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Academician of the Academy of Sciences of the Azerbaijan SSR Yu. G. MAMEDALIEV, M. M. GUSEINOV

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Abstract

Full Text

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Academician of the Academy of Sciences of the Azerbaijan SSR Yu. G. MAMEDALIEV, M. M. GUSEINOV
and F. A. MEKHTIEVA

PRODUCTION OF CARBON TETRACHLORIDE BY CHLORINATION OF METHANE IN A FLUIDIZED BED OF CATALYST

Carbon tetrachloride is used as a solvent for oils, resins, paraffin, and other organic substances; it serves as a starting material in the production of the refrigerant freon, is included in various fire-extinguishing compositions, and serves as a starting substance for the synthesis of ethane. At present, the principal method for producing carbon tetrachloride is the method based on the chlorination reaction of carbon disulfide, which is distinguished by the complexity of the technological process and by explosion hazard.

One of the authors of the present article, as early as 1936, developed and tested on a semi-industrial scale a method for producing carbon tetrachloride ([2], [3]) by catalytic chlorination of methane in the presence of carbon dioxide, which plays the role of a diluent in order to avoid the explosive nature of the reaction. For the same purpose, in the installations described in the literature ([4], [5]), chlorination is provided for under conditions of formation of all chlorinated methane derivatives and stepwise chlorination.

Investigations in the field of catalytic chlorination of alkanes carried out up to the present time provide for the reaction to proceed in the presence of a fixed bed of catalyst or molten salts. An exception is the work of A. V. Topchiev and co-workers ([6]) on the chlorination of propane on a moving contact. Strictly speaking, the investigations of the latter authors cannot be assigned to the category of catalytic processes, since the moving contact was a molten stone—mullite—which played the role of a chemically inert heat carrier.

The chain mechanism of the alkane chlorination reaction and its strongly exothermic character exclude the possibility of modeling the process; as a result, carrying out the process in large reactor systems is accompanied by serious complications. When the chlorination reaction is conducted under conditions of an excess of chlorine in the reacting mixture, the reaction is accompanied by frequent explosions with formation of soot, which disrupts the normal course of the reaction. In order to avoid the explosive nature of the chlorination reaction, various authors proposed diluting the reacting mixture with inert gases—nitrogen, hydrogen chloride, carbon dioxide, etc. Dilution of the reacting mixture with inert gases, although it eliminates the danger of explosion, creates additional difficulties connected with condensation of the products from the diluted gas mixture, circulation of the inert gas, and so forth.

The most effective method eliminating the above-mentioned shortcomings is to carry out the halogenation reaction in a fluidized bed of a finely dispersed catalyst. When this method, proposed by us, is used, as a result of collisions of radicals and atoms with particles of the powdered catalyst, inhibition of the halogenation chain reaction occurs, and its explosive development is stopped.

In this connection we carried out studies on the production of carbon tetrachloride by chlorination of natural gas in a fluidized catalyst bed over a wide range of variation of the process parameters. The natural gas used in this study was gas from the Duvanny field of the Azerbaijan SSR, containing 97–98% methane. Of the catalysts tested, pumice showed the greatest activity, and therefore the data presented refer to this catalyst. The experiments were carried out in the apparatus shown in Fig. 1.

Natural gas from cylinder *1*, passing through flow-rate regulator *2*, sulfuric acid absorber *3*, flowmeter *4*, and calcium chloride bottle *5*, enters the lower part of reactor *6*, which acts as a mixer. Chlorine follows an analogous path. The lower part of the reactor is separated from its main part by a glass filter. This filter serves as a regulator

Table 1

Characteristics of the experiments	7	8	6	15	5
Experimental conditions					
temperature, °C	380	400	420	380	410
mole ratio $CH_4 : Cl_2$	1 : 4	1 : 4	1 : 4	1 : 4	1 : 4
CH_4 rate, l/h	6.35	6.35	6.35	7.8	6.35
Cl_2 rate, l/h	25.4	25.4	25.4	31.1	25.4
contact time, sec	5.1	5.0	4.9	4.2	4.9

Characteristics of the experiments	7	8	6	15	5
duration of experiment, h	3.5	3.0	3.0	3.0	3.0
Fed to the reactor (N.T.P.):					
CH_4	20.4	17.4	17.4	21.4	17.4
Cl_2	81.6	69.8	69.8	85.6	69.8
Obtained					
catalyst, g	140	96.4	79	142	109
HCl, g	122	104	125	140	113
Cl_2, g	2	20	25	2.4	8.0
gas, l	0.8	0.4	—	—	—
Properties of the catalyst					
d_4^{20}	1.6028	1.6028	1.6071	1.5905	1.5996
n_D^{20}	1.4608	1.4640	1.4650	1.4616	1.4618
Fractional composition					
initial b.p., °C	59	72	72	59	63
fraction 59–63°—yield, %	0.2	—	—	1.7	—
fraction 63–74°—yield, %	6.4	1.6	5.2	8.8	6.6
d_4^{20}	1.5699	1.5710	1.5712	1.5695	1.5674
n_D^{20}	1.4582	1.4588	1.4589	1.4584	1.4580
fraction 74–78°—yield, %	85.8	88.5	83.6	82.0	86.5
d_4^{20}	1.5940	1.5932	1.5940	1.5942	1.5948
n_D^{20}	1.4615	1.4614	1.4613	1.4612	1.4626
Residue					
yield, %	5.6	9.0	10.0	5.0	6.1

Fig. 1

Figure 1: Fig. 1

Characteristics of the experiments	7	8	6	15	5
losses, %	2.0	0.9	1.2	2.5	0.8
Material balance for chlorine, %					
in catalyst	49.0	41.0	33.0	48.2	45.4
for formation of HCl	49.2	45.6	54.7	50.2	49.7
free Cl_2	0.8	8.0	11.3	0.9	3.6
losses	1.0	5.4	1.0	0.7	1.3

Fig. 1

Labels visible in the figure: 1–10; “Rheostat” ; “8 atm.”

uniform feed of the mixture into the reaction zone, and also eliminates the possibility of catalyst entering the mixer.

The mixture of chlorine and methane passes through a filter into a reactor with a fluidized bed of powdered catalyst. The reactor is a glass tube 3 cm in diameter and 100 cm long, heated by means of an electric winding. The reactor temperature is regulated with a laboratory autotransformer and measured with a thermometer placed inside the reactor.

The products from the reactor enter receiver-coolers 7, cooled with a mixture of ice and salt. To remove hydrogen chloride, the exit gases pass through column 8, irrigated with water. The gases freed from hydrogen chloride, after passing through a bottle with calcium chloride, enter charcoal adsorber 9 to trap the uncondensed portion of the reaction products, and are collected in gasometer 11.

After the experiment, the wash waters were analyzed for the content of chlorine and hydrogen chloride, and the catalyst was subjected to detailed examination. The results of typical experiments are given in Table 1.

As is evident from the data presented in Table 1, at a temperature of 380–400°, a ratio of $Cl_2 : CH_4 = 4 : 1$, and a contact time of 5 sec, in a fluidized bed of finely dispersed pumice the chlorine reacts completely, forming up to 90% carbon tetrachloride. The remaining 5–10% consists mainly of tetrachloroethylene and hexachloroethane.

The method developed for the synthesis of carbon tetrachloride by chlorination of methane in a fluidized catalyst bed can also be applied to exhaustive chlorination of other alkanes.

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