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THE EFFECT OF GAMMA RADIATION
ON SOME CHEMICAL REACTIONS
OF POSSIBLE INDUSTRIAL IMPORTANCE

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For the past four years this laboratory has been investigating chemical reactions promoted by gamma radiation. The work has been carried out as part of a broad program to find uses for the large amounts of radioactive fission products that are expected to be made available from the operation of nuclear reactors. However, because development programs for packaging and shipping fission product sources have not been completed, the studies have been conducted with artificial cobalt-60.

Two cobalt-60 sources of gamma radiation have been employed in this investigation. The first source is an aluminum-clad hollow cylinder of cobalt about 3.5 cm. in diameter and 35 cm. long. It was activated by neutron radiation in the pile of the Brookhaven National Laboratory and was given a nominal rating of 1000 curies. Later calibration indicated its true radiation strength to be about one-third this value. The cylinder of cobalt was mounted in a heavy lead container so that objects to be radiated were simply placed in the center of the cylinder. This permitted only small volumes to be treated at any one time. A second cobalt-60 source was installed which made provision for radiation of large volumes of material. This source consists of 100 aluminum-clad rods of cobalt about 0.6 cm. in diameter and 25 cm. long. These rods are mounted in two close concentric circles in an aluminum rack of about 15 cm. internal diameter. The whole unit is stored under water about 5 meters deep. When it is to be used, the unit is raised by remote control into a chamber where the various materials to be radiated have been stacked. The radiation chamber is constructed with concrete walls about 1.2 meters thick. The cobalt rods were activated in the pile at Chalk River, Canada, and were nominally rated at 10,000 curies; though, as with the other source, calibration indicated the radiation strength to be about one-third this amount.

In selecting chemical reactions to be studied in the presence of gamma radiation, emphasis has been placed on those which might have commercial applications. When a reaction was found to be promoted only minutely by radiation, it was discarded in favor of other reactions that proceeded vigorously. Two classes of chemical reactions that result in appreciable yields of products in the presence of gamma radiation are (1) polymerizations, and (2) chlorinations. In the former category this paper presents information on the polymerization of ethylene. In the latter category the chlorination of a series of aromatic compounds is considered. Also, the economics of a plant to chlorinate benzene are presented and a

comparison is made between the use of ultraviolet and gamma radiation.

I. POLYMERIZATION OF ETHYLENE

The gas-phase polymerization of ethylene has been studied in the presence of alpha radiation¹⁶, ultraviolet radiation^{2, 12}, and gamma radiation^{9,13,14,15}. The data presented here were taken in a continuation of the work of Lewis^{13,14}, and cover a pressure range of 50 to 100 atm. and temperatures from 6 to 220° C.

(a) Experimental Work

The high pressure stainless steel reaction vessel of Lewis was used in all runs. This reactor, shown in Figure 1, could be maintained at any desired high temperature by a set of electrical resistance heaters which fitted around the outside. A uniform procedure of loading and cleaning was followed in each test. The reactor was sealed at the flanges and pressure tested with nitrogen at 1000 psi. for 12 hours. The nitrogen was vented and the reactor evacuated, after which ethylene gas was charged at room temperature. The loaded vessel was placed in the radiation chamber and controlled to the desired temperature before raising the ten-kilocurie cobalt-60 source to initiate the reaction. Runs in the one-kilocurie source could be made only at room temperature as there was no room for the electrical heaters on the outside of the reactor. During the runs, pressure and temperature measurements were made at various intervals. At the conclusion of the run the reactor was removed from the radiation field and the excess ethylene was vented. The flanges were opened and the polymer product was removed mechanically and weighed. The reactor was cleaned by washing with boiling xylene, acetone, and distilled water. The ethylene was about 97% pure with a gas analysis showing it to contain 1.7% N₂, 0.8% C₅H₁₂, 0.37% CO₂, 0.05% CO, and 0.02% O₂. The amount of ethylene charged to the reactor was determined from the measured temperature, pressure, and volume by means of the thermodynamic properties of ethylene²⁰. The radiation received by the reactor during a run was calculated by the dosimetry techniques of Lewis, et.al.^{14,15}.

(b) Product Yields

A summary of the reaction conditions and the polymer yields is given in Table I. White, curdy, solid polymers were formed at reaction temperatures from 6 to 130° C. A white wax formed at about 160° C. and above this the product was an opaque liquid that separated into two layers after standing awhile. The top layer was colorless and the bottom layer contained a finely divided solid. The yield of polymer is presented as the A value¹³, gm. moles of ethylene reacted/ (metric ton of ethylene charged) x (megarep of gamma radiation). The rep is based on the absorption of 93 ergs per gram. From the scatter of the data it is difficult to determine the effect

of temperature on the yield since largest yields were at 39 and 217° C.

TABLE I. PRODUCTS FROM THE IRRADIATION OF ETHYLENE

Run	Reaction Temp. °C.	Reaction Pressure Ave. psia	Total Radiation, Dose Megarep.	Radiation Yield A*	Polymer State	Tensile Strength Psi
839	6	755	4.20	1340	Solid	3050
833	8	985	5.46	1630	Solid	3075
800	13	1145	4.10	1530	Solid	3350
801	13	875	5.28	2270	Solid	3100
807	39	1380	4.47	3040	Solid	2520
808	88	1325	1.90	490	Solid	
812	90	1300	5.85	433	Solid	
845	132	1700	4.05	955	Solid	
712	160	1490	2.76	945	Wax	
848	190	1125	2.88	1300	Liquid	
814	217	1100	3.77	4030	Liquid	
813	220	1175	4.86	1400	Liquid	

$$*A = \frac{\text{gm moles reacted}}{(\text{metric ton charged}) (\text{megarep})}$$

(c) Evaluation of the Polymer Products

Melting points of the solid and waxy products were measured on a melting point bar³. Melting points of the liquids were observed in small tubes of the polymer which were allowed to warm up after being frozen in a dry ice bath. Because each product is a composite of polymers of varying molecular weights, a range of melting points was found. The points at which melting could first be detected have been plotted as a function of the reaction temperature in Figure 2.

Solid products produced in appreciable quantity were pressed in a one-compartment mold at 1500 psi and 150° C. for 5 minutes. Specimens were punched from the molded polymer and placed in an Instron Tensile Test Machine. The measured tensile strengths are presented in Table I. Densities of the solids were determined by the Archimedes principle while those of the liquids were measured by weighing in a calibrated pipette. Figure 3 shows the densities as a function of the reaction temperature. Crystallinities or the degree to which the molecules are arranged in parallel positions were determined from the densities¹¹, and these are also shown in Figure 3.

Melt viscosities of solid products were obtained in a parallel plate plastometer at about 137° C. Viscosities of liquid products were determined in a modified Ostwald pipette. Molecular weights were estimated⁴

from the viscosities and are shown in Figure 2 as a function of reaction temperature. The molecular weights are not considered very accurate, but the general trend is indicated.

TABLE II. CHLORINATION OF AROMATIC COMPOUNDS WITH GAMMA RADIATION

Run	Aromatic Chlorinated	Temp. Reaction °C.	Dose Rate Kilo-rep/hr	Cl ₂ add. moles/liter	Cl sub. moles/liter	Average G* addition	Average G* _{substitution}
1	30% Benzene	20	61.0	35.20	---	234,000	---
2	20% Benzene	20	61.0	32.60	---	252,000	---
3	10% Benzene	20	61.0	33.30	---	90,000	---
4	30% Benzene	-10	61.0	13.70	---	90,000	---
5	10% Benzene	-10	61.0	32.70	---	57,000	---
6	Toluene	20	14.0	17.42	7.54	523,000	226,000
7	Toluene	- 5	14.0	14.12	6.59	900,000	420,000
8	Toluene	35	14.0	10.35	6.12	812,000	480,000
9	Toluene	20	None	3.23	.85	---	---
10	Xylene	20	13.7	5.90	3.48	462,000	272,000
11	Xylene	- 5	13.7	7.45	2.94	448,000	177,000
12	Xylene	20	None	3.20	2.63	---	---
13	Mesitylene	20	13.7	4.20	15.10	210,000	827,000
14	Ethyl Benzene	20	13.7	1.81	.47	137,000	35,000
15	Ethyl Benzene	20	None	1.61	.13	---	---

* G = $\frac{\text{molecule reacted}}{100 \text{ ev absorbed}}$ based on Chlorine

From the above results it is clear that a wide variety of polymers of ethylene may be produced in the radiation reaction. The yields are sufficiently high to consider the process feasible for commercial applications. At this stage economic studies are in order to determine the possible competitive position of polyethylenes produced by radiation processing with those produced in conventional processes.

II. CHLORINATION OF SOME AROMATIC HYDROCARBONS

In general, chlorination of an aromatic hydrocarbon may result in three possible reactions: (1) substitution of chlorine for hydrogen in the benzene ring, (2) substitution in an alkyl group attached to the ring, and (3) addition of chlorine to the ring. Friedel-Craft catalysts promote substitution in the ring; high temperature in the absence of catalyst favors substitution in the alkyl group; and radiation appears to favor addition to the ring. Ultraviolet^{5,6}, roentgen rays¹⁷, alpha radiation¹, and gamma radiation^{7,8} have been employed to promote the addition reaction. In this laboratory Harmer⁷ initiated a study of the chlorination of benzene and

toluene in the presence of gamma radiation. This has been extended to include xylene, mesitylene, and ethyl benzene.

(a) Experimental Work

Figure 4 is a flowsheet of the equipment developed by Harmer for carrying out chlorinations in the presence of gamma radiation. The glass bulb is the reactor which holds the aromatic liquid to be chlorinated. This was equipped with inlet and outlet tubes for passage of gases, a steel cooling jacket, glass baffles to promote mixing and a thermocouple well. Constant temperature was maintained by circulating cold methanol through the cooling jacket. The temperature of the methanol was controlled by a thermocouple potentiometer which governed the periods of operation of heaters and cooling coils. The reactor unit was placed in a portable hood in the ten kilocurie radiation chamber and connected to the cooling and gas analysis equipment by glass tubing that passed through ports in the concrete shielding wall.

In starting a run nitrogen was passed through the system to sweep out all air. Then the chlorine flow was started and the cobalt-60 source was raised into the radiation chamber. The reaction time was measured from the moment the source was raised to the midpoint of the period during which a sample of gas was collected. Radiation dosages were determined by the time and dosimetry calibrations.

Rates of reaction between chlorine and the aromatic hydrocarbons were determined by chlorine balance. The amount of chlorine into the system was measured with a rotameter. Excess chlorine was passed through the reactor at all times to maintain saturated conditions. At certain intervals samples of the exit gas were absorbed in a solution of 0.2 N. sodium arsenite and 3.0 N potassium hydroxide. The amount of free chlorine was determined by titrating the excess arsenite with ceric sulfate and total chloride ion was measured by the Volhard method. In this way the amount of substitution and addition could be determined.

(b) Results of Chlorinations

Benzene, Toluene, xylene, and mesitylene reacted vigorously with chlorine in the presence of gamma radiation. Addition of six chlorine atoms to the ring and alkyl substitution appeared to be the primary reactions. The ratio of addition to substitution was different from that obtained in chlorination reactions without radiation. In general this ratio appeared to be increased by radiation and decreased by increasing the temperature. The radiation yield is reported as G value (molecules chlorine reacted per 100 e. v. of radiation absorbed) in Table II. For some reason radiation had little effect on the reaction with ethyl benzene. Whether this is due to inherent inactivity or to inhibiting impurities is not known.

Harmer⁹ demonstrated the inhibiting properties of small amounts of benzyl chloride and oxygen in the chlorination of benzene and toluene.

TABLE III. COST ESTIMATE FOR PRODUCING 454 kg/day
OF GAMMA ISOMER OF BENZENE HEXACHLORIDE
WITH FOUR RADIATION SOURCES

	Gross Fission Product 0.5-yr.	Radiation Gross Fission Product 1 - yr.	Source Gross Fission Product 2 - yr.	Cesium- 137
Half-life, years.	0.2	0.3	1.1	33
Total Curies Req'd.-5 years.	84,000	57,000	19,000	5,000
Selected High Cost/Curie, \$.	0.0005	0.10	0.25	5.00
Radiation Cost 5 yr., \$.	4,200	5,700	4,800	25,000
Initial Investment in Radi- ation Source.	250	500	1,250	25,000
Radiation Chamber Cost, \$.	22,000	22,000	22,000	22,000
Process Equipment Cost, \$.	49,000	49,000	49,000	49,000
Total Investment, Including Radiation.	71,250	71,500	72,250	96,000
Annual Charges on Investment at 80%, Depreciation, Taxes, Interest, Maintenance, Etc.	57,000	57,200	57,800	76,800
Annual Radiation Replacement Cost.	800	1,000	700	0
Salaries of Workers, \$/yr.	21,000	21,000	21,000	21,000
Chlorine & Benzene, \$/yr.	109,000	109,000	109,000	109,000
Utilities, \$/yr.	3,000	3,000	3,000	3,000
Sales and Marketing, \$/yr.	8,000	8,000	8,000	8,000
Total Annual Cost, \$.	199,000	199,000	200,000	218,000
Annual Production, 290 Working Days, kg. Gamma Isomer	131,500	131,500	131,500	131,500
Cost/kg. Gamma Isomer, in 12% Mixture, \$.	1.51	1.51	1.52	1.66

Radiation chlorination of benzene takes place so quickly that temperature control is difficult. Also the production of the solid addition product tends to plug up the reactor unless the benzene is diluted with carbon tetrachloride. Toluene, xylene, and mesitylene do not react quite so fast and may be charged to the reactor in a pure condition. However, in all cases reaction under gamma radiation takes place so rapidly as to make it very attractive for commercial application. This is particularly true where the addition product might be desired, for radiation favors the

addition reaction. Chlorination of many other compounds may also be accelerated by gamma radiation.

III. ECONOMICS OF RADIATION CHEMICAL PROCESSING

The laboratory studies on the polymerization of ethylene and the chlorination of aromatic hydrocarbons have demonstrated the feasibility of promoting chemical reactions with gamma radiation. It is of interest to examine the costs of such radiation processes. The chlorination of benzene is well suited to cost estimation and comparison because the reaction is presently conducted on a commercial scale using ultraviolet radiation.

The addition product of benzene and chlorine is technically known as 1, 2, 3, 4, 5, 6 hexachlorocyclohexane, but it is usually referred to as benzene hexachloride. The gamma isomer of this compound is a powerful insecticide^{10,21} which is sold under various trade names. In the usual radiation reaction this isomer constitutes about 12% of the total addition product. The present commercial process utilizes small quartz equipment necessary for transmission of the ultraviolet. The following calculations are made for the gamma radiation process using a single larger reaction vessel made of nickel alloy. Costs are estimated for four different gamma radiation sources derived from fission products.

(a) Design of a Chlorination Process Using Gamma Radiation

In a typical batch run at 20° C. and 62 kilorep/hr. of radiation, Harmer⁷ obtained 63.6 gm. of benzene hexachloride in 0.333 hr. from a charge of 20 ml. of benzene and 80 ml. of carbon tetrachloride. The theoretical yield is 65.6 gm. based on the benzene density of 0.88 gm./ml. Neglecting the actual increase in volume of the reactor contents, the benzene concentration decreased from 20 to 0.6% by volume. Assuming the reaction is first order with respect to benzene concentration C, the rate is $dC/d\theta = -kC$, with k being the reaction velocity constant and θ the time. Integrating this from the beginning to the end of the batch reaction gives $\ln(20/0.6) = -k(0.333)$, or $k = 10.6 \text{ hr.}^{-1}$.

As a basis it will be assumed a plant is to be designed to produce 454 kg./day of the gamma isomer. This corresponds to a production of 541 gm. moles/hr. of mixed isomers. A cylindrical agitated flow reactor is to be employed with a uniform benzene concentration of 80%. The gamma source is to be placed in a center hole according to the scheme shown in Figure 5. The source is to be of such strength that the mean reaction velocity constant is 1.0, so the reaction rate is (1.0)(0.8) ml. benzene/hr. -ml. solution. This is equivalent to 9.02 gm. mole benzene/hr. -liter solution. Since a gm. mole of benzene makes a gm. mole of product, the volume of the reactor is 541/9.02 or 60 liters. This volume may be realized in a cylinder 50 cm. high and 50 cm. in diameter, with a hole 20cm. in

diameter for the radiation source and cooling coils circling the inside of the walls.

The reaction velocity constant is assumed to vary directly with radiation intensity I (Harmer⁸) showed the chlorination of toluene to vary as \sqrt{I} which is conservative for intensities less than that of the laboratory experiment. Thus, $k = mI$, or $k = 0.171 I$ from the fact that $k = 10.6$ at $I = 62$. For rough estimation assume the cylindrical reactor is the equivalent of a 25 cm. radius sphere with a point source of radiation at the center. There will be a spherical hole of 10 cm. radius at the center to account for the volume occupied by the actual source. If the radiation intensity on the surface of the hole at 10 cm. from the center is 50 kilorep/hr., and if the intensity decreases according to the inverse square law and the exponential absorption law, the average k throughout the reactor volume may be calculated as

$$k_{ave} = \int_{10}^{25} \frac{0.171(50)(10)^2 e^{-0.064(0.88)(r-10)} (4\pi r^2) dr}{r^2(4/3)\pi (25)^3 - (10)^3} = 1.0$$

Here 0.064 is the gamma absorption coefficient and 0.88 is the density of the benzene. In order to obtain an intensity of 50 kilorep/hr. at 10 cm. from the center for a fission-product source, about 1250 curies would be required¹⁸. This is multiplied by a factor of four to account for self-absorption, absorption by the wall and the agitator between the source and the benzene, and losses of radiation from the cylinder through the hole. Therefore, 5000 curies will be taken as a conservative estimate.

The radiation chamber housing the reactor will be made 3 meters square to provide adequate working space. To insure that the intensity of radiation is less than 0.5 millirep/hr. outside this chamber with a 5000-curie source, the concrete walls must be 85 cm. thick¹⁹. The other units in the system are calculated by conventional means. The process is straightforward, with the benzene being saturated with chlorine before entering the reactor, and excess chlorine bubbling through the reactor to keep the contents saturated. The product from the reactor is flashed to separate out the solid benzene hexachloride. The benzene is condensed and returned to the chlorine saturator. Refrigerated coolant is required to maintain the reactor feed and contents at 20° C.

(b) Cost Estimations

The costs of fission-product sources are not yet available. Therefore estimations are made for a range of values that seem reasonable. Because of varying half-life of different sources, it will be assumed that charges are made approximately according to the radiant energy delivered. Since the energy E of a radioactive source is given by $\int I_0 e^{-\lambda \theta} d\theta = I_0(1 - e^{-\lambda \theta})/\lambda$, at large values of time θ the energy varies inversely as the disintegration constant λ . But λ is the reciprocal of the half-life, so the energy varies directly as the half-life. The costs will

therefore be selected in proportion to the half-life. The cost of long half-life sources is to include shipping. Short half-life sources would involve excessive shipping costs and are assumed to be used in the vicinity where they are produced. If the source intensity is not to fall below say 80% of its initial strength, short half-life materials will require frequent replacement. These factors have been considered in Table III, where the costs of producing the mixed isomers of benzene hexachloride are given as a function of the type of radiation source. In estimating the total radiation required, the source is to be composed of five sections. Whenever the intensity falls off 20%, one section is replaced with fresh radioactive material. In the case of cesium-137, it is apparent that no replacements are necessary. In fact, at the end of a five-year period, the cesium activity is still more than 90% of its initial value. In selecting costs for radiations sources, ten-fold ranges were estimated for each case, but only the highest value is given in the table. It is noted that the variation in costs of radiation actually has only a small effect on the product cost.

The costs of benzene and chlorine are taken from the latest trade journals. These also give the cost of commercial benzene hexachloride as \$1.90 to \$3.00 per kg. of gamma isomer in 12% mixture with the other isomers. The gamma radiation process evidently can compete with the ultraviolet process for making this compound. Of course, the true comparison between the two should be made on the basis of the comparative costs of the reactors and radiation sources, since all other equipment is the same. What this comparison does show, however, is that gamma radiation processing is not out of line with other processing methods and that it should be given serious consideration by industry.

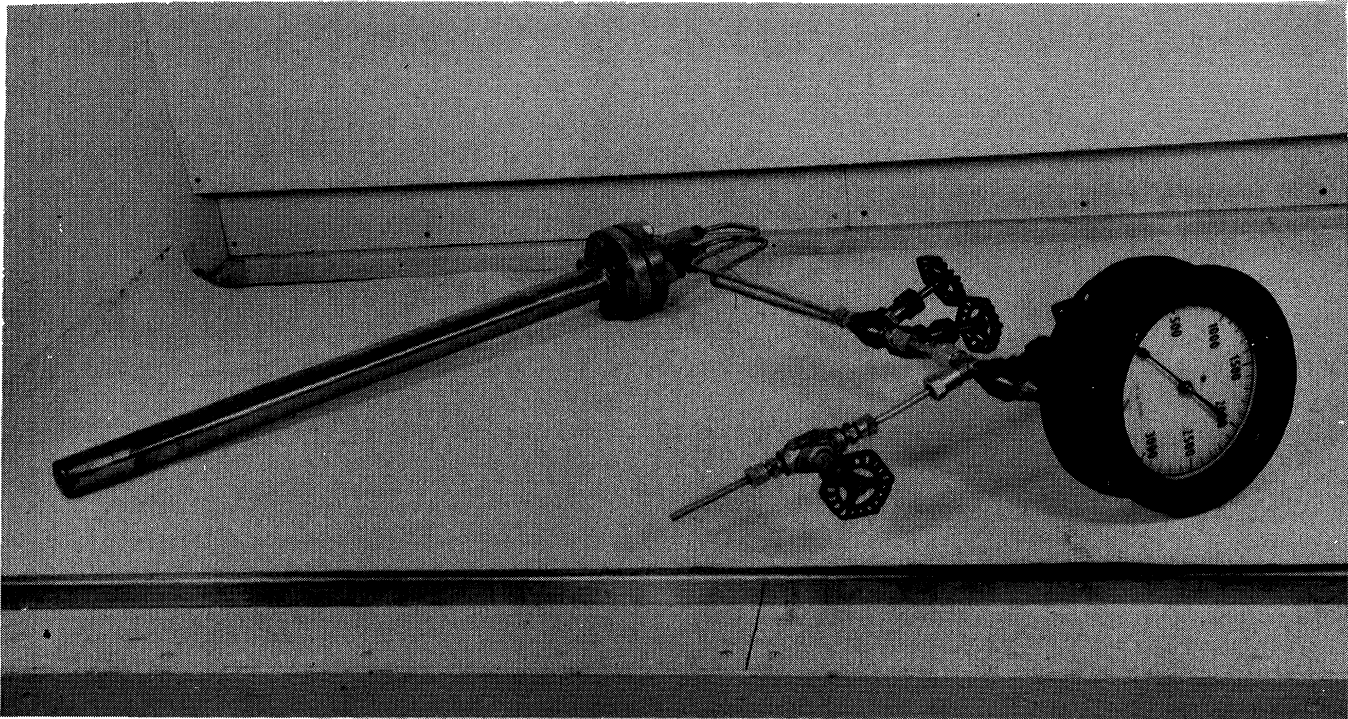


Figure 1. High-Pressure Polymerization Reactor with Fittings

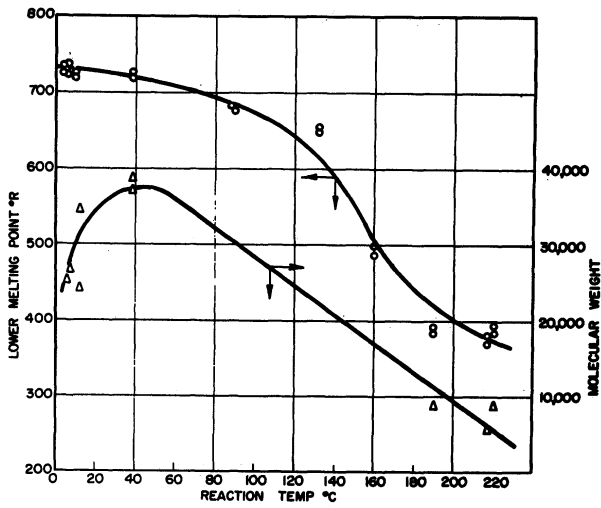


Figure 2. Melting Point and Molecular Weight of Polyethylene

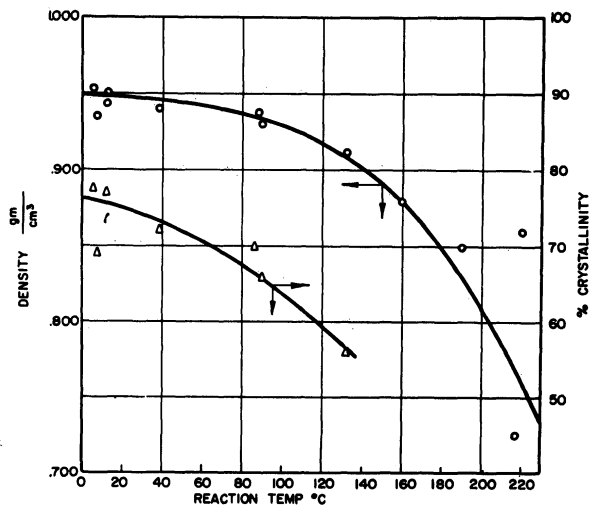


Figure 3. Density and Crystallinity of Polyethylene

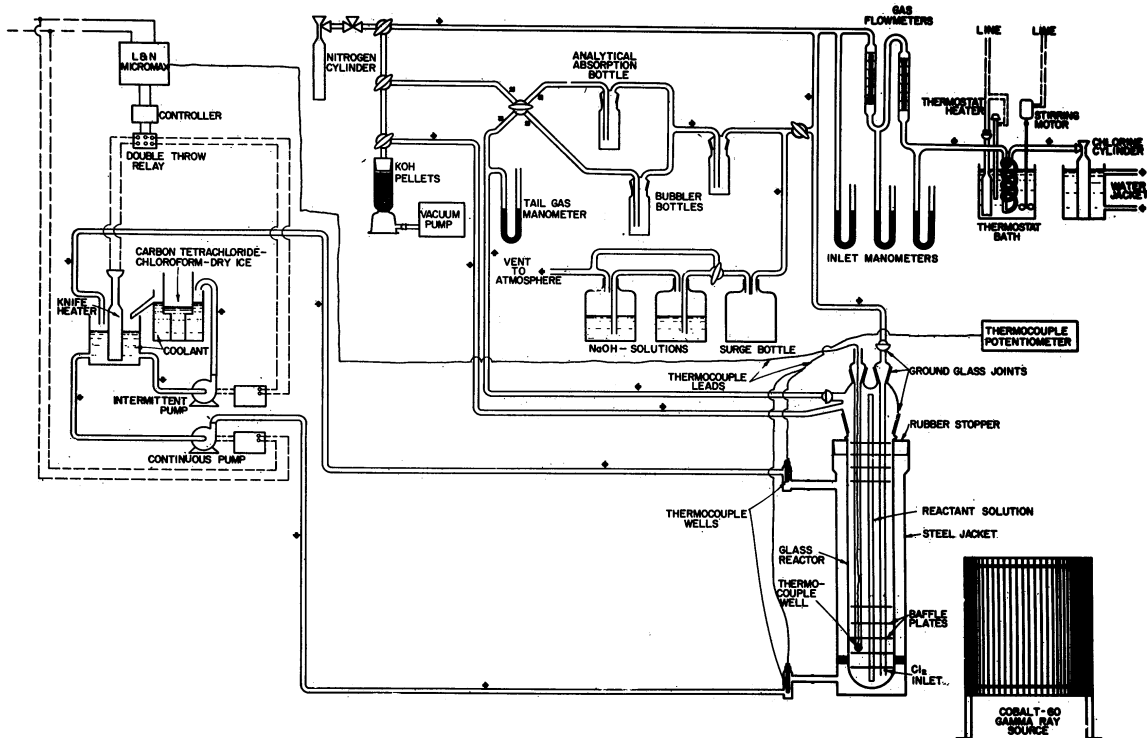


Figure 4. Schematic Diagram of Laboratory Equipment for Aromatic Chlorinations

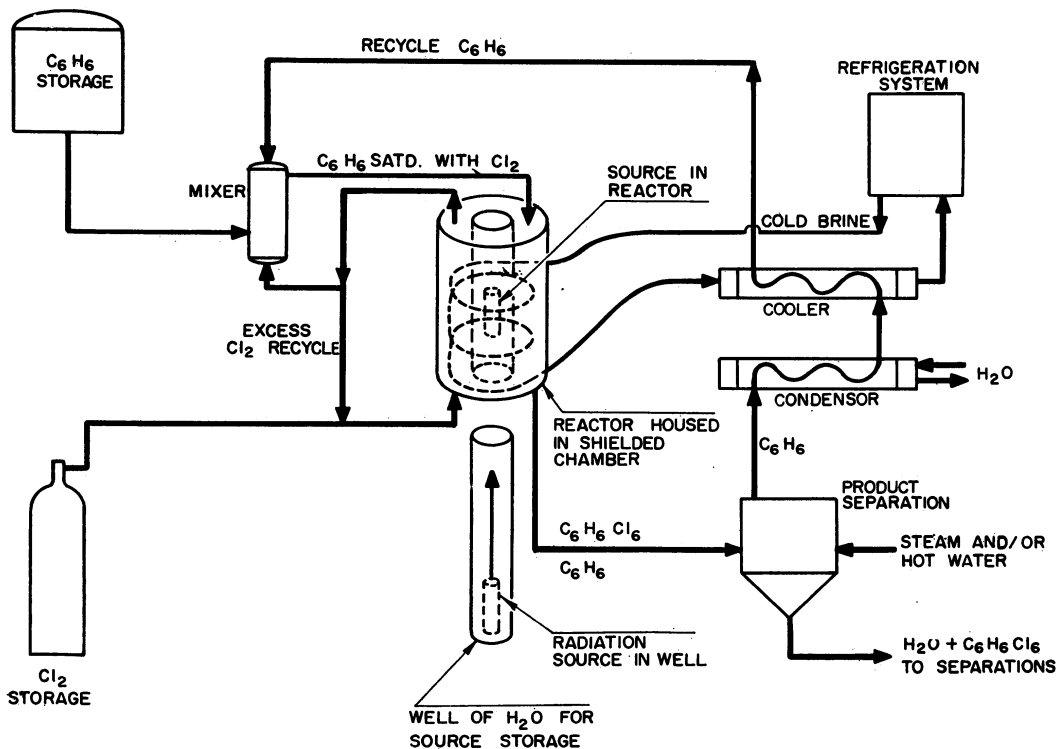


Figure 5. Flowsheet of Proposed Plant Design for Producing Benzene Hexachloride

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