

SOME TECHNOLOGICAL ASPECTS OF THE CHLORINATION OF DAUDKHEL 'GASOLINE'

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'Gasoline' a waste industrial product from ammonium sulphate industry, has been chlorinated to obtain a pesticide named as Makrolin. Chlorine gas-rates when increased from 50 to 150 litres/hr/250 ml. of the 'gasoline', lower the first-stage chlorination period from 1.192 to 0.634 hours but do not appear to have any effect on the second-stage of chlorination. Caustic soda when used in 0.5 to 4 percent concentration lowers the overall period of chlorination from 44 to 22 hours. Higher concentration namely 5 to 10 percent do not further reduce the chlorination period. Catalytic chlorination in presence of anhydrous ferric-chloride (0.2 g. Fe/250 ml. of the partly chlorinated 'gasoline') has been found useful in reducing the overall chlorination period down to 24 hours. The aqueous phase separated after the chlorination contains about 20-30 g. of hydrochloric acid per 100 ml. of the solution which can be used as pickling-agent.

Introduction

At Daudkhel ammonium sulphate plant, water gas is produced by the gasification of low grade sulphuraceous coals. Along with it cracked volatile matter is carried over which when condensed yields a pale yellow oily product named as 'gasoline'. Gasoline, having specific gravity of about 0.8 g./cc. and b.p. range 60—200° C., is a mixture of unsaturated aliphatic and aromatic hydrocarbons. Since it contains 3-5 percent of sulphur, mostly in the form of thioethers, 'gasoline' cannot be used as a motor fuel. But by chlorinating 'Gasoline' a useful application has been found as a pesticide. Direct chlorination did not prove successful because it resulted in the formation of a thick resinous material due to the formation of chloro-sulphur compounds known to have polymerising effect on

hydroaromatic bodies. This difficulty has been overcome by making use of oxidative chlorination i.e. chlorination in presence of hypochlorite solution. Since the gas-rate, concentration of caustic-soda and a number of metal catalysts have a pronounced effect on the overall period of chlorination, the present work has been restricted to the study of these variables. The new pesticide developed has been named Makrolin which compares favourably with D.D.T. in its insecticidal values, and copper naphthenate and colloidal copper in its fungicidal properties.¹

Experimental

Apparatus and Procedure.—The chlorination apparatus which consists of a number of vertical condensers arranged in a row is shown in Fig. 1.

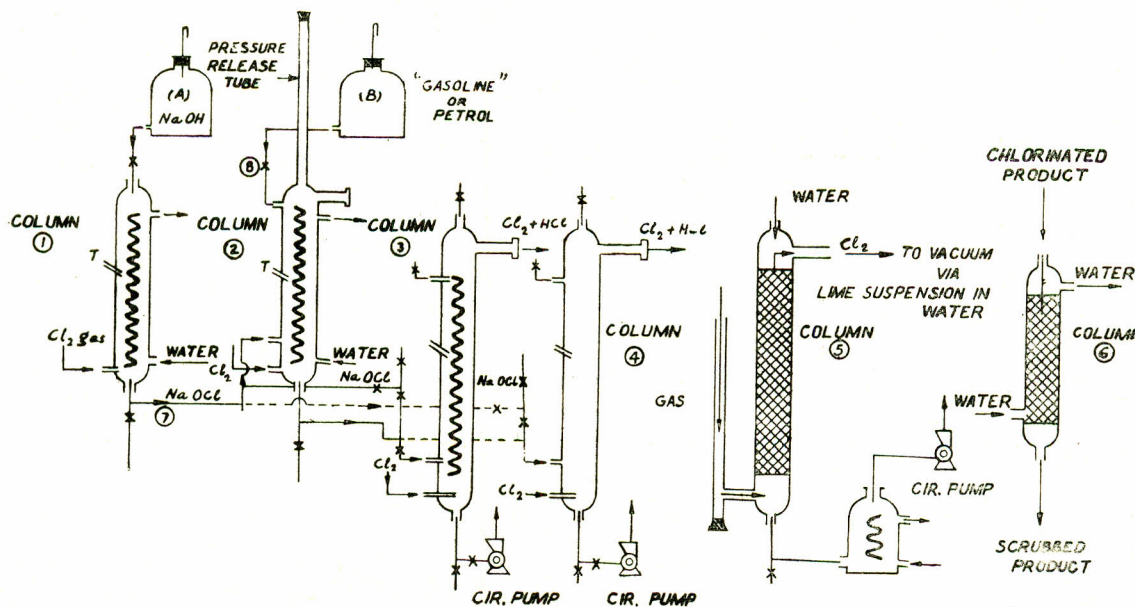


Fig.1.—Chlorination Apparatus.

Column I is a 5×60 cm. condenser with a free volume of 700 ml. and a cooling surface of 0.1 M². Column II similar to column I is used for chlorinating 'gasoline' in presence of hypochlorite solution at 10–15°C. Columns III and IV are identical and are employed for the second stage chlorination of the 'gasoline'. Column IV, packed with Rasching rings, is used for absorbing unreacted chlorine and hydrochloric acid gas from the preceding columns. The excess chlorine from the absorber is fixed as calcium chloride in lime water suspension.

In order to prepare chlorinated gasoline, equal volumes of hypochlorite solution and 'gasoline' are fed in column II and chlorinated at 10–15°C. till the specific gravity rises to 1.2 g./cc. The partly chlorinated gasoline is next transferred to column III or IV and re-chlorinated in the presence of fresh hypochlorite solution till the specific gravity rises to 1.415 g./cc. The chlorinated gasoline is then scrubbed free of chlorine and hydrochloric acid gas and dried over anhydrous calcium chloride or sodium sulphate.

Results and Discussion

1. *Effect of Gas-Rates on Chlorination Period.*—In order to have a better control over the chlorination process, the overall chlorination period has been divided into two stages, namely the first stage where the specific gravity of the gasoline rises from 0.815 to 1.2 g./cc., and the second stage where the rise is from 1.2 to 1.415 g./cc. Since in the first stage the reaction is highly exothermic, proper control over gas rates is essential. For a given temperature, low gas rates unnecessarily prolongs the chlorination period, while high rates result in explosion and fire. Gas rates varying from 50 to 150 litre/hour were used and the results are reported in Table 1.

TABLE I.—EFFECT OF GAS-RATES ON FIRST STAGE CHLORINATION PERIOD.

Initial specific gravity	=	0.815 g./cc.
Final specific gravity	=	1.20 g./cc.
Concentration of alkali	=	4%
Temperature of the reaction mixture	=	10–15°C.

No.	Gas-Rates litres/hour/1250 ml. gasoline	Chlorination period in hours
1.	50	1.192
2.	80	0.855
3.	110	0.750
4.	150	0.634

The results show that as the gas rate increase from 50 to 150 litres/hour, the chlorination period falls from 1.192 to 0.634 hours. Suitable gas rates can be selected, keeping in view the cooling water temperature and the cooling surface available. Since the gas absorption is fairly slow in the second stage, gas rates are preferably maintained between 5–10 litres/hour/250 ml. of the chlorinated 'gasoline'.

2. *Effect of Caustic Soda Concentration on the Overall Chlorination Period.*—As already mentioned, direct chlorination of 'gasoline' results in the formation of a thick resinous material which makes the chlorination process difficult. This difficulty was gradually overcome by making use of oxidative chlorination. Water may be used to furnish hypochlorite ions but preference is given to dilute alkalis where the required hypochlorite concentration can be obtained conveniently. The chlorination process may be divided into three parts namely the preparation of hypochlorite solution, the first and the second stage of chlorination in presence of hypochlorite.

Sodium hypochlorite is prepared by passing chlorine gas through solution of caustic soda at 10–15°C. The influence of concentration of alkali on quality of the hypochlorite which is presented in table 2 shows that:

TABLE 2.—INFLUENCE OF CAUSTIC SODA ON QUALITY OF SODIUM HYPOCHLORITE

No.	NaOH %	Cl ₂ from ClO ₂ g./ 100 ml.	Cl ₂ from ClO ₂ g./ 100 ml.	Cl ₂ from ClO ₃ g./ 100 ml.	Total available chlorine (Arsenite method) ² g./100 ml.
1.	0.492	0.725	—	0.037	0.749
2.	0.998	1.700	0.02	0.120	1.771
3.	2.005	2.059	—	0.219	2.080
4.	2.992	2.098	0.031	0.057	2.272
5.	3.908	2.415	—	0.027	2.534
6.	9.840	2.432	—	0.278	2.643

with the increase in the concentration of caustic soda from 0.5 to 4 and 10 percent the available chlorine content increases from 0.749 to 2.643 g./100 ml. of the solution. When analysed for ClO, ClO₂ and ClO₃ (determined by sodium thiosulphate method³), the hypochlorite range between 0.725 to 2.432, chlorite is almost absent and the amount of chlorate varies from 0.027 to 0.278 g./100 ml. of the solution.

In the first stage the rise in specific gravity is rapid and independent of the concentration of caustic soda solution (see Table 3). This may be due to the reason that nearly all the hypochlorite which brings about reduction in chlorination period is consumed in destroying chloro-sulphur compounds known to have polymerising action on hydroaromatic bodies. The analysis of the aqueous phase from the first stage of chlorination indicates, that the hydrochloric acid (see Table 4) is present from 20-30 percent and the amount of sulphuric acid, produced by the oxidation of the organic sulphur, is independent of the hypochlorite concentration and varies between 0.485—0.582 g./100 ml. of the solution,

In the second stage of chlorination where the chlorine absorption is slow, the hypochlorite concentration has a significant effect on reducing the chlorination period, e.g. with the rise in the concentration from 0.442 to 9.840 percent the time of chlorination falls from 44.5 to 22.2 hours. (see Table 3). Referring to Fig. 2, where the caustic soda percentage is plotted against the period of chlorination, it will be noted that for the first 2 percent rise in caustic soda concentration, the fall in overall period of chlorination is 39 hours; for a subsequent rise of 2 percent, the fall is 7.5 hours; and for a rise from 4 to 10 percent the fall is only 2 hours. This suggests that an economic concentration of caustic soda solution

TABLE 3.—EFFECT OF THE CAUSTIC-SODA STRENGTH ON THE CHLORINATION PERIOD.

Chlorination period hours.	0.5% NaOH		1% NaOH		2% NaOH		3% NaOH		4% NaOH		10% NaOH	
	S.G. g./c.c.	Temp. °C.	S.G. g./c.c.	Temp. °C.	S.G. g./c.c.	Temp. °C.	S.G. g./c.c.	Temp. °C.	S.G. g./c.c.	Temp. °C.	S.G. g./c.c.	Temp. °C.
2	1.18	27	1.20	26	1.85*(2.5)	25	1.22*(3)	25	1.225	29	1.205	29
4	1.22	26	1.24	25	1.215	26	1.24*(5)	25	1.245	25.5	1.240	30
6	1.24	25	1.27	25	1.235	26	*(7)1.26	25	1.270	23	1.270	29
8	1.26	25	1.29	25	1.255	25	*(9)1.28	25	1.290	26	1.300	29
10	1.27	26	1.31	25	1.275	25			1.310	24	1.315	28
15	1.30	25						24			1.316	28
20	1.315	26	1.35	25	1.355	25	*(25)1.385	25	1.38	27	1.395	27
30	1.39	26	1.385	25	1.405*(29.5)	27	*(27)1.410	26	1.405*(24)	23	1.41*(22)	27
40	1.40	27	*(38)1.405	25								
50	*(46.5)1.415	26										

S.P.: Specific gravity of 'gasoline' = 0.815 g./c.c.;
of Chlorinated-Gasoline = 1.415 g./c.c. at 15°C.

(*Figures in brackets indicate hours.)

TABLE 4.

No.	NaOH %	Chlorination stage	Hydrochloric acid g./100 cc	Sulphuric acid g./100 cc H ₂ SO ₄
1.	0.442	I	26.833	0.582
		II	24.133	0.534
2.	0.998	I	28.433	0.561
		II	29.30	0.458
3.	2.005	I	25.054	0.485
		II	22.094	0.494
4.	2.992	I	23.80	0.491
		II	23.48	0.434
5.	3.908	I	23.420	0.559
		II	24.366	0.559
6.	9.840	I	25.200	0.574
		II	—	0.444

These results further indicate that the reaction between hypochlorite and 'gasoline' in the presence of chlorine is irreversible i.e. the hypochlorite is not regenerated during chlorination but almost destroyed as shown in Table 5.

lies around 2 percent and that above 2 percent the chlorination process is more or less wasteful. Here in the second stage, as in the first one, the

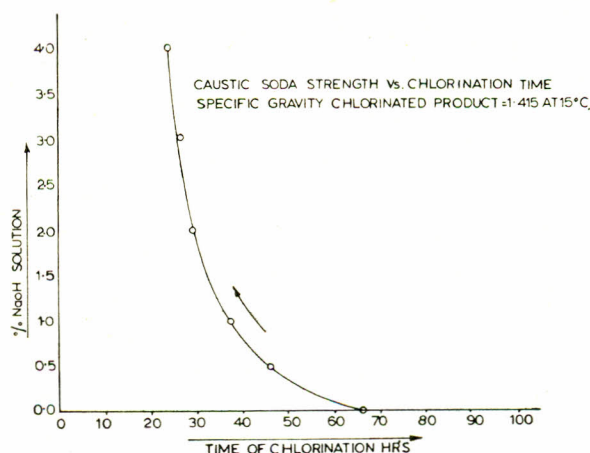


Fig. 2.

hypochlorite is not regenerated which is manifest in Table 5, where the quantities of the available chlorine in the aqueous layer are tabulated. The yield of hydrochloric acid in the second stage varies between 20-30 g./100 ml. and that of from 0.434 sulphuric acid to 0.559 g./100 ml. (see Table 4).

TABLE 5.—HYPOCHLORITE, CHLORITE AND CHLORATE CONTENTS OF THE CHLORINATED CAUSTIC SODA SOLUTION AFTER FIRST AND SECOND STAGE OF CHLORINATION.

No.	Alkali per cent	Chlorination Stage	Cl ₂ from ClO	Cl ₂ from ClO ₂	Cl ₂ from ClO ₃
1.	0.442	I	0.019	0.014	0.006
		II	0.017	0.00	0.054
2.	0.998	I	0.052	0.031	0.087
		II	0.009	0.009	0.032
3.	2.005	I	0.037	0.022	0.072
		II	0.010	0.004	0.030
4.	2.992	I	0.031	0.02	0.030
		II	0.28	0.007	0.030
5.	3.908	I	0.078	—	0.021
		II	0.025	0.003	0.044
6.	9.840	I	0.121	0.019	—
		II	0.014	0.013	0.024

3. *Effect of Metal or Metal Halides on the Chlorination Period.*—In the present process of chlorination, equal volumes of 'gasoline' and hypochlorite solution are taken which seriously limit the capacity of the chlorination apparatus. So far, the use of an alkali appears indispensable but experiments are in progress to minimize its use in the process. This has been partly achieved by introducing a metal catalyst namely iron, chromium, lead, copper, palladium or zinc in 0.016 to 0.333 per cent concentrations in the second stage of chlorination. The results in Table 6 show that at 30°C. with the increase in iron content from 0.1 to 0.5 g./250 ml. the specific gravity of the partly chlorinated gasoline rises from 1.2 to 1.35-1.42 g./cc in 24 hours. At 45°C., the target specific gravity of 1.415 g./cc. is reached using 0.2 g. of iron per 250 ml. of the gasoline.

Aluminium is not particularly active at 30°C. but it is effective at 45°C. in 0.05 and 0.1 g. concentration. Chromium, lead, copper, palladium and zinc are almost ineffective.

Fresh Makrolin (sp. gravity 1.415 g./c.c. at 15°C.) is an orange coloured syrupy liquid, which on exposure to air becomes opaque and gradually changes to dark red (heating at 100°C. also darkens the colour but produces no opacity). Makrolin is immiscible with water but readily goes into solution with a number of solvents.

TABLE 6.—EFFECT OF THE CATALYSTS ON THE SECOND STAGE OF CHLORINATION PERIOD.

No.	Catalyst	g./250 ml.	Specific Gravity in 24 hours at Chlorination Temp.	
			30°C.	45°C.
1.	Iron	0.1	1.360 g./	1.400 g./
		0.2	1.390	1.410
		0.25	1.280	1.410
		0.5	1.420	1.405
2.	Alluminium	0.05	1.370	1.410
		0.1	1.360	1.405
		0.5	1.380	—
		1.0	1.360	—
3.	Chromium	0.1	1.335	1.385
		0.15	1.310	1.360
		0.2	1.340	1.375
		0.25	1.325	1.375

Loss in weight of Makrolin when allowed to stand over anhydrous calcium chloride at room temperature is about 0.0276 per cent and at 100°C. the loss is 9.350 per cent per 24 hours. Being hygroscopic in nature Makrolin absorbs moisture from air and liberates hydrochloric acid. Since hydrochloric acid is also hygroscopic, more and more moisture is absorbed from air, accelerating thereby the reproduction of hydrochloric acid. This cycle continues till almost all the available chlorine in Makrolin is exhausted.

Conclusion

The foregoing experimental study of the effect of the variables such as gas rates, alkali concentration and certain metal catalysts on the overall chlorination period, has yielded encouraging results. On the basis of these results, it now appears possible to continue the present work to a stage where the production of Makrolin on a pilot plant scale would be feasible.

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