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FACTORS AFFECTING THE DESIGN OF A CHLORINATOR IN PHOTOCHEMICAL CHLORINATION OF LOW-BOILING PETROLEUM HYDROCARBONS

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Photochlorination of low boiling petroleum hydrocarbons between C_4 and C_{12} (b.p. range 60–150°C), involving the study of the effect of the rates of chlorination, the mode of agitation and bubble size at the liquid-gas interphase, on the design of a commercial chlorinator where optimum conditions or values for these factors have been applied, is presented.

Literature survey shows that considerable amount of work has been done on the photochlorination¹⁻¹⁰ of benzene, toluene, cyclopentadienes and certain fractions of turpentine oil, mainly for the production of insecticides. Most of the workers have used conventional type round bottom flasks fitted with agitator and thermometer and immersed in ice bath. Presumably constant gas rates and UV or actinic radiations have been used to catalyse the reaction.

Relatively little work appears to have been carried out on the chlorination of the mixtures of low boiling hydrocarbons i.e. the petroleum-cut (C_4 - C_{12}) of the composition shown in Table I, though the chlorination mechanism of some of the individual hydrocarbon such as methane, ethane, propane and butane has been reported by Hass *et al.*¹¹⁻²¹ without giving details of the apparatus used or describing the variables effecting the process of chlorination. The limited information available on polychlorination shows that Weizvich²² polychlorinated the petroleum hydrocarbons (b.p. upto 320°C) at 10–18°C, to a chlorine content of 20–40%. The fraction up to 140°C of the chlorinated product was used as a solvent, addition of lubricants and fireproof mixtures e.g. paints. These authors appear to have used the usual round bottom flask apparatus and they have not studied the variables affecting the chlorination process. Desai and Metha²³ obtained solid compound (insecticide) by chlorinating petroleum-cut (b.p. range 90–200°C), using the same type of apparatus as used by the preceding workers. Iodine has been used as a catalytic agent but the factors such as the rate of chlorination (chlorine reacted), the mode of agitation and the bubble size have not been studied. Gault and Lauchec²⁴ chlorinated long chain hydrocarbons (paraffinic series) and hydrolysed the products with aqueous

and alcoholic potash, presumably for the production of unsaturated hydrocarbons. The work of these authors mostly revolves round the chlorination followed by the hydrolysis of the derivatives and not the variables involved in the process. Keefer²⁵ chlorinated the lubricating oils, kerosene, paraffin wax and isopentane in a 3-inch column provided with means for introducing chlorine, stirrer (mechanical agitation), temperature measurement and control and gas exit. The author studied the effect of heat, light, dilution and iron catalyst. None of these factors form a part of the present study. Moreover, the types of compounds chlorinated by the author are mostly above C_{12} .

The present paper deals with the polychlorination of mixture of petroleum hydrocarbons with particular reference to the study of the factors such as the rates of chlorination (absorption or chlorine reacted), the method of agitation and the bubble size, for an improved design of a chlorinator. The final product, i.e. the polychlorinated petroleum-cut which contains about 60% chlorine, finds its application primarily as an insecticide²⁶ which is comparable to B.H.C. and Toxaphene in its insecticidal properties.

TABLE I.—PHYSICAL PROPERTIES AND CHEMICAL COMPOSITION OF PETROLEUM FRACTIONS.

Physical property	Petroleum fraction (A)	Petroleum fraction (S)	Petroleum fraction (I)
B.p. range °C	41–150	60–150	40–155
Specific gravity	0.729	0.731	0.730
Paraffins	84.9	88.0	67–83
Naphthenes			12–25
Olefins			0.0–0.35
Aromatics	12–17	12	1–20

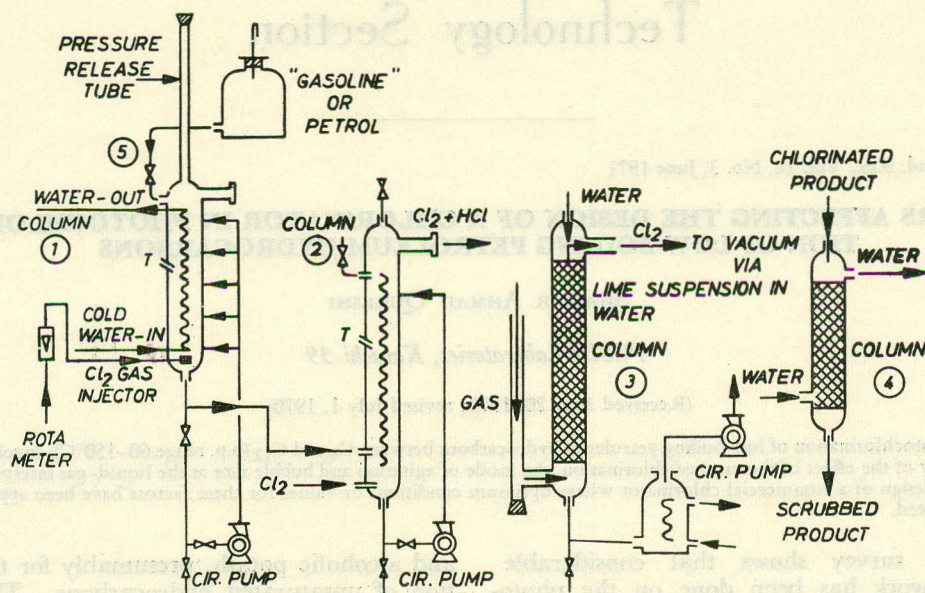


Fig. 1.—Chlorination apparatus.

Apparatus and Experimental

Rate of Chlorination.—The apparatus used may be seen in Fig. 1, where column I is used for the chlorination of the petroleum-cut from 0.729 to 1.2 g/cm³ and column II, to further increase the density from 1.2 to 1.415 g/cm³. Both these columns are connected with an HCl absorber and finally led to a water jet-pump via a lime suspension flask, to maintain flow of gases in the apparatus.

About 50 ml of the petroleum-cut is fed to column I and cooled to 15–20°C. Chlorine gas is first passed at the rate of 0.05 lb/hr (lb cut) and gradually increased to 0.25 lb/hr (lb cut) in the presence of sunlight or Hg lamp. When the density rises to 1.20 g/cm³, the partly chlorinated petroleum-cut is transferred to column II where it is rechlorinated to a density of 1.415 g/cm³. (The chlorination has been split up into two parts as safety measure.) The product is then scrubbed free of dissolved HCl and chlorine gases and finally dried (Na₂SO₄).

Method of Agitation—Turbulence.—The process of chlorination may roughly be divided into 3 stages, namely (i) where minimum amount of the Cl₂ is used in the reaction i.e. 0.05 lb/hr, (ii) where maximum amount of Cl₂ is consumed i.e. 0.25 lb/hr and (iii) where finally the Cl₂ reacted drops to 0.1 lb/hr (lb cut), as indicated in Fig. 2. The corresponding amounts of heat liberated, as plotted in Fig. 3, shows that the heat evolved varies from minimum of 84 to a maximum of 377 and again drops to a value of 165 Btu/hr (lb cut). These varying heat loads will alter the cooling water requirements and subsequently the mode of agitation-turbulence in the column. In order to meet the requirements of all the stages especially the first stage of chlorination where the Cl₂ must pass through an aqueous layer before escaping into the petroleum-cut, two types of 'circulations' i.e. gravity and forced circulations, were used which gave satisfactory results. Both these arrangements have been shown in Fig. 1. In the first case, the recycle liquid is simply allowed to escape at the surface of the petroleum-cut whence it flows

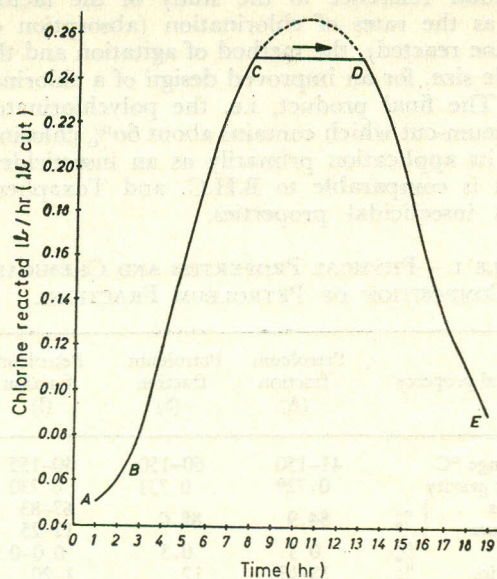


Fig. 2

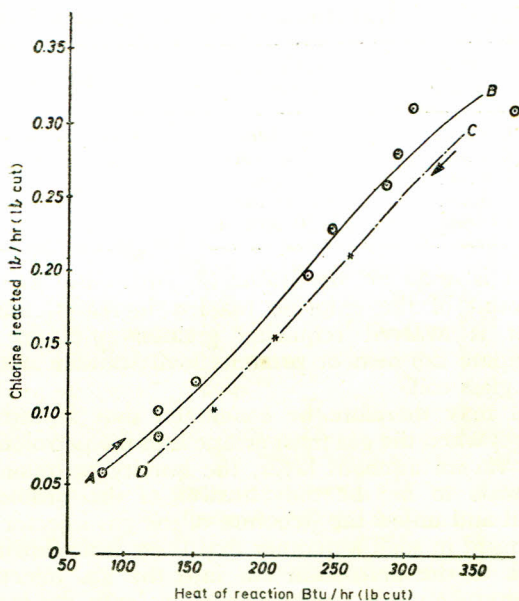


Fig. 3.

down the column under the influence of gravity in the form of drops, while in the second case, the recycle liquid is forced into the petroleum-cut at 'excessive-heads', i.e. heads greater than that of the pump, to bring about desired degree of agitation in the column.

The Chlorine-Gas Bubble Size (at interface).—At the initial and final stages of chlorination where the chlorine absorption is very low as compared to the other two stages, the bubble size play an important role and should be reduced to minimum within the practical limits.

Chlorine-gas injectors, namely, cindered-glass plates 100–120 μ i.e. 0.1–120 mm pore size and simple glass tubes with perforation varying from 0.2 to 4 mm were used to study the effect of bubble size on gas absorption. Perforations or nozzles with diameters higher than 3 mm were not used as they give rise to very large bubbles.

Results and Discussion

The Variable Gas-Rates.—Chlorination of a single hydrocarbon is relatively simple and the experimental conditions can be determined easily. But in case of a mixture of hydrocarbons such as the petroleum-cut, it is unsafe to stick to one set of conditions which keep on varying in the process of chlorination. Thus it is imperative to determine the limits of the variable conditions to ensure a better control over the process.

Of the variables, the flow rates of gas into the petroleum-cut was considered most important and as such has been studied at length for the given values of the rest of the variables, i.e. the pressure was atmospheric throughout, temperature set at

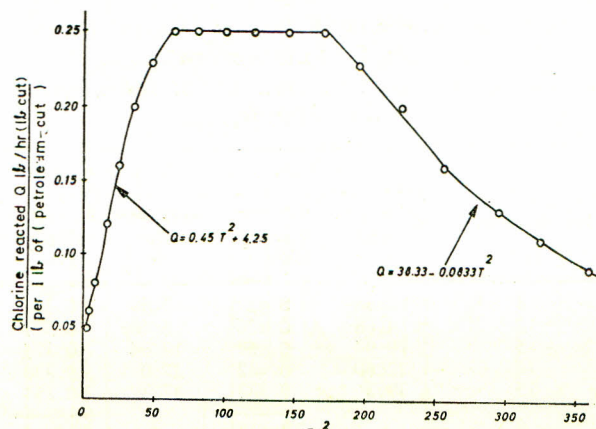


Fig. 4.

20°C and the intensity of the radiations was equivalent to that emitted by 150W Hg-vapour lamp.

When the chlorination rate (chlorine reacted/hr) is plotted against time, a bell-shaped curve (Fig. 2) is obtained. At point A the gas absorption is minimum, i.e. chlorine rate is 0.05 lb/hr (lb cut) which gradually rises to 0.25 lb/hr over a period of nearly 8 hr. From point C to D the chlorine absorption is maximum, i.e. 0.25 lb/hr and remains constant over a period of nearly 5 hr and thereafter falls to 0.1 lb/hr at point E in 6 hr. At point E the density of the final product is 1.415 g/cm³ with chlorine content of about 60%.

Any change in these chlorination rates, will build up an unreacted chlorine potential within the petroleum-cut and a point will reach when the desorption of the gas accompanied by the evolution of heat will start, resulting in vigorous boiling of the petroleum-cut at 60–70°C, either culminating into explosion or fire.

In Fig. 4 the left-hand side of the curve, i.e. AC which is almost a straight line, may be represented by a relationship: $Q = 0.45 T^2 + 4.25$ where Q is the rate of chlorination in lb/hr (lb cut) and T is the chlorination period in hr. Thus in the first 8 hr the rate of chlorination is proportional to T^2 . Similarly in the falling-rate period i.e. the right-hand side of the curve, is represented by $Q = 38.33 - 0.0833 T^2$, Q falls in proportion to T^2 .

A very low rate of absorption at the initial stage may be attributed to the low affinity of the paraffinic compounds towards chlorine. Once the chlorine has entered the molecule, the subsequent substitution becomes quicker but diminishing again towards the end probably due to the saturation of the molecule. According to Hass and his coworkers,¹¹ hydrogen atoms are substituted at a rate which are in the order primary < secondary < tertiary and are independent of the hydrocarbons. This would mean that the tertiary position is most vulnerable, less so is secondary, followed by the primary position.

TABLE 2.—GRAVITY FLOW OF WATER DROPS THROUGH PETROLEUM-CUT.
(Dia of the nozzle=2 mm dia of the drops=8 mm approx).

Liquid height (Petroleum-cut) ft	Column (plain)		Column (with coils)	
	Average time sec	Average velocity ft/sec	Average time sec	Average velocity ft/sec
1	2.38	0.42	2.94	0.352
2	4.68	0.426	6.70	0.597
5	10.94	0.467	13.34	0.375
10	22.60	0.442	27.0	0.370
15	39.3	0.382	42.3	0.354
	Av. = 0.427		Av. = 0.4096	

Degree of Agitation—Turbulence.—In both the cases, i.e. gravity and forced circulations, centrifugal pump sucks in the material from the base and discharges it at the top of the column either at atmospheric or higher pressures. Forced circulation is decidedly a better approach for bringing about higher turbulence and improved heat-transfer rates. But at the initial stages where the chlorination rate is very low, the gas is absorbed in the petroleum body via an aqueous layer, use of forced circulation would mix both the components with the result that some of petroleum-cut will enter the gas-injector and cause sparking. This situation could be averted by recycling the aqueous layer alone over the column and fall through the petroleum-cut under gravity, bringing about a restricted type of turbulence. When once the density has risen beyond 1 g/cm³, forced circulation will then become imperative. There is no danger of sparking even if a part of the chlorinated product flow back into the injector.

Agitation in open vessels by means of an impeller is well known but there is no satisfactory method to introduce turbulence in a column fitted with cooling coils, other than a recycle pump. In such a system when the recycle liquid is allowed to discharge at the top of the column liquid at atmospheric pressure, it will cause agitation while falling through the liquid under gravity in the form of drops. The agitation brought about in this manner is very small as shown in Table 2, where the time of fall of a water drop of a selective known size in vertical columns, one with and the other without coils but both filled with petroleum-cut, have been recorded. These results show that the drop falls with an average velocity of 0.427 ft/sec in the plain column (Re=104) and 0.41 ft/sec (Re=100) in the coiled condenser. The value of Re being less than 2000, indicates a streamline-flow. As already stated higher values of Re can only be obtained by introducing forced circulation by a recycle pump with excessive heads. This is not necessary at initial stages of chlorination where the amount of the heat liberated per

TABLE 3.—GAS-ABSORPTION VS. BUBBLE SIZE.

Diameter of the nozzle	Diameter of the bubble	Remarks
0.1 mm	≈ 0.2 mm	Totally absorbed
0.2 mm	≈ 0.4 mm	" "
1.0 mm	≈ 3 mm	Partly "
2.0 mm	≈ 8–10 mm	" "
3.0 mm	≈ 20–30 mm	" "

hour is small i.e. 84 Btu/hr (lb cut). But as the amount of the chlorine reacted increases, more heat is evolved requiring greater agitation to dissipate the heat or promote heat transfer across the glass coil.

It may therefore be concluded that at initial stages when the gas must escape into the petroleum cut via an aqueous layer, the gravity turbulence appears to be the only answer of the problem until and unless the structure of the gas injector is changed in such a manner that there is no flowing back of the petroleum cut into the gas injector (nonreturn valves always develop leaks at later stages).

The water drops from the recycle pump vary in size between 1–20 mm where the bigger drops break into smaller ones i.e. between 2–10 mm during the fall. In view of this, a common size of 8 mm has been chosen for the present study.

The Chlorine-Gas Bubble Size (at interface).^{27,28}—Since the gas absorption is very low initially, it is necessary to reduce the bubble size in order to increase the interfacial area to promote reaction between the two phases. The effect of the bubble size on gas absorption is tabulated in Table 3.

It will be seen from these results that the chlorine absorption is complete when the bubbles size is 4 mm or less. Bubbles larger than 4 mm are only partly absorbed. It has been further observed that all or most of the mass transfer takes place at the water-petroleum-cut interphase but no quantitative study of this aspect of the phenomena has been made.

Thus while designing a gas-injector for initial stage of chlorination, canted glass plate with pore size 100–120 μ and for the second stage where the gas-absorption is relatively much higher, nozzle type injectors as described earlier will be most suitable.

The Chlorinator Design—Some Other Aspects

Safety Measures.—Although the foregoing study on the chlorination rate, the agitation and the bubble size have considerably streamlined the process but a safe and hazard-free working design of chlorinator still needs some further considerations which have been explained below one by one.

In the laboratory scale chlorination where the effective height of the column (a coiled condenser) was limited to 12 in the time of contact at initial

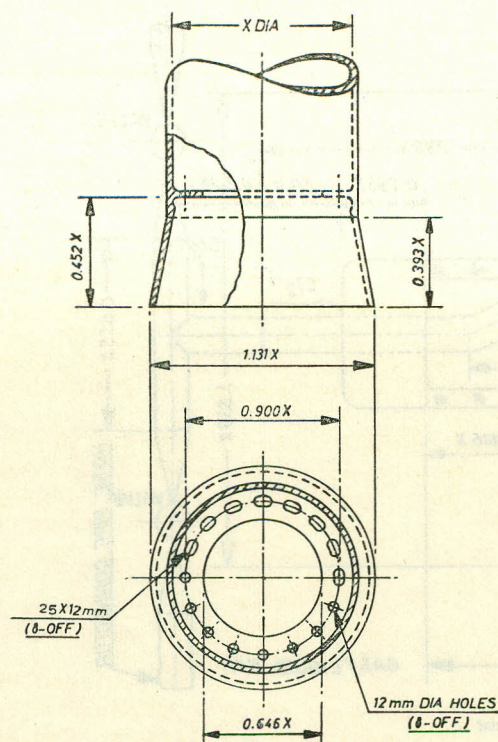


Fig. 5.—Glass heat exchanger.

stage of chlorination was nearly 2–3 sec. Bubbles larger than 8 mm had the tendency to escape from the top unreacted. Round-bottomed vessels or flasks have proved most unsatisfactory piece of equipment for the chlorination of petroleum-cut because the time of contact as compared to the vertical column is very small e.g. less than 1 sec. As already mentioned, withholding of the gas bubble at a particular place, e.g. by introducing a packing material, results in the production of hot spots which are difficult to remove without strong agitation. Imparting a free zig-zag or swirling movement to the rising gas bubbles could prolong the residence time but introducing a device for bringing about such a motion appears to be a remote possibility. The only alternative, at the moment, lies in increasing the height of the chlorinator subject to an economic limit.

In a smaller chlorinator, the chances of the formation of heat pockets are slim but in commercial ones where the heavy glass condensers with cooling coils, are mounted on each other, there is an inherent danger of the formation of heat pockets. The construction of these condensers is such that the coils are supported on a circular glass-strip fused onto the main glass shell. When the gas rises, a part of the bubble steam is trapped below the strip, with the result that at such dead corners where the effects of agitation are minimum, the formation of hot-spots becomes imminent. It was found that the support with elliptical or circular

performations as shown in Fig. 5 gave an unobstructed passage to the ascending stream of bubbles, removing thereby the stagnant petroleum layer below the glass support. With this arrangement, even a slight agitation is sufficient to dislodge the heat-pockets.

Another discomforting factor in the chlorinator design is its chlorine injection point i.e. the chlorine injector. Conventional gas injectors have failed in emergency, i.e. when a part of the petroleum-cut has leaked into the injector or its connecting tube, in course of chlorination. Being in immediate contact with the chlorine gas, and that the reaction is exothermic, the heat accumulates within the injector and may at any time initiate sparking or fire. This danger has been mostly obviated by tapering the injector upward and introducing an offtake valve near the injector as shown in Fig. 6.

Heat of Reaction.—Since the percentage of the individual hydrocarbons present in the local petroleum-cuts is not known and that the data on the heat of reaction (or chlorination) of these components is equally scant, it appears to be rather difficult to ascertain the exact amount of heat evolved per pound of the chlorine reacted during the chlorination period. The unsaturated hydrocarbons i.e. olefins are almost absent from all the cuts, while the saturated hydrocarbons belonging to the paraffinic, naphthenic and the aromatic series, constitute 99.7% of the petroleum-cut (Table 1). Consequently the heat given out is mostly due to the substitution reaction and that the heat generated by way of addition is insignificant. The compounds present in a typical petroleum-cut²⁹ and some of the corresponding chlorine compounds³⁰ are numerous and difficult to reproduce. The heats of formations or chlorination^{31–32} of these compounds (for mono- and the poly-substitution products), vary over a small range for methane, ethane, propane, butane, pentane and hexane. This could also possibly be true for higher homologues of the paraffin series (data not available). Thus it will be seen that the optimum heat of chlorination by way of substitution comes to 911 Btu/lb of chlorine and in case of addition reaction e.g. $C_6H_6Cl_6$, 836 Btu/lb of the chlorine reacted (Groggin³¹ gives this value as 892 Btu/lb.).

The empirical value of the overall heat of reaction (heat of reaction + the losses) during the peak period determined on a 0.5 ton/day chlorination plant comes to about 36,500 Btu/hr per 250 lb polychlorinated cut or 350 lb of Cl_2 reacted (=104.2 Btu/lb of the chlorine reacted per hr). This value included the cold losses from the chlorinator in the form of atmospheric vapour condensation and the heat radiated by mercury-lamps which amounts to 28.6 Btu/lb Cl_2 reacted per hr. These losses can be minimised by totally

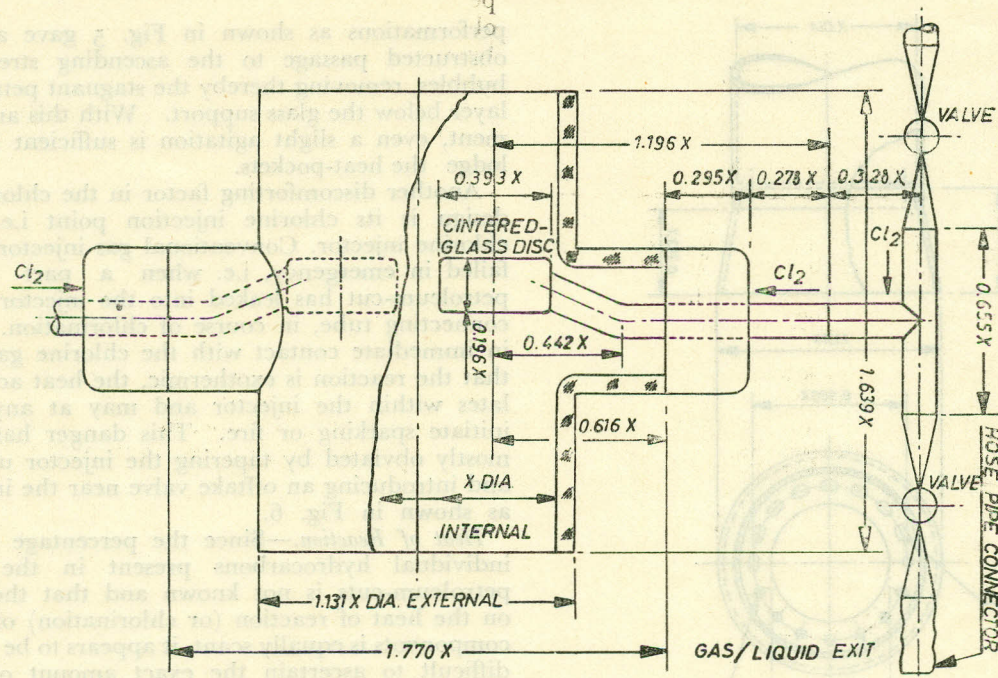


Fig. 6.—Gas injector

enclosing the chlorinators in such a manner that the air circulation is reduced to bare minimum but sufficient enough to expel the heat generated by the mercury lamps or the tubes surrounding the column.

Materials of Construction.—The choice of glass as a material of construction for the chlorinators is due to its resistance towards the hydrochloric acid and the photosensitive nature of the reaction. Apart from the fragile nature of the glass, which can be taken good care of, the other drawback is the poor thermal conductivity of glass which results in low values of the overall heat transfer coefficient. The heat transfer coefficient across the cooling-heating coils as reported³³ varies between 10–155 Btu/hr (ft²) (°F) but in the present case an average figure of 50 Btu/hr (ft²) (°F) may be considered safer for calculating the overall heat transfer area. For higher heat transfer rates coils made from special metals or alloys, e.g. tantalum or Hastelloy-B, could be substituted but their fabrication in a glass cylinder may pose a problem which needs investigation on the part of the manufacturers. In case this is feasible, the introduction of a metal coil within the reactor will considerably reduce the heat transfer area and consequently the overall height of the chlorinator.

Other Considerations.—Apart from what has been discussed above, great care is to be exercised so that the rise in temperature does not exceed the determined limits and that under no circumstances an excess of Cl₂ is admitted to the column. Should this happen, the petroleum hydrocarbons-gas

mixture begins to boil and give out considerable amount of heat which may develop to explosion or fire. In such an event, bursting-disc provided at the top, will burst open and save the apparatus from damage. An expansion chamber located at the top of the bursting disc will help in preventing the overflow of the material. It would perhaps be advisable to have the opening outside the building so that the spilled material does not spoil or impair the surrounding chlorinators and the machinery.

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