



OXIDATIVE DEGRADATION OF SPENT ION-EXCHANGE RESINS IN ACID MEDIUM

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ABSTRACT

In the present study hydrogen peroxide was used for the oxidative degradation of spent ion-exchange resin simulate in sulphuric acid medium. Heating the organic resins in sulphuric acid results in its carbonization and in partial oxidation of only 1.7% of the carbon added. The results obtained show that the oxidation reaction is a relatively slow process of first order with K-value in the order of $10^{-4} \text{ min.}^{-1}$ and the main oxidation product was carbon dioxide.

The production of carbon oxides in the off-gas stream increased very sharply by the addition of hydrogen peroxide to the hot sulphuric acid-resin mixture. The results obtained show that more than 97% of the added carbon was oxidized to carbon dioxide and carbon monoxide. The rate constant value (K) of this reaction was calculated and was found to be $(1.69 \pm 0.13) \times 10^{-2} \text{ min.}^{-1}$.

The results of gas chromatographic analysis indicate that no significant amounts of hazardous organic materials were detected in the off-gas stream.

INTRODUCTION

Volume and weight reduction of spent ion-exchange resins received increasing importance due to the increase in storage cost⁽¹⁾ and also to the unstable physical and chemical nature of the organic bead resins⁽²⁾. A number of processes to reduce the volume and weight of spent ion-exchange resins have been proposed e.g. drying⁽³⁾, compaction⁽⁴⁾, pyrolysis⁽⁵⁾ and incineration⁽⁶⁾.

To avoid the drawbacks of dry oxidation processes⁽⁷⁾, oxidative degradation of spent ion-exchange resins in hot sulphuric acid medium and using nitric acid as oxidant has been investigated on both laboratory and industrial scales in many nuclear centers and in different countries⁽⁸⁻¹⁰⁾.

In the present work oxidative degradation of ion exchange resin in hot sulphuric acid medium using hydrogen peroxide as oxidant was carried out on large scale to study the kinetics and mechanism of this process.

EXPERIMENTAL WORK

Two forms of ion-exchange resins supplied by Bayer (Germany), were subjected to oxidative degradation in acid medium. The bead cationic one is an acidic resin in H-form and has sulphonic acid as functional group. The molecular formula for the basic unit is assumed to be $C_8H_7SO_3H$. The anion resin has a

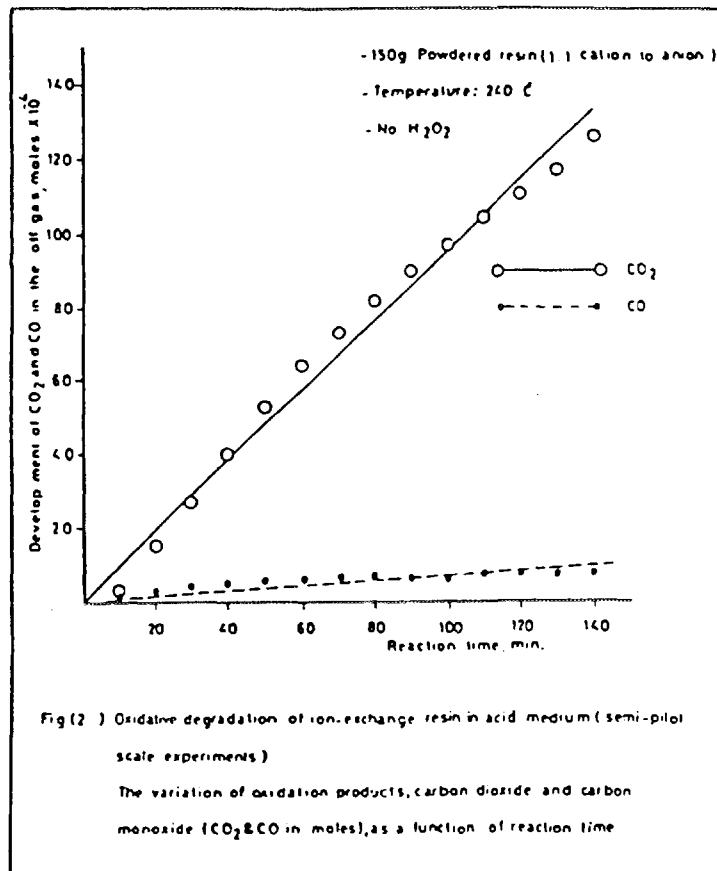
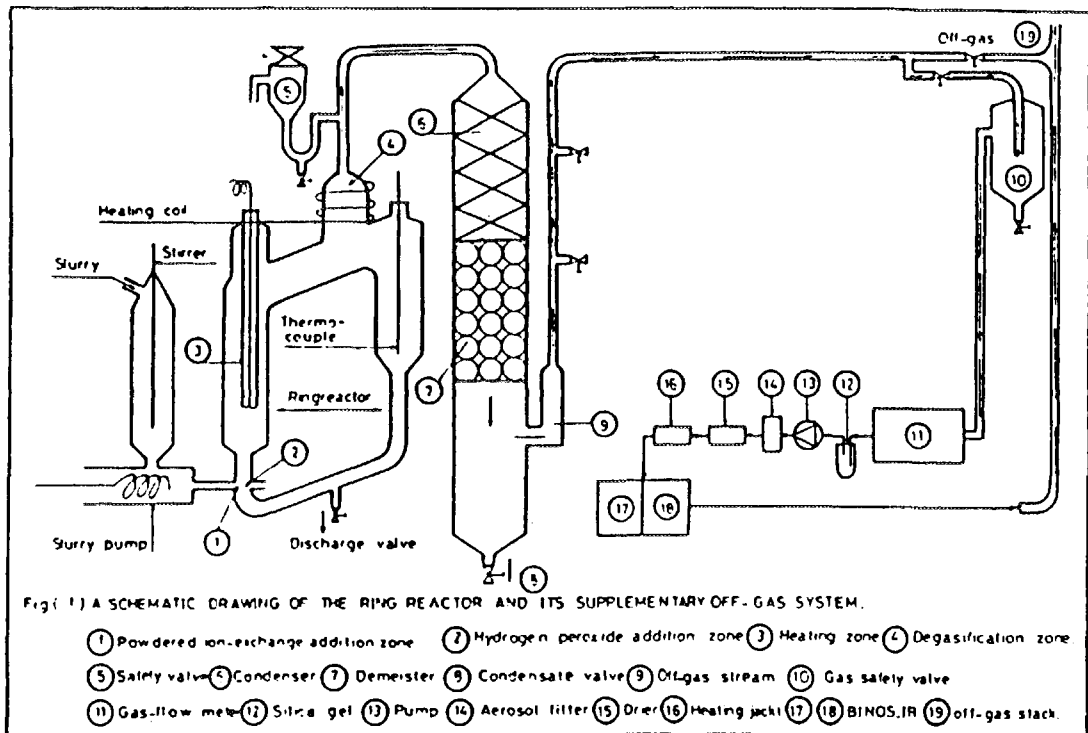
quaternary ammonium as functional group and its basic unit has the formula $C_{12}H_{19}ON$. The elemental analysis and water content, in weight %, of both anion and cation resin were represented in Table 1. The beads resins were ground using a ball mill grinder and the resulted powder was sieved. The fraction of grain size 0.125-0.250 mm was used for all oxidation experiments otherwise indicated.

Table 1 : Water Content and Elemental analysis of ion-exchange resins

resin type	water content, wt%	C%	H%	N%
Anion	56.63	74.6	8.6	4.1
Cation	45.25	51.8	5.2	0.8

A ring digester has been developed in Nuclear Research Centre Karlsruhe in Germany and used in this study for oxidative degradation of ion-exchange resins. The digester consists of glass tube which is curved to form closed loop and a schematic drawing of the apparatus is shown in Fig. 1.

The ring reactor was loaded with five litres concentrated sulphuric acid and heated to the required temperature. Calculated weight (150 g) of powder ion-exchange resin mixture (1 : 1 cation to anion by weight) was mixed with 500 ml cold concentrated sulphuric acid and the resulting slurry was pumped into the ring digester below the hot sulphuric acid (5 l) followed by hydrogen peroxide (35%) addition with adjusted rate (1 l/hr.) beneath the acid surface. The acid circulation in the ring digester was achieved by the air-lift effect of gases generated during the decomposition of hydrogen peroxide and the oxidation of ion-exchange resins. The oxidation process of ion-exchange resins takes place in the whole digester but most intensive in the heating zone.

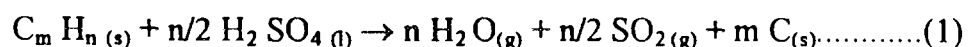


The oxidation process of ion-exchange resin was followed by determining the percentage of both carbon-dioxide and carbon monoxide in the off-gas stream using two BINOS-Infrared Gas Analyser supplied by Leybold-Heraeus Co.. The gas flow during the oxidative degradation process was measured by a Flow Meter U-70 SETARAM. The off-gas temperature was kept at 30°C using extra heaters, to optimize the process of measurements. The number of moles of carbon dioxide and carbon monoxide were calculated from the corresponding gas flow rate and the measured percentage of each.

RESULTS AND DISCUSSION

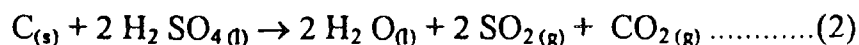
The oxidative degradation process studied is a method that utilizes the dehydration action of concentrated sulphuric acid to carbonize solid ion-exchange resins and to oxidize the resulting carbon by hydrogen peroxide. The proposed technique aims at achieving reasonably weight and volume reduction, transforming the organic resin materials to an inorganic form suitable for their subsequent immobilization and disposal processes and, at the same time, preserving the environmental resources by avoiding the well known drawbacks of the dry oxidation processes.

The study of kinetics and mechanisms of oxidation reaction aims at defining the oxidative degradation process of ion-exchange resins in acid medium. If the organic portion of ion-exchange resin is presented by $C_m H_n$, its reaction in concentrated sulphuric acid could be described according to equation (1).



Continuous heating of the sulphuric acid-resin mixture at 240°C before the addition of hydrogen peroxide aims at studying its role on the oxidation of the

carbonized ion-exchange resins. Quantitative analysis of off-gas stream results from this reaction show that the main oxidation product at 240°C was carbon dioxide. The results, represented in Table 2 and illustrated in Fig. 2, show that carbon dioxide represents about 94% of the total oxidation products.



The rate constant (K) of the reaction in equation (2) was calculated by plotting the logarithmic values of the unreacted carbon fraction $[- \log \frac{a-x}{a}]$ versus the reaction time in minute where :

[x] = number of moles of oxidation products evolved in the off-gas stream ,

[a] = the total numbers of moles of carbon contained in the ion-exchange resin added,

[a-x] = the unreacted carbon in mole.

The linear relation obtained and shown in Fig. 3, indicates that the reaction is first order reaction and the K-value was $(1.25 \pm 0.1) \times 10^{-4} \text{ min.}^{-1}$, which was in good agreement with figures previously given in the literatures⁽¹¹⁾. From the data obtained in Table 2, it was observed that a relatively small fraction of the added carbon was oxidized by concentrated sulphuric acid. The total amount of oxidation products evolved in the off-gas stream due to the chemical reaction calculated in moles of carbon represent only 1.7% of the total carbon contained in the ion-exchange resin added. (94% of this oxidation products as carbon dioxide and 6% as carbon monoxide).

To improve the rate of oxidation reaction a powerful oxidizing agent as hydrogen peroxide was used. The production of carbon dioxide and carbon monoxide in the off-gas streams was increased sharply by the addition of hydrogen peroxide to the reaction mixture (sulphuric acid and ion-exchange

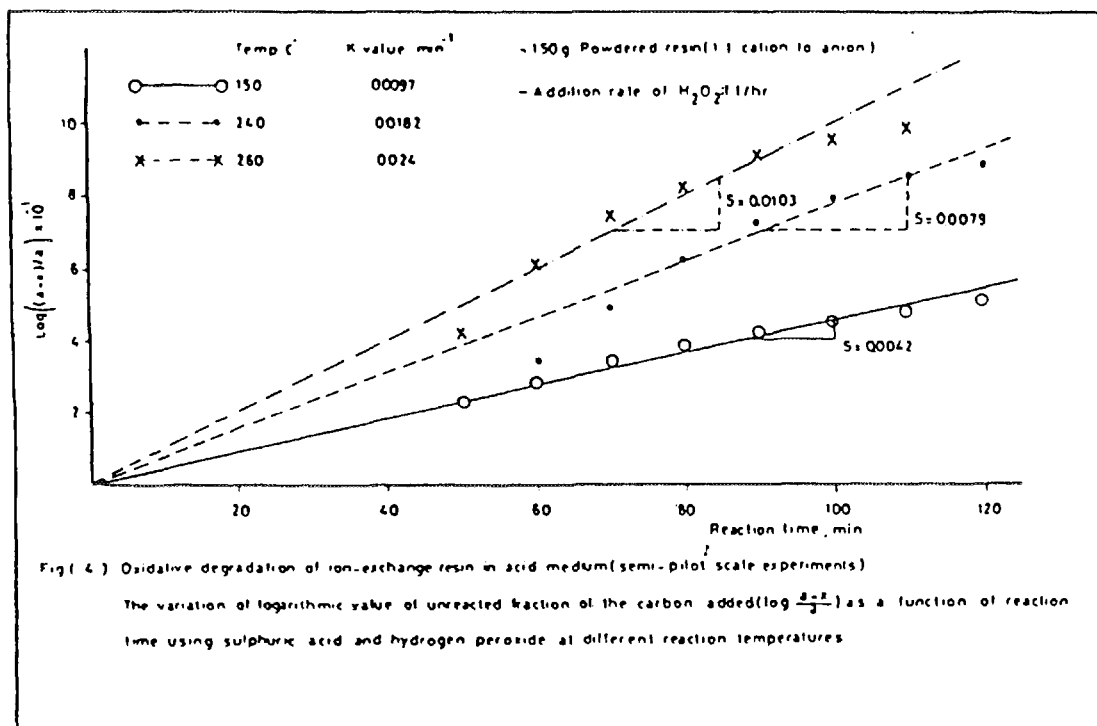
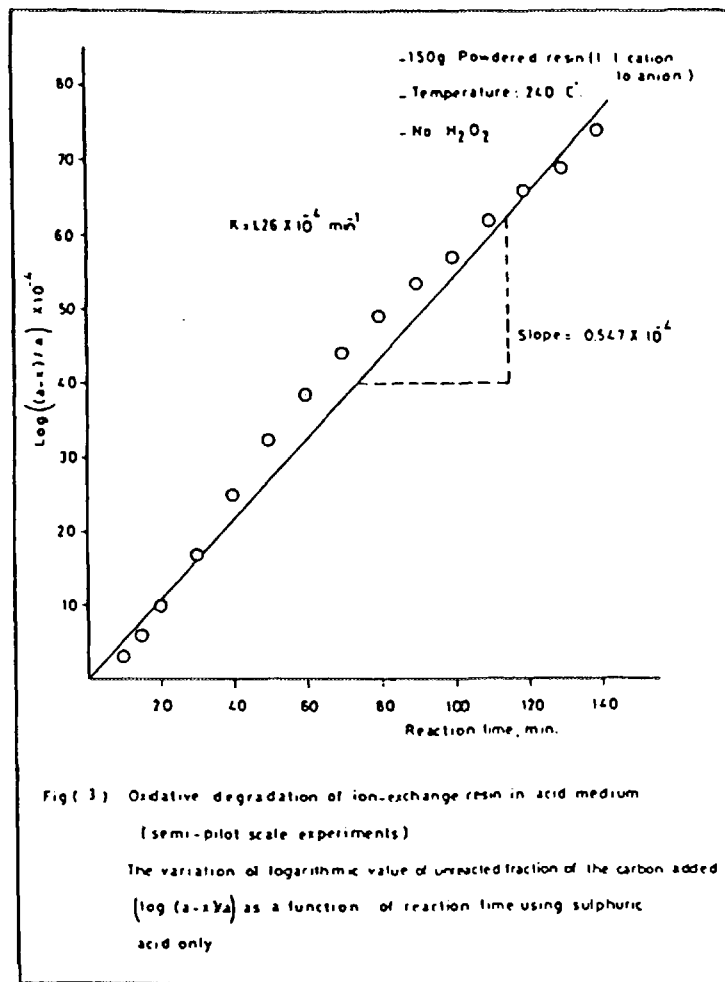


TABLE 2 : OXIDATIVE DEGRADATION OF ION-EXCHANGE RESIN IN

ACID MEDIUM (SEMI- PILOT EXPERIMENTS) .

Oxidation effect of sulphuric acid on the variation of off-gas composition as a function of reaction time .

reaction time (min.)	CO ₂	CO	{ CO ₂ + CO
	% (4)	%	%
10	3.0	0.8	3.8
15	6.0	1.0	7.0
20	4.5	1.1	5.6
30	4.0	0.6	4.6
40	4.0	0.2	4.2
50	3.0	0.2	3.2
60	3.0	0.2	3.2
70	2.5	0.2	2.7
80	2.5	0.1	2.6
90	2.0	0.1	2.1
100	2.0	0.1	2.1
110	2.0	0.1	2.1
120	2.0	0.1	2.1
130	1.5	0.1	1.6
140	1.5	0.1	1.6

oxidation products. (5)			
moles	0.126	0.008	0.134
(6)			
" , %	1.59	0.11	1.7
(7)			
Percent fraction, %	94 %	6 %	

(1) 150 g powder resin (1:1 cation to anion by weight) contain 7.925 mole carbon.

(2) Reaction temperature : 240 °C. (3) No use of H₂ O₂ .

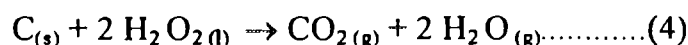
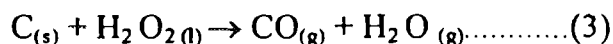
(4) The percent of oxidation gas in the off-gas sample.

(5) The cumulative concentration in moles of the oxidation gas evolved .

(6) The percent of oxidation gas in moles from the total carbon added.

(7) The percent fraction of carbon dioxide or carbon monoxide from the total oxidation gas evolved .

resins). More than 97% of the total carbon added was oxidized to carbon dioxide representing about 74% of the oxidation products, and carbon monoxide representing about 26% of the oxidation products. Table 2. The evolution of both carbon dioxide and carbon monoxide due to oxidation of ion-exchange resin followed equations (3) & (4) respectively



The average overall rate constant (K) of oxidation reactions was calculated from the first order reaction equation and was found to be $(1.69 \pm 0.13) \times 10^{-2} \text{ min}^{-1}$ at 240°C. It could be observed that the oxidative degradation of ion-exchange resins took place via two different reaction mechanisms namely oxidation by sulphuric acid and by hydrogen peroxide. However the sulphuric acid oxidation was relatively slow compared with that of hydrogen peroxide where the rate constants were of the order 10^{-4} and 10^{-2} min^{-1} respectively. The fact that the rate constant of hydrogen peroxide was 100 folds more than that of sulphuric acid may be explained by the difference in oxidation potential (sulphuric acid 0.17 volts and hydrogen peroxide 1.77 volts). The data obtained in Fig.4 show that the overall rate constant (K) increased by raising the reaction temperature (150°C-260°C). This trend was in good agreement with those previously mentioned in the literatures⁽¹¹⁾.

To determine the influence of reaction temperature on the reaction velocity, the energy of activation (E*) of the oxidative degradation of ion-exchange resin in acid medium using hydrogen peroxide as oxidant was calculated on basis of Arrhenius equation⁽¹²⁾. The value E* between 240°C-260°C was found to be 1.7136 K cal/min..

It was clear from Fig. 5 that the maximum evolution of carbon dioxide was reached in a shorter time compared with that of carbon monoxide for the different temperature studied Fig.6.

Gas chromatographic analysis of off-gas samples was performed to prove the absence of significant amounts of hazardous organic materials expected from the oxidation reaction of ion-exchange resins. Samples collected from the off-gas stream at the reactor outlet every 15 minutes during the oxidation process (at 240°C) show that a very low percentage of methane, not higher than 0.003%, ethane and ethylene have less than 0.001% while propane could not be detected. Table 3.

In conclusion, it could be stated that, the process is a promising technique as far as the pollution of the environment is concerned.

ACKNOWLEDGMENT

It is worth mentioning that the ring digester used was developed in Karlsruhe, Nuclear Research Centre (KFK-INE) Germany. Thanks are due to Dr. H. Wieczorek and Mr. B. Osar for all kinds of facilities provided.

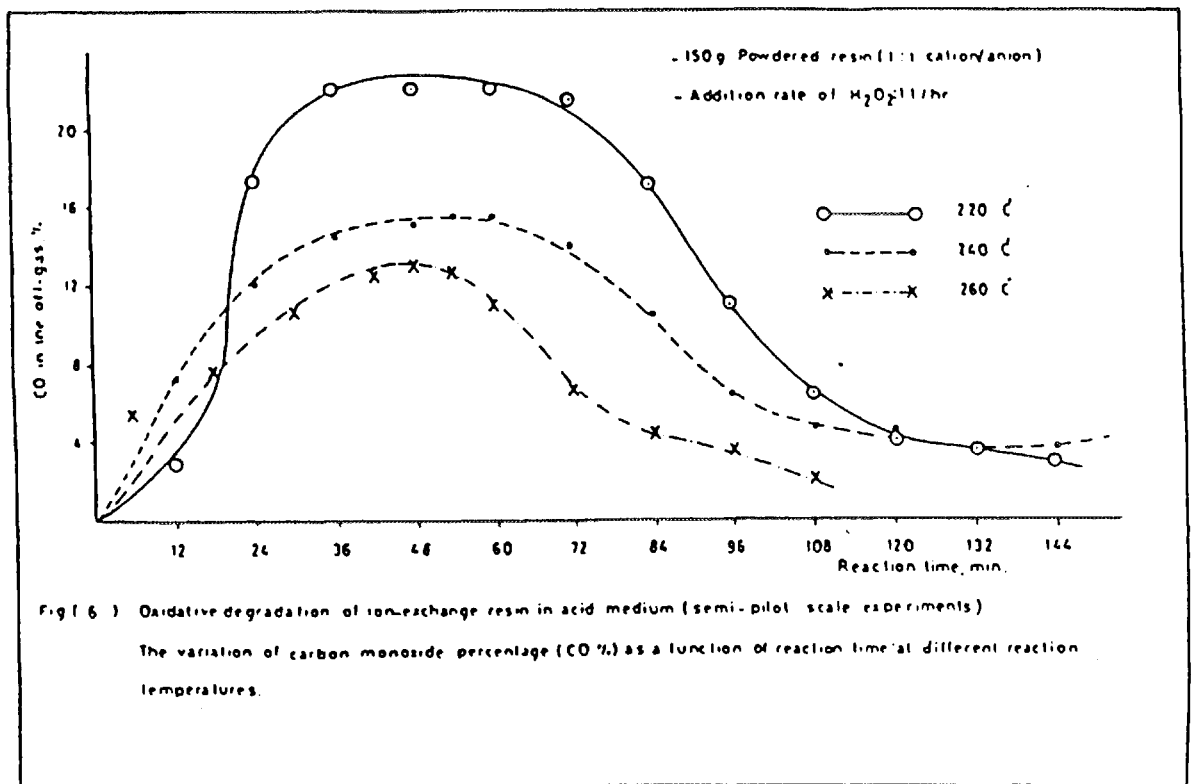
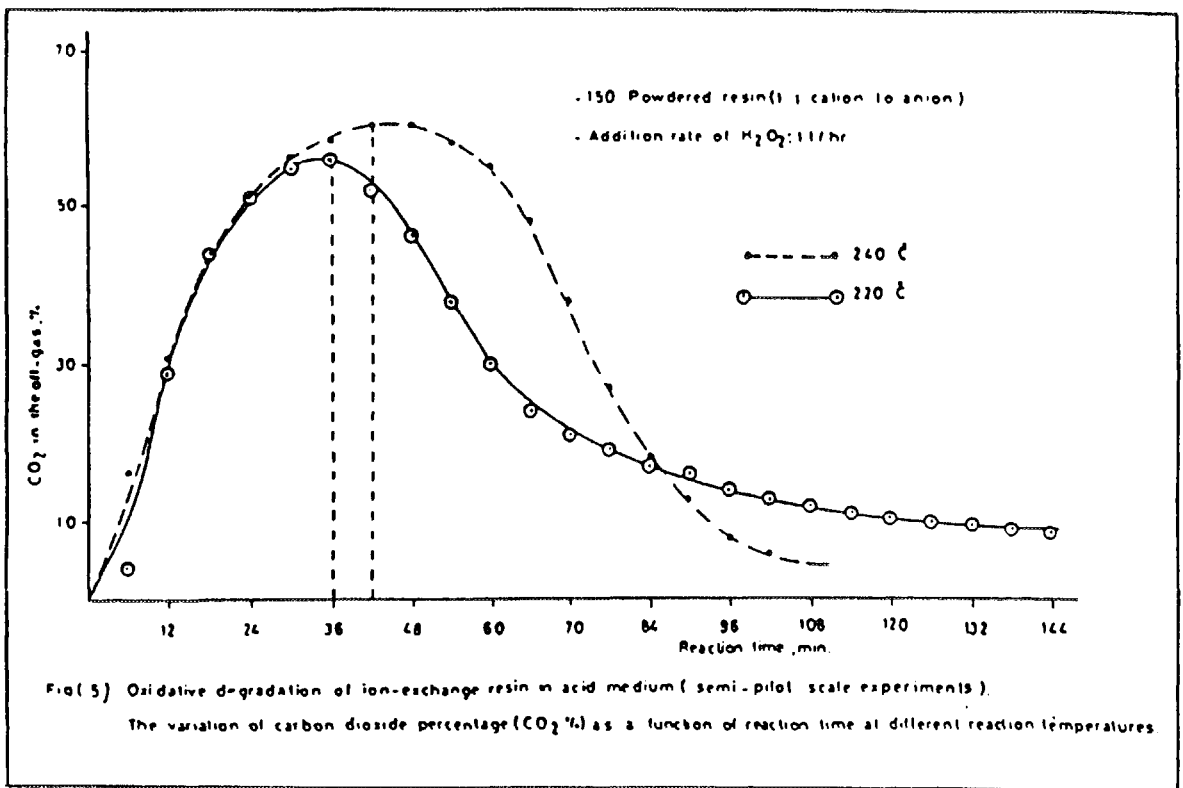


TABLE 3 : OXIDATIVE DEGRADATION OF ION-EXCHANGE RESIN IN

ACID MEDIUM. (SEMI-PILOT EXPERIMENTS).

Effect of sulphuric acid : hydrogen peroxide mixture on the variation of off-gas composition as a function of reaction time.

Time min.	development of CO ₂		development of CO		Σ (CO ₂ + CO)	
	% (4)	mole	%	mole	%	mole
10	2.08	0.16	1.49	0.11	3.51	0.17
20	8.72	0.67	2.92	0.23	11.64	0.90
30	16.02	1.23	4.37	0.34	20.39	1.57
40	23.76	1.84	5.83	0.46	29.60	2.30
50	34.31	2.63	8.01	0.62	42.32	3.27
60	44.98	3.47	10.49	0.81	55.47	4.29
70	55.27	4.26	13.09	1.01	68.36	5.27
80	62.82	4.84	15.43	1.19	78.25	6.03
90	66.08	5.13	16.87	1.30	82.95	6.43
100	68.68	5.29	17.63	1.36	86.33	6.63
110	69.85	5.38	18.30	1.41	88.15	6.79
120	70.76	5.45	18.69	1.44	89.45	6.89
130	71.41	5.50	19.08	1.47	90.49	6.97
140	71.94	5.54	19.47	1.50	91.41	7.04
150	72.46	5.58	19.73	1.52	92.39	7.10
160	72.98	5.62	20.12	1.55	93.10	7.17
170	73.50	5.66	20.25	1.79	96.75	7.45
180	73.76	5.68	26.24	2.02	100.00	7.70
(5) oxidation products, M		5.68		2.02		7.70
(6) " " ,%		71.67		25.49		97.16
(7) Percent fraction ,%		73.77		26.23		---

- (1) 150 g powder resin (1:1 cation to anion by weight) contain 7.925 mole carbon.
- (2) Reaction temperature : 240 oC.
- (3) Rate of H₂O₂ addition : 1 l/h.
- (4) The percent of oxidation gas in the off-gas sample.
- (5) The cumulative concentration in moles of the oxidation gas evolved .
- (6) The percent of oxidation gas in moles from the total carbon added.
- (7) The percent fraction of carbon dioxide or carbon monoxide from the total oxidation gas evolved .

TABLE 4 : OXIDATIVE DEGRADATION OF ION-EXCHANGE RESIN

IN ACID MEDIUM . (SEMI-PILOT EXPERIMENTS)

The variation of organic compounds composition

in the off-gas as a function of reaction time.

Time (min)	Methane %	Ethane %	Ethylene %	Propane %
15	<0.001	--	--	not detected
30	0.003	<0.001	<0.001	" "
45	0.003	<0.001	<0.001	" "
60	0.003	<0.001	<0.001	" "
75	0.003	<0.001	<0.001	" "
90	0.003	<0.001	<0.001	" "
105	0.002	--	<0.001	" "
120	0.003	<0.001	<0.001	" "

(1) 150 g. powdered resin (1 : 1 cation to anion by weight)

contain 95.1 g carbon.

(2) Reaction temperature : 240 C.

(3) Rate of H₂O₂ addition : 1 l / hr.

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