

CHLORINATION OF PETROLEUM HYDROCARBONS

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Different low boiling petroleum cuts both indigenous as well as imported have been chlorinated under varying conditions of gas-rates, sunlight or ultraviolet radiations and temperature, and in the presence of hypochlorite solutions. Low gas-rates namely 0.133 L/min./litre at initial stages of chlorination favour smooth absorption. In the presence of direct sunlight the gas-rates increase from 0.0033 to 0.1805 L/min./100 ml. at 10 mm. Hg, while higher rates namely 0.0033-0.216 L/min./100 ml. result in sparking and blackening of the product. Ultraviolet radiations effects the second-stage where otherwise the gas-absorption is low. Chlorination in the presence of caustic-soda varying in concentration from 0.5 to 4 percent, does neither promote smooth absorption nor helps in reducing the overall period of chlorination. The addition of the final chlorinated product in 5 to 25 percent concentration, promotes the smooth absorption of chlorine. Of all the methods used, chlorination in the presence of poly-chlorinated hydrocarbons has proved beneficial in promoting smooth absorption of chlorine. Less so is the chlorination in the presence of direct sunlight. A combination of the two gives satisfactory results.

Introduction

Pakistan is importing pesticides to the tune of about Rupees one and a half crores annually which satisfies only a fraction of her requirements.¹ All the commercial pesticides namely D.D.T., B.H.C, heptachlor, aldrin, dieldrin and toxaphene are chlorinated products of benzene, cyclopentadienes and certain fraction of the turpentine-oil. With the exception of turpentine-oil, all the remaining hydrocarbons are imported and consequently, insecticides based on these hydrocarbons will cost more when compared with those based on cheaper indigenous raw-materials. In view of this, chlorinated pesticides from petroleum-hydrocarbons have been developed at these laboratories. These insecticides have proved effective against cock-roaches, houseflies and mosquito larvae.²

Literature survey shows, that relatively less work has been done on the chlorination of low-boiling hydrocarbons. Weizvich³ chlorinated petroleum-hydrocarbons (B.P. 0-230°C.) at 10-18°C. to a chlorine content of 20-40 percent. The fraction upto 140°C. of the chlorinated product was used as solvent in lubricants and fire proofing. Desai and Mehta⁴ obtained a solid insecticide and larvaecide by chlorinating petroleum cuts (B.P. 90-200°C.) at 5°C. Keefer⁵ and many other workers chlorinated petroleum cuts such as kerosene, paraffin-wax and lubricating oils to obtain fire-proof materials, detergents, antioxidants for mineral oils and high pressure lubricants. Gault and Lauchec⁶ chlorinated long chain hydrocarbons and hydrolysed the chlorinated product with alcoholic potash for the preparation of organic substances other than insecticides.

The present investigation relates to the experi-

mental study of the different methods of chlorination of petroleum-hydrocarbons (for physical properties see Table I),⁷ namely direct chlorination i.e. chlorination in the presence of a poly-chlorinated petroleum cut, which is the final chlorination product (sunlight and ultraviolet radiations) and oxidative chlorination.

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

No.	Physical Property	Petroleum Fraction (A)	Petroleum Fraction (S)	Petroleum Fraction (I)
1.	B.P. Range °C.	41-150	60-150	40-155
2.	Specific gravity	0.729	0.731	0.730
3.	Paraffins	84.9	88.0	67-83 %
4.	Napthenes			12-25
5.	Olefins %	0.3	0.3	0.0-0.35
6.	Aromatics %	12-17	12	1-20

Apparatus and Experimental Procedure

Apparatus used for the chlorination of the petroleum cuts is similar to that used for the chlorination of 'Gasoline'.⁸

About 50 ml. of water and 200 ml. of the petroleum cut containing 5-25 percent of the poly-chlorinated hydrocarbons is transferred to the first column and chlorinated at 15°C. till the density rose from 0.9 to 1.3-1.4. The partly chlorinated petroleum fraction is then removed to the next column for second-stage chlorination where it is re-chlorinated to a density of 1.515 at 15-20°C. The end product is then scrubbed free of dissolved chlorine and hydrochloric acid with water and dried over anhydrous sodium sulphate in the usual manner.

Results and Discussion

Effect of the Gas-Rates.—Gas absorption in petroleum cuts is poor in the absence of either the sunlight or the poly-chlorinated hydrocarbons. The use of direct sunlight results in high reaction velocity which may initiate sparking and consequently fire. The desirable procedure comprises adding 5-25% of the final chlorination product and then chlorinating at a controlled temperature range of 15-25°C. Under these conditions, the absorption rates have been found to vary between 0.133 to 1.332 litre for the first stage and 1.332 litre/min./litre of the mixture for the second stage of chlorination as shown in Table 2.

TABLE 2.—EFFECT OF THE GAS-RATES ON THE OVERALL CHLORINATION PERIOD.

No.	Gas-Rates (litre/min./litre)	Duration (hours)	Specific gravity g./c.c.
1.	0.133	4	—
2.	0.666	5	1.29
3.	1.332	6	1.30
4.	1.332	9	1.41
5.	„	14	1.435
6.	„	22	1.475
7.	„	28	1.51

Initial Specific gravity=0.940 g./cc. Final Specific gravity=1.515 g./cc. Temperature of Chlorination=15-25°C.

The above results indicate that the chlorine absorption is slow at initial stages but gradually increases to about ten times the original rate. This may be due to the gradual formation of a 'carrier', which is believed to be responsible for the smooth and quick absorption of the chlorine-gas at initial stages.

Effect of Direct Sunlight and Ultraviolet Radiations.—The use of sunlight has been found beneficial in promoting chlorine absorption. It was observed that the gas absorption varies with the intensity of the light i.e. in the presence of sunlight, reaction velocity is higher while in indirect or diffused light the velocity is low. Effect of the sunlight for a given gas-rate and the composition of the feed solution is shown in Table 3.

It is manifest from Table 3 that in the presence of direct sunlight when the gas-rate is increased from 0.003 to 0.1805 L/min., the 'sparking time' rises from 5 to 90 minutes and thereafter the 'sparking' is almost eliminated. When the gas-rates are increased from 0.0033 to 0.216 L/min., the danger of 'sparking' persists and is not eli-

minated even by using a mixture containing 25 percent of poly-chlorinated petroleum cut. This would mean that for given experimental conditions, there is an optimum gas-rate beyond which the 'sparking' becomes imminent. This gas-rate may be called as the 'Critical-Gas-Rate'. Further work on this aspect of the problem is in progress.

TABLE 3.—EFFECT OF THE SUNLIGHT ON GAS-ABSORPTION.

No.	Composition	Optimum Gas-Rate (litre/min./100 ml.)	Remarks
1.	Pure	0.0066	(a) Sparking after 10 mts. „ „ 15 „ „ „ 35 „ „ „ 90 „ No Sparking
2.	10%	0.011	
3.	15%	0.0299	
4.	20%	0.0365	
5.	25%	0.1805	
1.	Pure	0.0066	(b) Sparking after 0-35 „ „ 0-10 „ „ 2-20 „ „ 1-35
2.	15%	0.0231	
3.	20%	0.0365	
4.	25%	0.0231	

Chlorination temp.=15°C. Final Specific gravity=1.415 g./c.c.

As far as the effect of the ultraviolet-radiation is concerned, no effect on gas-absorption could be noticed in the first-stage of chlorination while in the second-stage, the use of these radiations has an appreciable effect on the gas-absorption and consequently on reducing the overall period of chlorination down to about 20 hours.

Effect of the Temperature.—Temperature plays a very important role in the first-stage of chlorination. Chlorine-absorption is an exothermic reaction and if not properly controlled may give rise to explosion or fire. This could be avoided if the proper temperature is maintained during the chlorination period. Using 5,10,15,20 and 25 percent of the final chlorination product in the mixture, chlorination was conducted at 15,20 and 25°C. in the presence of diffused sunlight.

These results show that at 15°C. the chlorine absorption is related to the amount of the final chlorination product present in the mixture. The colour of the mixture remains pale to yellow throughout the experiment which indicates that for a given gas-rate of 0.00332/min./100 ml., the physical absorption exceeds the chemical reaction. At 20°C., it is observed that the ab-

sorption is smooth but some physical absorption does take place towards the end. At 25°C., the absorption is partial and incomplete which results in the appearance of paleness. Thus it would be seen that chlorination at 20°C. favours smooth absorption while at 15 and 25°C., the chlorine-petroleum reaction is rather unsatisfactory.

Effect of the Concentration of Sodium Hydroxide on the Chlorination Period.—As in the case of the chlorination of 'Gasoline',⁸ the increase in the concentration of the caustic-soda decreases the overall period of chlorination, it was thought that higher concentrations might also help in

reducing the overall period of chlorination of the petroleum hydrocarbons. In view of this, caustic-soda of same concentration i.e. 0.5 to 4% was used and petroleum cuts chlorinated at 10-15°C.

The results as they appear in Table 5 show that a change in the concentration from 0.5 to 1 percent did not reduce the overall period of chlorination while higher concentrations, namely above 2 percent resulted in explosion. This was avoided when the first-stage chlorination (0.9 to 1.4 g./cc.) was carried out in the presence of 0.5 percent caustic-soda while second-stage of chlorination (1.4-1.5, g./cc.) was conducted with higher concentrations, namely

TABLE 4.—EFFECT OF THE TEMPERATURE ON THE CHLORINE-ABSORPTION IN PETROLEUM CUT.

No.	Temperature °C.	Percent Poly-chlorinated Hydrocarbon						Remarks
		Pure	5%	10%	15%	20%	25%	
1.	15	(0.715) P.A. C.A.	(0.750) P.A. C.A.	(0.790) C.A.	(0.830) C.A.	(0.875) C.A.	(0.916) C.A.	Pale Yellow
2.	20	C.A.	C.A.	C.A.	C.A.	C.A.	C.A.	Opaque Pale
3.	25	P.A. C.A.	C.A. P.A.	C.A. C.A.	C.A. P.A.	C.A. P.A.	C.A.	Light Pale

Gas-Rate=0.0033 litre/min./100 ml. at 100 mm. Hg. Chlorination Period=8 hours. C.A.=Complete Absorption. P.A.=Partial Absorption ()=Indicate Specific Gravity g./cc.

TABLE 5.—EFFECT OF THE CAUSTIC-SODA CONCENTRATION ON THE OVERALL PERIOD OF CHLORINATION.

No.	Caustic-Soda Concentration %	Petroleum (Indigenous)			Hydrocarbons (Imported)		
		1st Stage Hrs.	2nd Stage Hrs.	Total Hrs.	1st Stage Hrs.	2nd Stage Hrs.	Total Hrs.
1.		7	19	26	17	53	70
2.		4	22	26	6	26	32
3.	0.5	4	22	26	4	24	28
4.	1.0	4	18	22	5	22	27
5.	2.0 Explosion					
6.	0.5 1st Stage 2.0 2nd Stage	4	18	22	6	26	32
7.	0.5 1st Stage 3.0 2nd Stage	5	21	26	5	24	29
8.	0.5 1st Stage 4.0 2nd Stage—	5	19	24	6	22	28

2,3 and 4 percent caustic-soda solutions. Such a combination of the concentration of alkali, though eliminate the danger of explosion, did not prove useful in reducing the overall period of chlorination. It may as well be concluded that the quantitative absorption of chlorine in the first-stage is about seven times the second-stage absorption (i.e. rise in specific gravity from 0.7 to 1.4 g./cc. is in 4 hours while 1.4 to 1.5 g./cc. in 20-22 hours). It may as well be seen that the chlorination period in the presence of water is about the same as with caustic-soda, which also supports the previous conclusion that caustic-soda plays no part in reducing the chlorination period.

Chlorinated petroleum hydrocarbon (Specific gravity 1.515 g./cc. at 15°C.) is a colourless to pale yellow camphoric smelling viscous liquid, with the following distillation range at 5-6 m.m. Hg.

TABLE 6.—DISTILLATION OF CHLORINATED PETROLEUM AT 5-6 m.m. Hg.

No.	Name	B.P. Range °C.	Specific gravity at 30°C.	% Volume
1.	Attock Oil	95-150	1.443	31
		150-180	1.500	29
	Petroleum Cut (Chlorinated)	180-200	1.540	23.5
		Above 200°C.	—	10.0
			1.442	37.5
2.	Imported Petro- leum Cut (Chlorinated)	„	1.503	27
			1.549	21
			—	15

Steam distillation yields about 7-10 percent of the distillate while distillation at atmospheric condi-

tions results in a black solid spongy residue. The chlorinated petroleum fraction contains about 67 percent of chlorine and has been found stable at room temperature for a considerable period of time. Its viscosity is 14-20 centipoises and refractive index 1.5167-1.5217 at 20°C.

Chlorinated petroleum cuts with specific gravity varying from 1.4 to 1.5 may be used as pesticides.

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References

1. Private Communication (Department of Plant Protection, Govt. of Pakistan, Karachi.)
2. S. Siddiqui, S. A. Qureshi and S. H. Ashrafi, Pakistan Patent Application No. 39/64, January 14, 1964.
3. P.J. Weizvich and H.G. Vesterdal, U.S.P. 119, 873 (1938).
4. R.D. Desai and M.D. Mehta, Indian Patent, 33, 241, August 14, (1941).
5. R.W. Keefer, *Chlorination of Petroleum Fractions* (Ph.D. Thesis, Pennsylvania State College, December, 1942).
6. Gault and Lanchec, Chem. et. Ind. **81**, 881-4 (1959).
7. Private Communications (M/s. Attock Oil Ltd., Rawalpindi and M/s. Burmah Shell, Karachi.)
8. S.A. Qureshi and Salim Reza, Pakistan J. Sci. Ind. Res., **7**, 192 (1964).