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VINYL CHLORIDE PRODUCTION BY CATALYTIC DEHYDROHALOGENATION OF 1.2 DICHLOROETHANE[1/]

by

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CONTENTS

Title: Vinyl chloride production by catalytic dehydrohalogenation of 1.2 dichloroethane.

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The present paper is concerned with research on the production of vinyl chloride by dehydrochlorination of 1.2 dichloroethane.
Aluminas, with special promoted treatment were synthesized in the Instituto Mexicano del Petróleo and were used as catalysts.

In this particular dehydrochlorination reaction the influence of temperature (300, 325, 350°C) and the influence of space-velocity (0.63 1.86, 3.75 g/g/hr.) on conversion, yield and carbon deposit on the catalyst were studied.
Experiments were run in a pilot plant with a tubular fix bed reactor of 2.5 cm internal diameter, and charged with 20g of catalyst.
Each run took ten hours and included a gas chromatographic and volumetric analysis of the reaction products hourly.
Regeneration of the catalyst was measured also, and the results showed the possibility of operating in an intermittent cycle process by using at least two reactors. The conversion obtained (which still could be improved) was from 80 - 90% per pass, with a stochiometrical yield of vinyl chloride of 40 - 57% (theoretical yield is 63%) and a selectivity of 95 - 99%. Therefore, it appears to offer some competitive route to the classical thermal process.

I INTRODUCTION.

1.- Background.

In Mexico the demand for vinyl chloride is about 35,000 tons per year (1), and the current process is based on the use of a tubular furrace which produces vinyl chloride and hydrochloric acid from the pyrolisis of dichloroethane, with a maximum 60% conversion.

On the other hand, the remarkable development of the petrochemical industry has led to several attemps to obtain a better conversion in this process.

During the course of studies on the production of vinyl chloride by catalytic pyrolisis of dichloroethane, it was found that the process was quite effective in increasing the total yield of vinyl chloride.

2.- What is being investigated in the world ?

There are two main routes to vinyl chloride production. One is via the addition of hydrocl loric acid to acetylene; the other route is via the chlorination of ethylene producing dichloroethane which can be thenthermally decomposed, yielding vinyl chloride and hydrochloric acid. All of these processes have advantages and disadvantages, as is related in the literature (2, 3, 4, 5).

3.- Processes tha involve dichloroethane cracking.

The pyrolisis reaction involves a free radical chain mechenism (6,7) in which a free radical of chlorine starts the chain.

$$Cl + CH_2CL - CH_2CL \longrightarrow HCL + CH_2CL - \dot{C}HCL \quad ------ (1)$$

$$CH_2CL - \dot{C}HCL \longrightarrow CH_2 = CHCL + \dot{C}L \quad ------ (2)$$

These two propagation steps are thought to occur primarily, if not exclusively, in the gas phase. The first step for the above chain has not been established with certainty, but there is some evidence that part of the reaction initiation occurs at the wall of the reactor. When a catalyst is used, initiation apparently occurs at the catalyst surface; that means that characteristic properties of the catalyst (8, 9, 10, 11) such as the crystallographic morphology, the surface area, the pore volume, the acidity, etc., affect the reaction.

$$CH_2CL - CH_2Cl \longrightarrow CH_2CL - \dot{C}H_2 + \bar{C}L \qquad ---- (3)$$

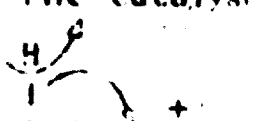
4.- Ionic mechanism considerations.

The mechanism of the catalytic reaction could be ionic because it has been proven the alumina surface, when heated, presents an acid character. Two possible ways for the reaction to take place are assumed:

a) The formation of a carbocation ion by acid centers,

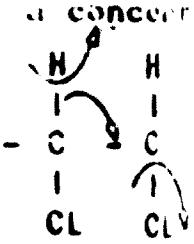
$$CH_2CL - CH_2Cl \longrightarrow CH_2CL - \overset{+}{C}H_2 + \bar{C}L \qquad ---- (4)$$

and the rearrangement of molecules by the elimination of the hydogen ions when the molecules are deadsorbed from the catalyst.



$$CHCL - \overset{+}{C}H_2 \longrightarrow CHCL = CH_2 + H^+ \qquad ---- (5)$$

b) By a concerated mechanism



$$CH_2 = CHCL + H^+ + CL^- \qquad ---- (6)$$

At present the I.M.P. laboratories are investigating the influence of the acidity in the reaction by controlling it on the alumina surface or by the addition of other compounds in the production processes.

5.- Catalytic dehydrohalogenation processes.

From the review of literature, it is possible to remark that there are no commercial catalytic processes in operation in spite of the numerous patents claimed in this area.

For example, some references (12, 13, 14, 15, 16) use a system $CuCl_2/Al_2O_3$, $CuCl_2/C$ for vinyl chloride obtentions , - others (17, 18) work with $HgCl_2/SiO_2$, $HgCl_2/C$ at low temperatures. And by utilizing Al_2O_3 (14, 19, 20) they obtain good yield and selectivity.

I: EXPERIMENTAL

6.- Production of catalysts.

The properties of aluminas used as catalysts depend on their preparation (8, 9, 21, 22, 23). In general they are obtained from the aluminium, the aluminium chloride and the aluminium sulphate, or from organometallic compounds such as the alkyl aluminium. In all the cases these compounds experiments an alkali treatment, and produce the precipitation of its hydroxide. Further heating yield alumina with sharp chemical characteristics.

Some aluminas (A-4, A-5) were synthesized in the Instituto Mexicano del Petróleo and their catalytic activity was compared with commercial aluminas.

7.- All the aluminas used were analized by X-Ray microdiffraction, electronic microscopy (E.M.) and surface adsorption. Also pore volume, particle, absolute density , bulk and compact density were measured. See table I.

8.- Production of vinyl chloride.

Pilot plant (figure 1) studies, carried out in a tubular fix bed reactor, were used to provide a measure of the distribution of products, and to correlate the space-velocity and - the temperature.

The feed of technical 1.2 dichloroethane from container A, is connected to pistón pump S, which has a device for controlling

the impulses of the pump and a micrometric control of piston displacement, so that the liquid pumping can change - rapidly from 0.3 ml/minute to 4.5 ml/minute. These changes were verified by turning on the valve V-3 an by measuring - the outlet liquid with a graduated cylinder. It also has a flow liquid rotameter F-1.

The reactor R is made of stainless steel with dimensions of 0.25 m. in length and 0.025 m. in internal diameter. It was heated by a tubular and electrical furnace H, and the temperature was regulated by a proportional control G. The reaction temperature was measured by a themocouple TP that is under the fix bed catalyst. In all the experiments 20 gr. of catalyst were used.

Each run started by heating the system with a N_2 as carrier controlled by a gas flow rotameter F-2. It took one hour for the fix bed catalyst to reach 350°C. Simultaneously, the flow feed was measured and was passed to the reaction zone. The products were collected in a cold trap C-1 and in special traps C-2 (figure 2).

9.- Analysis (24, 25, 26).

The reaction products were in the vapor phase were bubbled at room temperature through methyl 2 pirrolidone for 60-120 seconds. The special designs of the trap help the quantitative dissolution of reaction products without changes of pressure in the reactor.

The analysis of organic products (27) was made in a Perkin-Elmer F-11 gas phase chromatograph, with a flame ionization detector. It is composed of two steel columns having a length

of 0.15 m. and a 1/8 inch internal diameter, filled with solid porapak Q (80-100 mesh). The injector temperature program was from 30 to 200°C at a rate of 30°C/minute. The carrier gas was nitrogen (150 ml/minute).

Ethanol was used as an internal reference standar and 3 microliters of products were injected.

Under these conditions the analysis time was 9 minutes after which the N methyl pirrolidone was vented into the atmosphere through the backflush system of the chromatograph.

Vinyl chloride, 1.2 dichloroethane, ethanol, acetylene were identified.

Hydrocholoric acid was analyzed by pouring all the reaction products and solvent of the trap -2 (without the 3 microliters used for organic analysis) in an Erlenmeyer flask, washing with 50 ml of water and tritrating with 1.0N NaOH.

The content of carbon in the catalysts was determined by burning at 450°C, for 18 hours in the presence of air carrier gas.

10.- Catalyst activation.

The dehydrohalogenation reaction was carried out at relatively low temperatures (275-400°C), however, cracking reactions were detected by the gas phase chromatographic analysis and by the deposite of carbon on the alumina surface. This diminished the conversion with time and therefore the activation of catalysis was studied after 10-hour-runs. The results for some experiments are computed on table II.

III RESULTS.

Tables I to IV and Figures 1 to 6 show the experimental results. All the experiments were made at atmospheric pressure (585 mm. Hg in Mexico) and represent at least 2 runs with the same catalysts. They were analyzed by gas phase chromatography of each one of the 10 samples trapped in every experiment.

The calculation of yield, conversion and selectivity were obtained from the average of all the traps analyzed in every run.

The carbon deposited in catalysts was determinated after each 10-hour-runs.

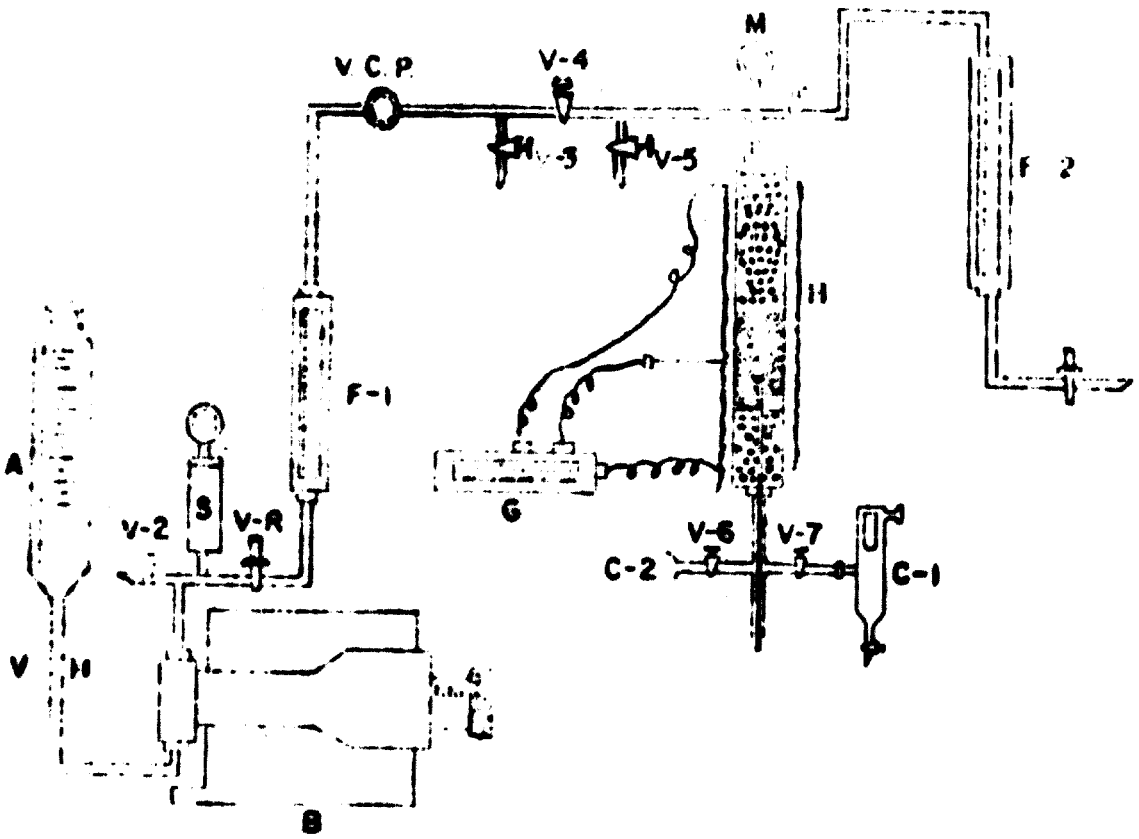


Figure 1: Pilot plant flow

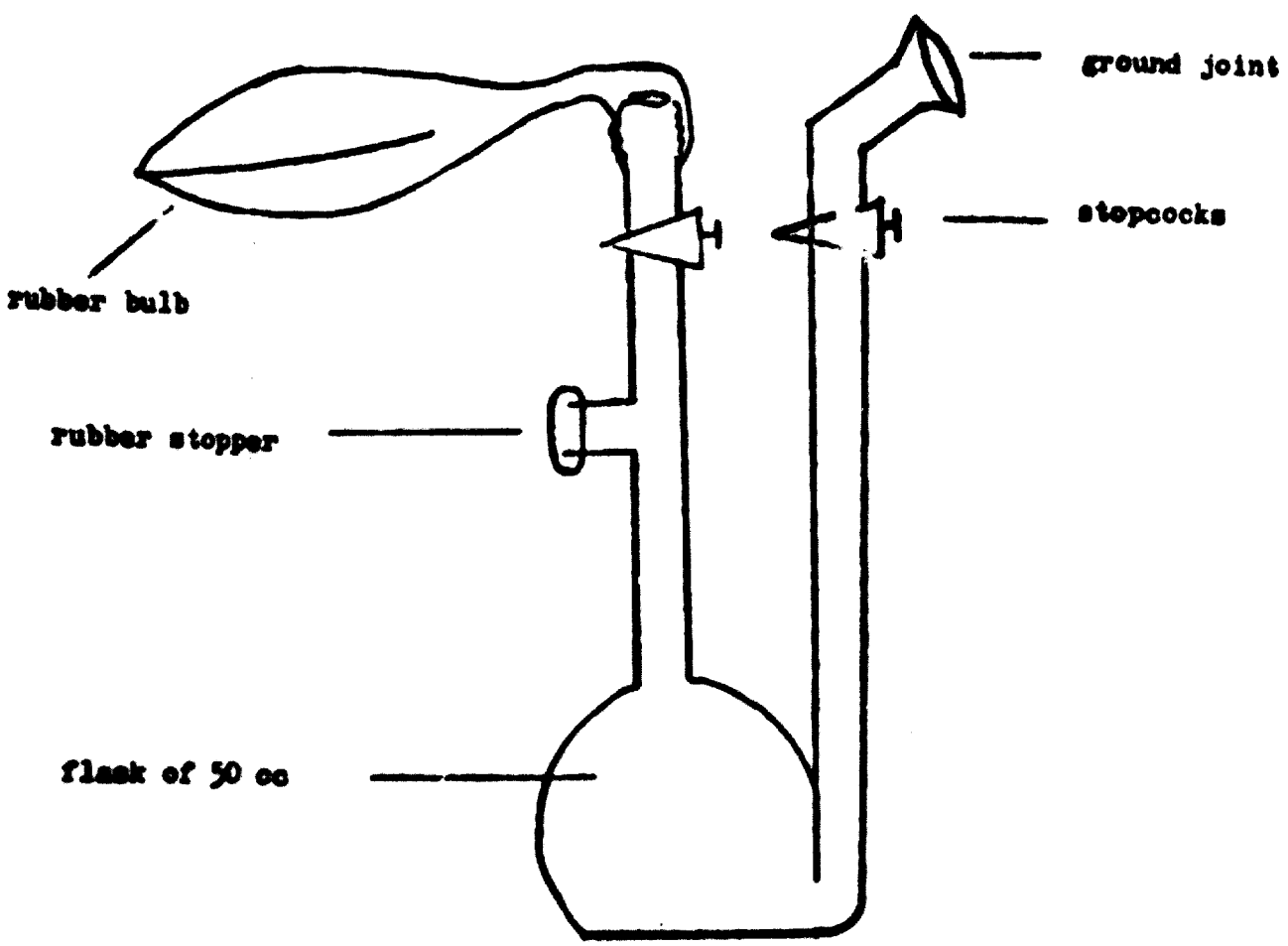


Figure 2: Special trap C-2

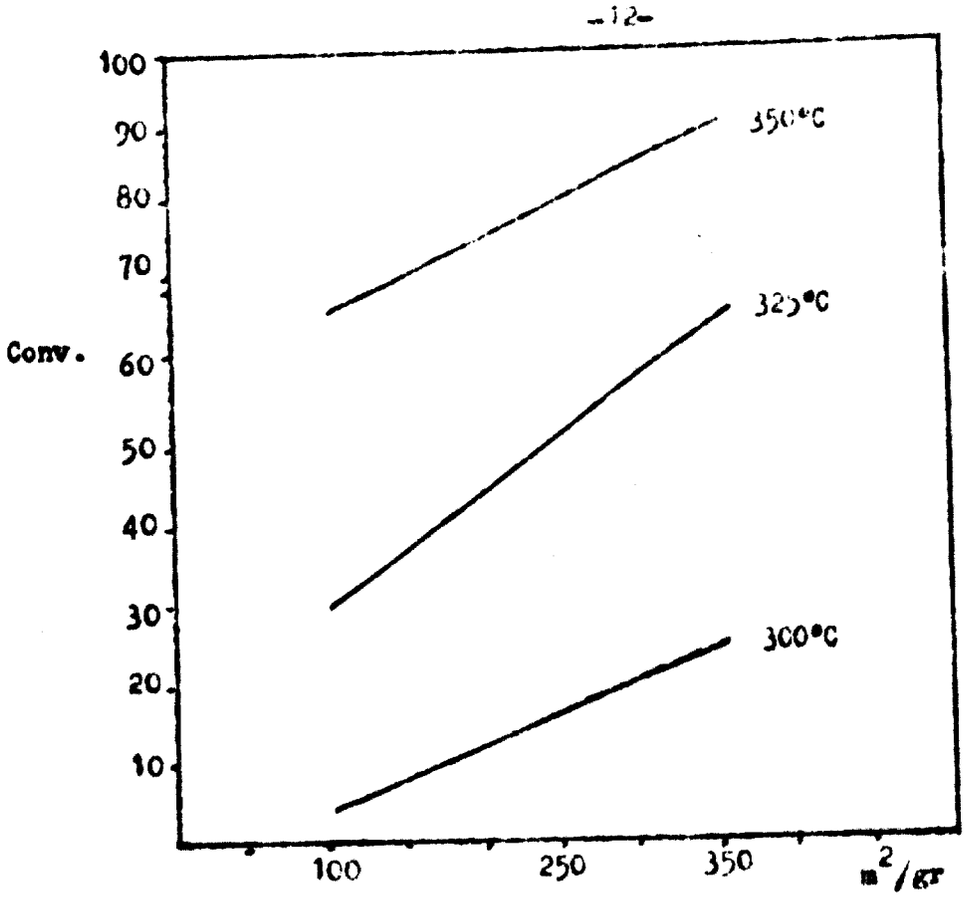


Figure 3: The effect of surface areas of catalyst

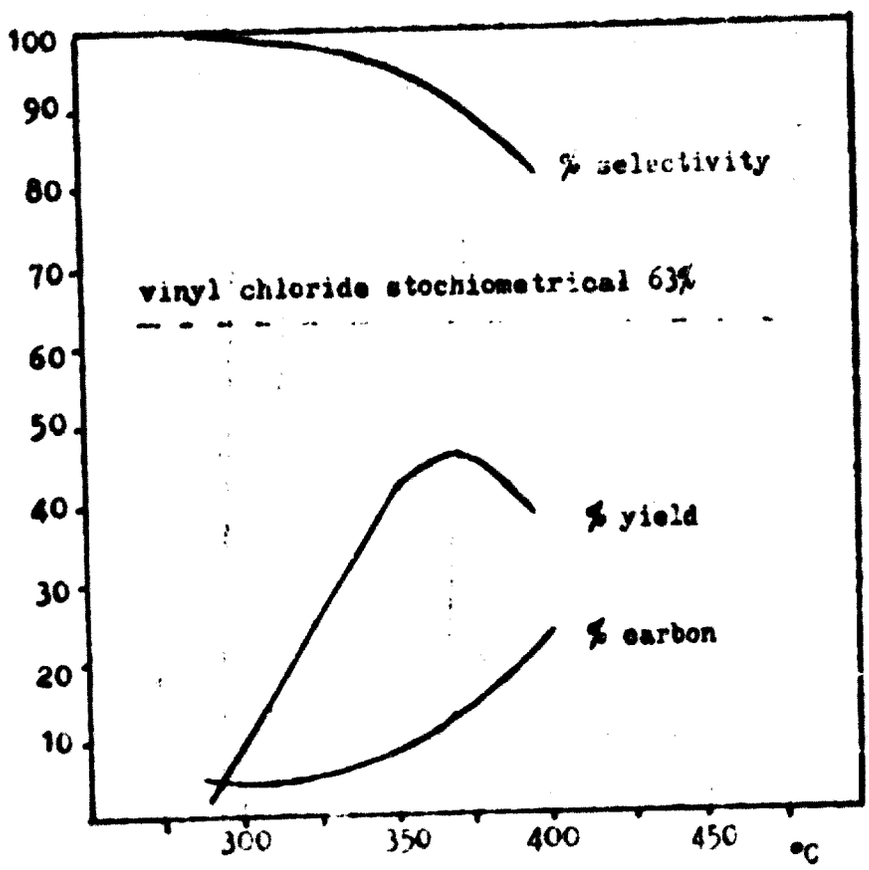


Figure 4: The effect of temperature

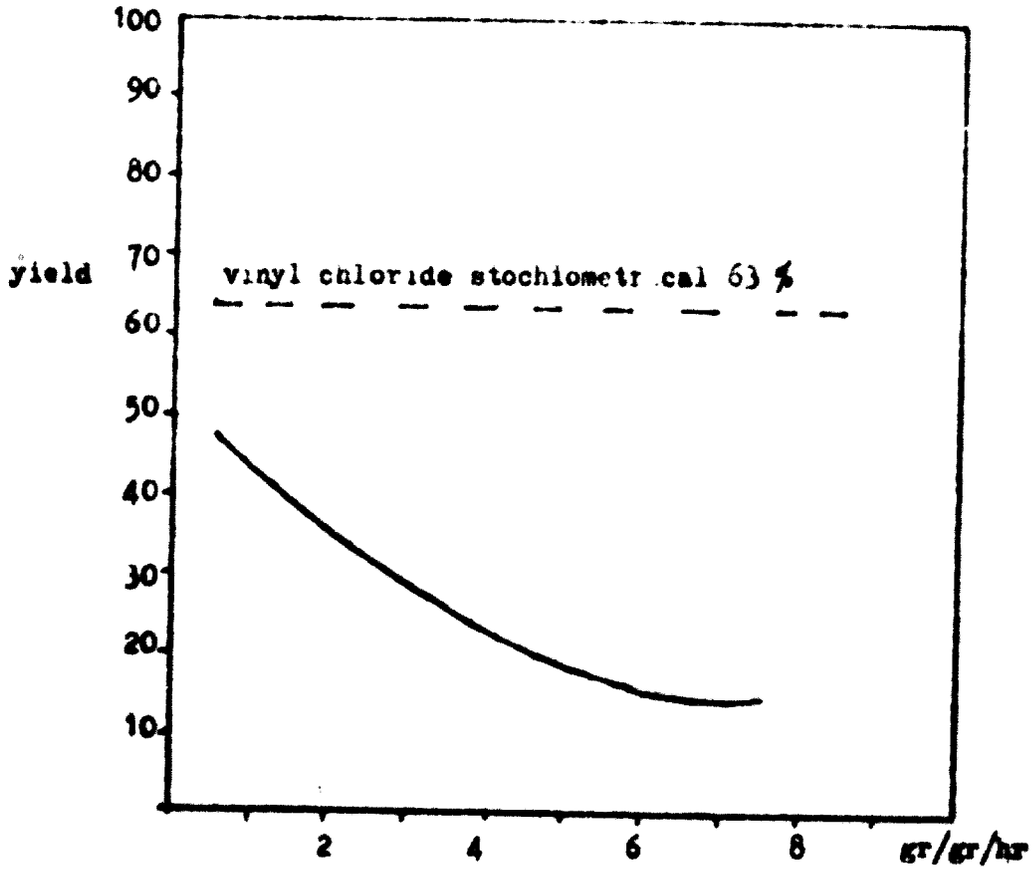


Figure 5: The effect of space-velocity

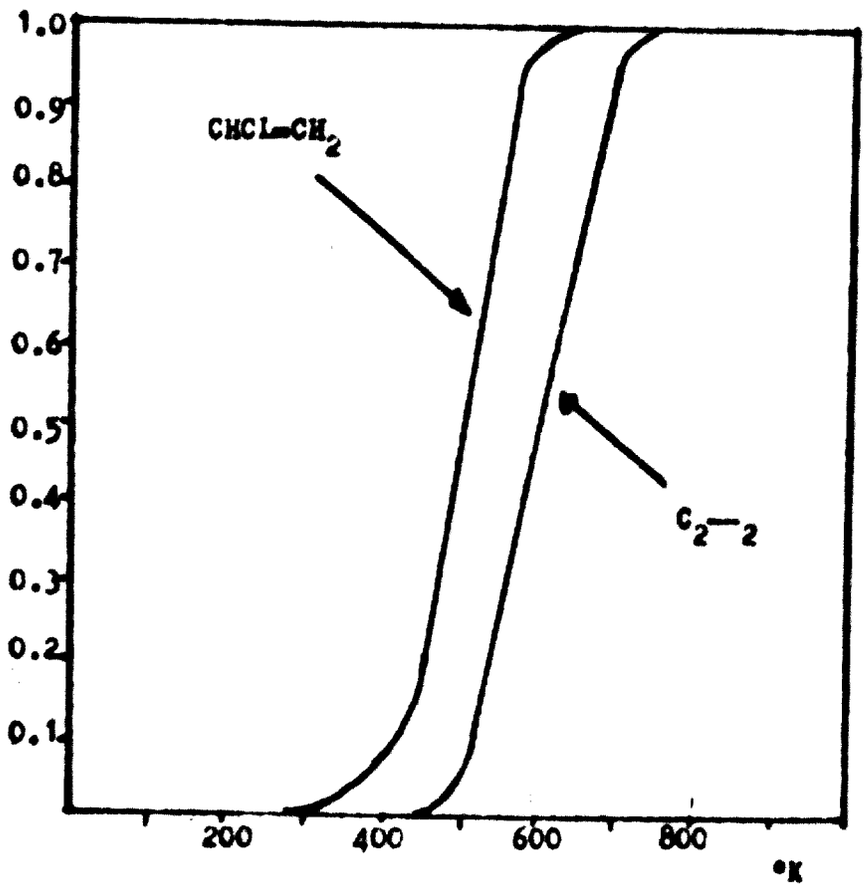


Figure 6: The concentration in the equilibrium

Physical property	A-1	A-2	A-3	A-4 *	A-5 *
Surface in BET m^2 gr	350	250	100	100	250
Pore volume A^0	65.0	90	120	——	——
Absolute density	1.38126	——	——	2.6321	1.0228
Bulk density	0.6097	0.6097	0.6410	0.7178	0.6931
Compact density	0.5614	0.5555	0.5814	0.6931	0.714
Size (mesh)	18-14	18-14	18-14	10-14	10-14
	spherical	spherical	spherical	rolls	rolls

Table 1: Physical properties of the catalysts

* These were produced in the Instituto Mexicano del Petroleo.

Regeneration

Exp.	time hr temp ℃	%Conv. 2 h.	%Conv. 4 h.	%Conv. 6 h.	%Conv. 8 h.	%Conv. 10 h.	%Conv. average
1	——	70.0	65.0	56.0	44.5	37.5	54.6
2	7/450	59.0	66.5	57.0	45.0	44.0	54.3
3	10/450	67.0	75.0	67.0	57.0	49.0	60.3
4	18/450	66.0	82.0	67.0	60.0	47.5	64.5
5	18/450	63.5	60.1	52.0	38.7	20.0	46.9
6	18/450	61.0	54.0	47.0	45.5	38.0	49.1
7	18/450	65.0	56.2	53.0	40.5	30.0	48.9

Table 2: The catalysts worked 70 h. and attained 7 regenerations

(1) Table III - Compute of experimental results

Catalyst A 1						
Exp.	Temp.C	e.v.	% Conv.	% Yield	% Select.	% Carbon
1	300	0.63	23.5	14.2	95.0	2.6
2	300	1.87	10.3	6.2	95.6	4.3
3	300	3.75	5.7	3.6	100.0	5.0
4	325	0.63	64.2	38.6	95.1	3.8
5	325	1.87	21.0	13.3	100.0	5.3
6	325	3.75	10.0	12.2	101.7	6.6
7	350	0.63	90.1	57.0	100.0	6.6
8	350	1.87	80.6	48.5	97.3	8.1
9	350	3.75	31.5	18.4	92.6	7.0
Catalyst A-2						
10	300	0.63	18.4	11.7	100.0	3.9
11	300	1.87	14.2	9.1	100.0	4.8
12	300	3.75	7.0	4.4	100.0	4.2
13	325	0.63	55.0	33.4	96.0	4.1
14	325	1.87	35.8	23.5	93.8	6.1
15	325	3.75	25.0	15.7	100.0	6.7
16	**350**	**0.63**	**80.0**	**47.4**	**94.0**	**6.1**
17	350	1.87	67.0	41.0	97.4	7.8
18	350	3.75	33.1	21.3	101.6	12.5
19	275	1.87	3.1	2.0	100.0	4.2

(2) Table III - Compute of experimental results

Exp.	Temp.C	e.v.	% Conv.	%Yield	%Select.	%Carbon.
Catalyst A-2						
20	350	1.25	80.5	41.2	81.4	6.9
21	350	5.60	27.1	15.9	92.9	8.9
22	350	7.50	33.5	15.5	73.2	12.0
23	375	1.87	80.7	45.0	88.3	16.6
24	400	1.87	75.6	38.6	80.8	23.6
Catalyst A-3						
25	300	0.63	2.3	1.4	100.0	1.2
26	300	1.87	1.9	1.2	100.0	1.6
27	300	3.75	4.5	2.8	100.0	4.9
28	325	0.63	28.0	17.6	99.0	4.3
29	325	1.87	4.0	3.0	100.0	2.7
30	325	3.75	3.8	2.4	100.0	2.9
31	350	0.63	19.0	49.0	97.0	7.3
32	350	1.87	51.3	3.36	97.7	13.2
33	350	3.75	36.9	23.7	101.5	6.2
Catalyst A-4						
34	300	0.63	19.9	12.0	95.3	1.34
35	300	1.87	2.4	1.5	100.0	1.34
36	300	3.75	12.4	7.8	100.0	4.56
37	325	0.63	69.6	36.9	84.1	1.65
38	325	1.87	43.5	30.5	113.10	4.7
39	325	3.75	58.0	34.8	95.8	4.6

(3) Table III - Compute of experimental results

Catalyst A-4						
Exp.	Temp.C	e.v.	% Conv.	% Yield	% Select.	% Carbon
40	350	0.63	81.1	44.2	86.3	3.2
41	350	1.87	52.5	31.0	95.0	8.2
42	350	3.75	64.1	39.7	98.1	5.2
Catalyst	**A-5**					
43	325	0.63	---	---	---	---
44	325	1.87	21.6	10.3	97.0	---
45	325	3.75	18.1	11.3	99.0	---
46	350	0.63	82.0	43.0	83.0	6.9
47	350	1.87	61.5	34.8	100.0	15.0
48	350	3.75	36.0	16.5	72.0	7.5

Table IV The degree of equilibrium dehydrochlorination for the next reactions

$CH_2Cl-CH_2Cl \longrightarrow CH_2=CHCl + HCl$			
T °K	Δ H cal mol	Δ G cal mol	kp
300	0.173×10^5	0.712×10^4	0.650×10^{-5}
400	0.174×10^5	0.370×10^4	0.946×10^{-2}
500	0.174×10^5	0.270×10^3	0.762×10^0
600	0.174×10^5	-0.316×10^4	0.142×10^2
700	0.174×10^5	-0.659×10^4	0.115×10^3
800	0.173×10^5	-0.100×10^5	0.546×10^3
900	0.172×10^5	-0.134×10^5	0.182×10^4
1000	0.171×10^5	-0.168×10^5	0.479×10^4
$CH_2Cl-CH_2Cl \longrightarrow CH \equiv CH + HCl$			
300	0.410×10^5	0.219×10^5	0.972×10^{-16}
400	0.415×10^5	0.155×10^5	0.323×10^{-8}
500	0.418×10^5	0.900×10^4	0.116×10^{-3}
600	0.420×10^5	0.242×10^4	0.132×10^0
700	0.420×10^5	-0.418×10^4	0.205×10^2
800	0.420×10^5	-0.108×10^5	0.893×10^3
900	0.419×10^5	-0.174×10^5	0.167×10^5
1000	0.417×10^5	-0.239×10^5	0.173×10^6

Effect of pressure: $K_p = P \frac{\alpha}{1-\alpha^2}$

equations for vinyl chloride

$\Delta H = 0.169 \times 10^5 + 0.168 \times 10 \times T - 0.152 \times 10^{-2} \times T^2$

$\Delta G = 0.174 \times 10^5 - 0.344 \times 10^2 \times T + 0.188 \times 10^{-2} \times T^2$

$\log K_p = -0.142 \times 10^2 + 0.373 \times 10^{-3} \times T - 0.197 \times 10^{-4} \times T^2$

IV CONCLUSIONS.

13.- The effect of catalyst.

Catalyst plays an important role in this dehydrochlorination reaction. With the aid of computed values in table I and in table III, it was possible to deduce the effect of the catalyst. In the case of the same catalyst preparation (A-1, A-2, A-3) the effect of the surface area is showed in figure 3. By comparing experiments 1 , 10 and 25 or 4, 13, 28 or 7, 16, 31 it is possible to infer that: if the surface area increases on the catalyst, the conversion percentage also increases.

14.- The effect of temperature.

Figure 4, (experiments 11, 14, 17, 19, 23 and 24) illustrates the effect of temperature on yield of vinyl chloride from 1.2 dichloroethane in a fixed catalyst bed, at weight velocity of 1.87 hour -1. Thus an increase from 275°C to 400°C augment the yield from 2.0% to 38.0%. Simultaneously, the selectivity decreased from 100.0% to 80.8% and this was corroborated by the increase of carbon deposit from 4.2% to 23.0%; however, the best yield in vinyl chloride was at 375°C. But 350°C is recommended as operation temperature - because the yield still is high and the carbon deposit is lower than that attained at 375°C.

15.- The effect of space-velocity.

The effect of space-velocity on results on dichloroethane dehydroclorination at 350°C in a fixed catalyst bed is shown in figure 5. Experiments with the increase of space-velocity (16, 17, 18, 20, 21 and 22) from 0.63 to 7.5 hr-1,

decreased the yield of vinyl chloride from 47.4 to 15.5 per cent wt.

Independently of the temperature, the ratio of vinyl chloride and carbon formed remained practically constant when the space-velocity was greater than 3.75 hr-1.

10.- Thermodynamic considerations.

It was shown earlier (28) that the reaction of the catalytic interaction of 1.2 dichloroethane which results in the formation of vinyl chloride and hydrochloric acid is peculiar not only to these simplest products, but to the - other different classes of dehidroalogenations.

The results of it will be the formation of molecules with less molecular weight by the substraction of hydrochloric acid.

As the thermodynamic calculations have shown (see table IV) (29) the reaction of dehydrochlorination of 1.2 dichloroethane can be successfully realized with the temperatura exceeding 500°K.

By comparing the concentrations in the equilibrium of the vinyl chloride curve with the acetylene curve (figure 6) under the given conditions, it was observed that the possibility of existence of both compounds in the mixture of reaction products is strong. It follows from this, that the selective realization of the process of dehydrochlorination demands the search for a catalyst which would be distinguishable for its selective action. We can confirm that the concentration of vinyl chloride in the process of dehydrochlorination at temperatures from 300 to 350°C and high contact time (low space-velocity) was close to the equili-

bromo, and the maximum yield of vinyl chloride might be expected.

The work described in this paper was carried out at Instituto Mexicano del Petróleo (Mex).

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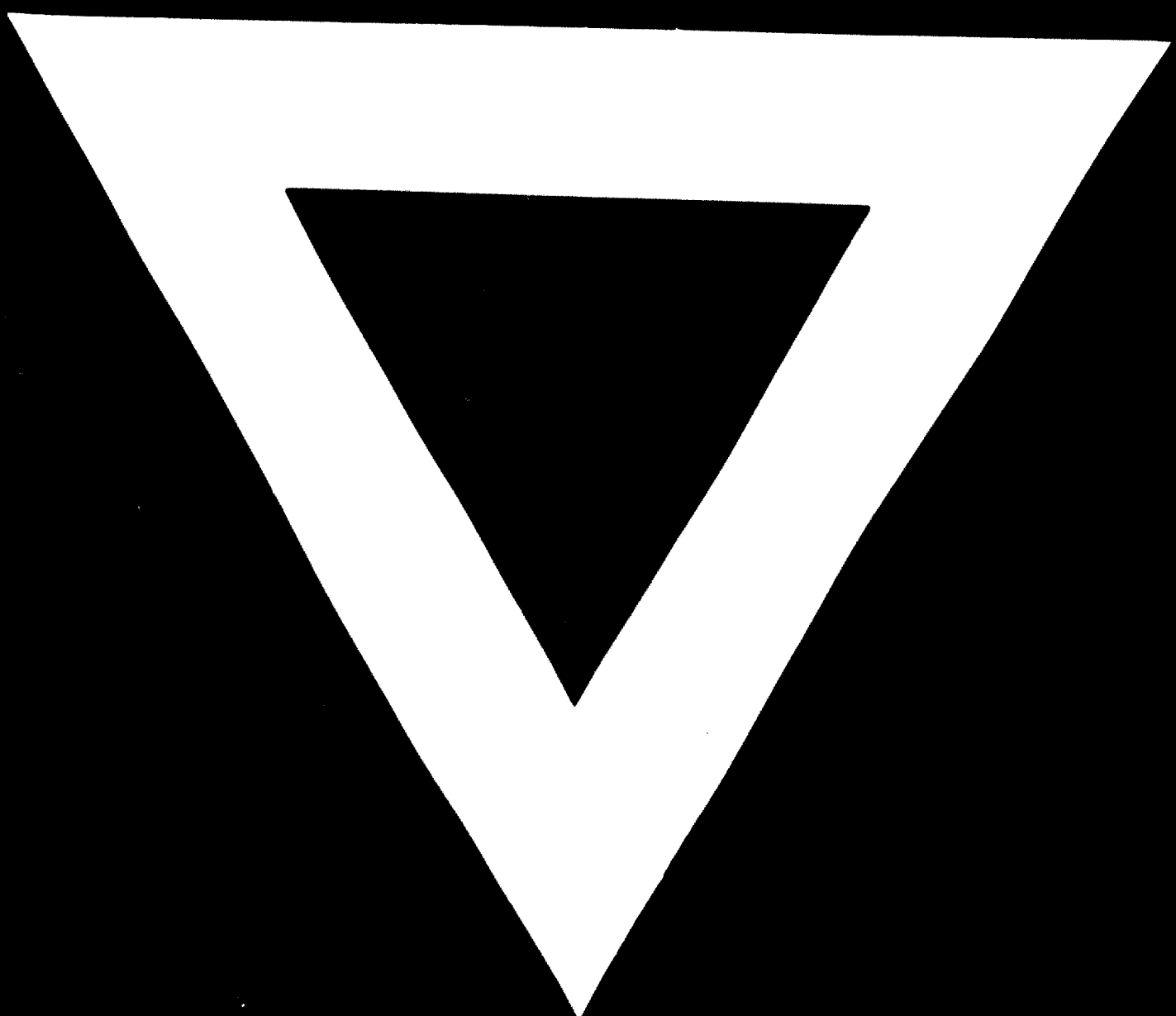

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