAF has transferred funds in the amount of $45,000 (see Enclosures 1 and 2) to the EPA-IPCS for the delivery of information as outlined in the Research Proposal (reference, letter from ARRT to Col. O.J. Sundstrom, HqUSAF, AF/LGS, Pentagon, dated July 10, 1972). If the EPA-IPCS determines that work called for in this agreement will be delayed, it will notify the USAF in writing immediately. Billing will be accomplished by the EPA to the U.S. Air Force on Standard Form 1080.

6. Authorization

Economy Act of 1932 as amended (31 U.S.C. 686)

Federal Water Pollution Control Act as amended (33 U.S.C. 466 et seq.)

7. Signature

Agreed: 6 SEP 1972

W. H. Fairbrother,
Brigadier General, USAF
Deputy Chief of Staff,
Distribution
Department of the Air Force
U.S. Air Force Logistics Command
Wright- Patterson Air Force Base
Dayton, Ohio 45433

Leland D. Attaway
Deputy Assistant Administrator for Resea
Office of Research & Monitoring
Environmental Protection Agency

Enclosures

DEPARTMENT OF THE AIR FORCE
HEADQUARTERS AIR FORCE LOGISTICS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433

10

REPLY TO ATTN OF: DS

28 JUL 1972

SUBJECT: Disposition of Herbicide Orange

TO: SAAMA/DS

1. The attached HQ USAF/LGSX letter, 18 Jul 1972, is forwarded for immediate action as requested in paragraph 3 thereof.

2. R&M funds under EEIC 586 in the amount of $45,000 will be provided your installation in the August change to the Operations Operating Budget (OOB).

3. It is recommended that obligation authority be provided to EPA in two increments of $35,000 and $10,000 each as discussed 27 Jul 1972 between Mr. G. Niska, SAAMA/DSM and Mr. S. Keaton of this office.

FOR THE COMMANDER

W. H. FAIRBROTHER, Brigadier General, USAF
Deputy Chief of Staff, Distribution

1 Atch
HQ USAF/LGSX Ltr,
18 Jul 1972

Cy to: HQ USAF/LGSX, w/atch
SAAMA/SF, w/o atch

PRIDE IN THE PAST FAITH IN THE FUTURE

OBLIGATION AUTHORITY	ADVICE NUMBER S73-59	CHANGE NUMBER

INSTRUCTIONS TO RECEIVING OFFICE

Duplicate copy hereof should be returned to the issuing office not later than the date specified above, or as soon as all obligations hereunder have been completed, whichever occurs first. Obligations incurred will be listed on the reverse.

A copy of each obligation document will be transmitted to the issuing office coincident with incurrence of the obligation. A copy of each paid voucher will be transmitted direct to the issuing office by the accounting and finance officer, and documents submitted to the accounting and finance office should contain instructions to that effect. The name, address, and accounting and disbursing station number of the issuing office and the number of the obligation authority will always be shown on all obligation and expenditure documents, the obligation authority number being shown in parentheses immediately after the document number.

When items are furnished from stock for which reimbursement is required, Standard Form 1080 will be prepared and processed by your office, charging the funds cited below.

ISSUED TO (Name, address, and accounting and disbursing station number of receiving office)	ISSUED BY (Name and address of issuing office)
United States Environmental Protection Agency Attn: Paul E. Deskosiers Washington, D C 20460	SAAMA/DSRA Kelly AFB TX 78241

YOU ARE HEREBY AUTHORIZED TO INCUR OBLIGATIONS UNTIL 9 November 1972 FOR THE PURPOSES AND WITHIN THE AMOUNT ($) STATED BELOW.

THE FUNDS CITED ARE PROPERLY CHARGEABLE AND HAVE BEEN RESERVED BY THIS OFFICE.

SIGNATURE, TYPED NAME, GRADE, AND TITLE OF INITIATING OFFICER (Optional)	SIGNATURE, TYPED NAME, AND GRADE OF ACCOUNTING AND FINANCE OFFICER (Required)
GS-12 Chief, Surveillance & Support Branch Directorate of Distribution	Catherine E. Solomon Funds Certifying Officer

DATE ISSUED	APPROPRIATION SYMBOL	MAJOR ACCOUNTING CLASSIFICATION: ALLOTMENT SERIAL	PROJECT	OBJECT	ACCOUNTING AND DISBURSING STATION NUMBER	AMOUNT[1]
10 Aug 1972	5733400	303 6300	28486F586		8504300	$35,000

AUTHORIZED PURPOSES AND DESCRIPTION

To conduct a study and perform tests for the disposal of Herbicide Orange. See attached SAAMA/DS letter, 7 Aug 1972, Disposition of Herbicide Orange, with attachments.

1 Atch
DS Ltr, 7 Aug 72, w/Atch

Encl 1

[1] Obligations WILL NOT exceed the amount of this authority.

AF FORM AUG 59 405 PREVIOUS EDITIONS OF THIS FORM MAY BE USED.

OBLIGATION AUTHORITY	ADVICE NUMBER S73-61	CHANGE NUMBER

INSTRUCTIONS TO RECEIVING OFFICE

Duplicate copy hereof should be returned to the issuing office not later than the date specified above, or as soon as all obligations hereunder have been completed, whichever occurs first. Obligations incurred will be listed on the reverse.

A copy of each obligation document will be transmitted to the issuing office coincident with incurrence of the obligation. A copy of each paid voucher will be transmitted direct to the issuing office by the accounting and finance officer, and documents submitted to the accounting and finance office should contain instructions to that effect. The name, address, and accounting and disbursing station number of the issuing office and the number of the obligation authority will always be shown on all obligation and expenditure documents, the obligation authority number being shown in parentheses immediately after the document number.

When items are furnished from stock for which reimbursement is required, Standard Form 1080 will be prepared and processed by your office, charging the funds cited below.

Mail Obligations to 2851ABGp/ACFSB-1

ISSUED TO (Name, address, and accounting and disbursing station number of receiving office)	ISSUED BY (Name and address of issuing office)
United States Environmental Protection Agency ATTN: Paul E. DesRosiers Washington DC 20460	SAAMA/DSRA Kelly AFB TX 78241

YOU ARE HEREBY AUTHORIZED TO INCUR OBLIGATIONS UNTIL 9 Nov 1972 FOR THE PURPOSES AND WITHIN THE AMOUNT ($) STATED BELOW.

THE FUNDS CITED ARE PROPERLY CHARGEABLE AND HAVE BEEN RESERVED BY THIS OFFICE.

SIGNATURE, TYPED NAME, GRADE, AND TITLE OF INITIATING OFFICER	SIGNATURE, TYPED NAME, AND GRADE OF ACCOUNTING AND FINANCE OFFICER (Required)
ARTHUR H. MATHIS GS-12 Chief, Surveillance & Support Branch Directorate of Distribution	GENEVIEVE R. SCLERANDI Funds Certifying Officer 2851ABGp/ACFSB-1

DATE ISSUED	APPROPRIATION SYMBOL	MAJOR ACCOUNTING CLASSIFICATION				AMOUNT[1]
		ALLOTMENT SERIAL	PROJECT	OBJECT	ACCOUNTING AND DISBURSING STATION NUMBER	
10 Aug 1972	5733400	303 6306 28	86F586		S504300	$10,000

AUTHORIZED PURPOSES AND DESCRIPTION

To conduct sampling tests as cited in US Environmental Protection Agency letter, 10 Jul 1972, addressed to HQ USAF AF/LGS. Copy filed with Obligation Authority (Advice No. S73-59) issued by SAAMA/DSRA, 10 Aug 1972.

Encl 2

[1] Obligations WILL NOT exceed the amount of this authority.

AF Form 105 PREVIOUS EDITIONS OF THIS FORM MAY BE USED

SELECTED WATER RESOURCES ABSTRACTS

INPUT TRANSACTION FORM

1. Report No. 2. 3. Accession No. W

4. Title

STUDY OF FEASIBILITY OF HERBICIDE ORANGE CHLORINOLYSIS

5. Report Date

6.

8. Performing Organization Report No.

7. Author(s)

Lavergne, Edward A.

10. Project No.

9. Organization

Diamond Shamrock Corporation
T. R. Evans Research Center
Painesville, Ohio 44077

11. Contract/Grant No.

68-01-0457

13. Type of Report and Period Covered

12. Sponsoring Organization

15. Supplementary Notes

Environmental Protection Agency report number, EPA-600/2-74-006, July 1974

16. Abstract

A process termed chlorinolysis (exhaustive chlorination) was applied to samples of USAF Herbicide ORANGE. The ORANGE (50/50 volume mixture of the n-butyl esters of 2,4-D and 2,4,5-T) contained a production impurity called dioxin - a powerful teratogen.

The research objective was to demonstrate the feasibility of converting such herbicides into marketable products, namely, carbon tetrachloride (CCl_4), carbonyl chloride ($COCl_2$), and hydrogen chloride (HCl), while destroying any dioxin present.

Bench scale (100 g/hr) chlorinolysis of ORANGE was evaluated over a range of reactor conditions. The critical reaction parameters were found to be: chlorine to carbon ratio (4.4 - 7.2); temperature (600 - 800°C); pressure (225 - 300 psig); and retention time (0.5 - 1.0 minute).

Thermodynamic analysis had indicated that CCl_4, hexachlorobenzene (HCB), and chlorine (Cl_2) would exist in equilibrium at the reaction conditions utilized. Because of the balance required between reaction rate (reactor size) and HCB content of the effluent, recycle of unconverted HCB from the product recovery system was found to be necessary. Recycle tests indicated that single pass HCB conversion rates of 80% could be realized.

17a. Descriptors

Chlorinolysis, Herbicide ORANGE, Exhaustive Chlorination, Dioxin, 2,4-D, 2,4,5-T, Chemical Conversion, Fractionation/Distillation, Chlorinated Still Bottom Residues

17b. Identifiers

17c. COWRR Field & Group

18. Availability

19. Security Class. (Report)

20. Security Class. (Page)

21. No. of Pages

22. Price

Send To:

WATER RESOURCES SCIENTIFIC INFORMATION CENTER
U.S. DEPARTMENT OF THE INTERIOR
WASHINGTON, D. C. 20240

Abstractor Dr. R. R. Swank

Institution SERL, Athens, Georgia

WRSIC 102 (REV JUNE 1971)