

VOLUME REDUCTION OF FLAME-RESISTING RADIOACTIVE WASTES

BY A NEW WET OXIDATION PROCESS

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ABSTRACT

A wet oxidation process newly developed in our research center was found to be effective in converting flame-resisting radioactive wastes such as ion exchange resin, active charcoal, polyvinyl chloride which are generated from nuclear facilities, to CO_2 and H_2O by 40 $\text{kg/cm}^2\text{G}$ oxygen at 200°C.

This process is characterized by the following results.

1. All types of inflammable and flame-resisting wastes can be treated by this process, compared with other wet oxidation processes which have limitations in their capabilities.
2. Radioactive nuclides as well as NO_x , SO_x and HCl gases are not dispersed to gas phase but are retained in liquid phase.
3. Consequently off-gas treatment is simplified remarkably and related facilities become compact and economical.
4. High volume reduction can be achieved.

Bench scale tests have been carried out with an 1 ℓ autoclave (batchwise) and a 3" dia. x 1.5 m bubble tower.

Pilot plant scale tests supported by the Science and Technology Agency in Japan are now under operation with a 5" dia x 5 m bubble tower.

§1. History of Research Development

Of various radioactive wastes generated from nuclear facilities, steady advances are being made in the volume reduction of gaseous and liquid wastes through development works on waste treatment technologies. However, it is evident that an adequate treatment techniques have not yet been developed for the treatment of flame-resisting radioactive wastes which, in reality, occupies the major portion of solid wastes.

In this context TEC has been advancing development works on radioactive wastes, especially on the following kinds of wastes, in which newly developed treatment techniques are highly desired:

- 1 Flame-resisting radioactive waste such as polyvinylchloride, natural rubber, active charcoal, spent ion-exchange resins.
- 2 Organic liquid substances, such as detergent, greases, oil and fats organic liquid wastes.

Through extensive survey on volume reduction techniques now in use for the above items, we conclude that a wet oxidation method, would be extremely advantageous since the method does not require any chemicals, but utilizes oxygen or air and under the presence of a special kind of catalyst. Therefore, with the aim of industrializing the above method, a research program was begun in December, 1980.

As the result of the basic tests with an autoclave from December, 1980 through March, 1982, it was confirmed that the organic substances in the waste were decomposed in a short time, to be converted into water and CO_2 gas and that the volumes of the waste were also remarkably reduced. On the basis of the above results, from April, 1982 to March 1983, in addition to the autoclave reactor, a bubble tower reactor with an inside volume of 5 ℓ (inner dia. 3 inches x 1.5 m height) was made for performing reaction testing. Possibilities for industrialization of this wet oxidation process were then confirmed.

Furthermore, from May 1983 to the present, testings aimed at the industrialization have been made with a pilot-scale bubble tower reactor with an inner volume of 50 ℓ (inner dia. 5 inches x height 5 m) financed with subsidies granted by the Science and Technology Agency in Japan. This article reports the result of decomposition tests on numerous kinds of wastes in bench-scale apparatus (autoclave, and bubble tower reactor) and also the results obtained with pilot plant reactors.

§2. Wet Oxidation Process and its features

2.1 Wet oxidation process is a method where carbon or hydrogen atoms in the waste materials are converted at high temperature (200 - 230°) and under pressure (20 - 40 $\text{kg/cm}^2\text{G}$) into carbon dioxide and water. This process has already been industrialized in the field of sewage treatment and plant waste water treatment. In this research a successful treatment of radioactive wastes has been achieved through the application of the wet oxidation process in the presence of catalysts.

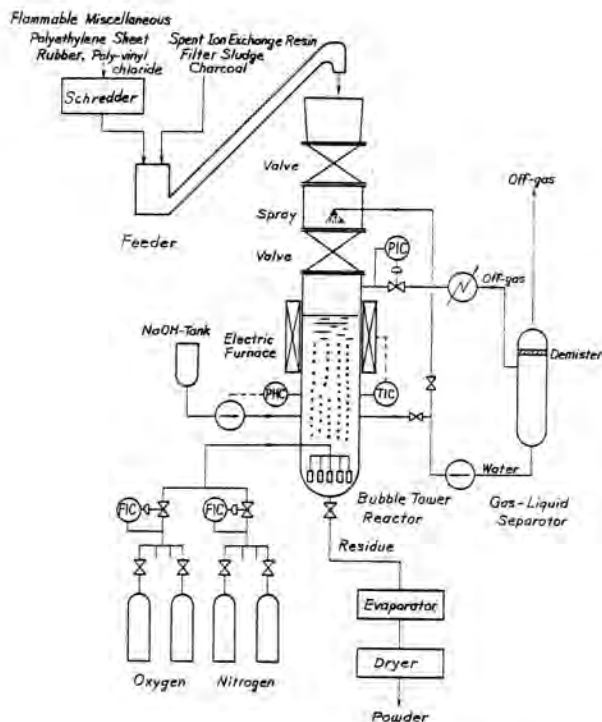


Fig. 1 PILOT PLANT FLOW SHEET

Fig. 1 represents an example of the flow-sheet in the abovementioned pilot plant. Flow sheet is quite similar for the bench-scale apparatus, (autoclave and 5L bubble tower).

Operating method in these apparatus are as follows:

1 First Stage

- (1) Feed the required quantity of catalytic solution to the bubble tower reactor by using a circulating water pump.
- (2) Feed the simulated waste ground to prescribed particle sizes with shredder from the top of the bubble tower while bubbling the content in the system with pressurized nitrogen gas.
- (3) After raising the system temperature and pressure to prescribed values, initiate the reaction by continuous feed of oxygen. pH in the reacting liquid is measured automatically and regulated to a prescribed value by being interlocking with NaOH liquid feed pump.
- (4) Exhaust gas containing decomposed CO₂ gas and steam are discharged through a pressure control valve. Steam is condensed in exhaust gas condenser, and the condensate is recirculated to the reactor again. Exhaust gas is made free from mist through a demister and then is subjected to a gas analyser before being discharged into the atmosphere.

2 Second Stage (Repetition of reaction)

After the first stage reaction is completed, feed the new waste into the reactor by changing over the two valves at the top of the reactor one

by one without dropping the inner pressure of the reactor and leave the reacting liquid as it is. Then repeat the procedures following the first stage (3) to effect the oxidation process again.

3 Third Stage

After the last reaction is completed, the reacting liquid is discharged from the reactor bottom. Waste liquid thus discharged is converted into powder to be solidified by concentrating and drying of the liquid.

2.2 Features of Wet Oxidation Process

This process provides the following features:

- (1) The process is capable of treating various kinds of wastes (inflammable) lumped together in the same system at the same time.

Various kinds of inflammable materials lumped together in the miscellaneous solid wastes (Polyvinyl sheet, wood, paper, rubber, active charcoal and etc.) and process wastes (ion-exchange resins, filter sludge etc.) can be treated with the same wet oxidation system and at the same treating conditions.

- (2) Highly safe and reliable operations can be achieved by improving the conditions of oxidation.

Much safer and more reliable operation regulation and control can be effected compared to the conventional dry combustion process, since the process is capable of achieving continuous control of pH in the reacting liquids in the reactor, and oxidation treatment at lower temperatures (around 200°C) compared with incineration process.

- (3) Remarkable reduction in initial cost of off-gas treatment systems can be made.

No dust and toxic gas such as SO_x, NO_x are generated in this process, since the wastes are treated by means of oxidation in a liquid phase. Consequently, the facilities necessary for removing dust and gases can be deleted (dust filter, scrubber etc.).

- (4) High decontamination factor (D.F.) reduces the load of the off-gas treating system (radiation exposure reduction).

From the reason stated in (3), emigration of radioactive substances into the off-gas side is very small (i.e. extremely high D.F. is obtained) in this process. The load of the off-gas treating system (radiation exposure is especially reduced) is remarkably mitigated.

- (5) High reduction of waste volume can be achieved

Fig. 2 indicates the results of the estimated waste generation in a case where this process is adopted in a BWR 1100 MW plant. The result shows that the waste volume is reduced to around 1/8 compared with those untreated, and to around 1/3 compared with those treated with the conventional incinerator.

Weight-reduction of Combustible Waste from BWR Plant

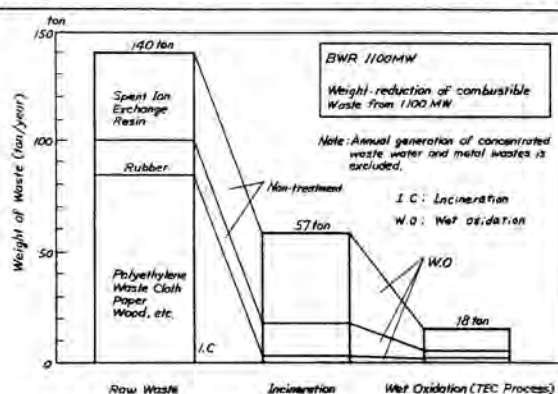


Fig. 2

53. Tests and Results

3.1 Results of Autoclave Tests

In the series of experiments of wet oxidation on radioactive wastes, we initially conducted the tests by using an 1ℓ autoclave. After oxygen gas was injected and sealed up to a prescribed pressure in the autoclave having the required amounts of water, test samples and catalysts, the reaction was started. After the reaction was completed, the conversion of the samples were obtained by measuring the Total Organic Carbon (TOC) of the reacting liquid.

The results illustrated in Table 1 indicates that the inflammable miscellaneous solids (polyethylene, waste cloth, wood) have conversion of 90% or more, and flame resisting miscellaneous solids (polyvinyl chloride, ion-exchange resins, rubber tapes, natural rubber gloves) have a conversion of 85% or more, and that even active charcoal has a conversion of 90% or more through 5 HR reaction.

Table-1 Conversion of Wastes in Autoclave

Species	Conversion (%)
High density polyethylene	95.1
Waste cloth	97.5
Cotton glove	91.7
Wood	97.7
Newspaper	99.8
Neoprene	86.2
Polyvinyl chloride	83.7
Machine oil	94.0
Grease	90.4
Active charcoal	89.8
KC floc	98.7
Rubber glove	90.9
IR-120B	97.1
PAO	85.0
Adhesive tape	91.9

$$\text{Conversion} = \frac{[\text{TOC}]_i - [\text{TOC}]_f}{[\text{TOC}]_i} \times 100$$

Reaction Condition: *) 230°C, 1hr 230°C, 5hr

The Table 2 illustrates the weight-reduction through this process, which is given by comparing the decomposition residue weight with the initial waste weight. The weight reductions were found to be in the order of one part to thirty for inflammable miscellaneous solids, and around one-tenth for flame-resisting miscellaneous solids. On the other hand, ion-exchange resins showed a weight-reduction ratio as low as one-third, which is possibly due to the fact that a large

amount NaOH was added to the reacting liquid to adjust pH values, and that the resins originally contain a large amount of inorganic substances. On the basis of the above basic test results, a bubble tower reactor with an inside volume of 5ℓ was manufactured, and the following wet oxidation or decomposition test was begun.

Table-2 Weight Reduction

Species	Weight Ratio
*) Waste mixture	1/31
Waste cloth	1/42
Adhesive tape	1/3.5
KC floc	1/45
Ionexchange resin	1/3
Rubber glove	1/6.5
Active charcoal	1/10

*) { Polyethylene 10.6 g
Waste cloth 7 g
Paper 2 g
Wood 0.4 g

Weight ratio :

Wt. of Dry-up Residue / Wt. of Raw Material

3.2 Test Results with Small Scale Bubble Tower

Based on the autoclave test results mentioned above, a series of tests were conducted with ion-exchange resins. An apparatus with an inner diameter of 3 inches and height of 1.5 m was used. Outlines of the apparatus are analogous to the flow-sheet mentioned before.

After feeding the required quantities of the test samples and reacting liquid and raising the temperature and pressure in the reactor up to the prescribed values, the reaction was sustained by a continuous supply of oxygen to the reactor in the form of bubbles in the reacting liquid. Similar to the case in the above autoclave, conversion were obtained by measuring TOC.

Fig. 3 represents one of the test results used to evaluate the effect of temperature and time on the decomposing reaction. The curves demonstrates that conversion become higher with rising temperatures, while the temperature varies from 180°, and that the reaction is nearly completed in 1 hour.

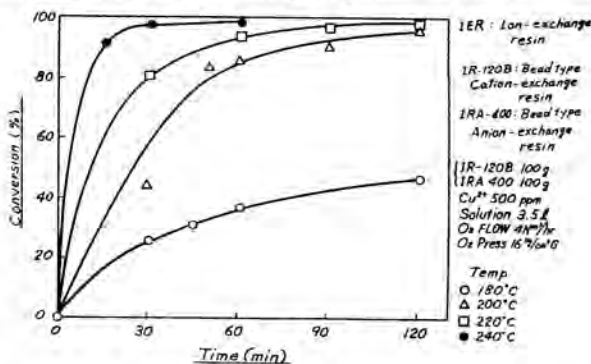


Fig.3 Time Course of IER Mixture Decomposition

Furthermore, the reaction is found to be a primary reaction for the given concentrations of the

samples in the initial and middle stage of the reaction and is expressed by the following formula

$$-\frac{d(TOC)}{dt} = A \left(\exp \frac{-\Delta E}{RT} \right) \cdot PO_2 \times (TOC)$$

where $A = 4.74 \times 10^{-6} \text{ min}^{-1} \times \text{KG/cm}^2\text{G}$, $\Delta E = 24.75 \text{ Kcal/mol}$.

The effects of the initial charge quantity on the decomposition rates were then surveyed and the results are shown in Fig. 4. When the initial charges exceed 7.5 wt% or 250g/3.5% for bead resins (IR-120, IRA-400) and 10 wt% for powdered resins, some decrease in conversion in 1 HR are observed.

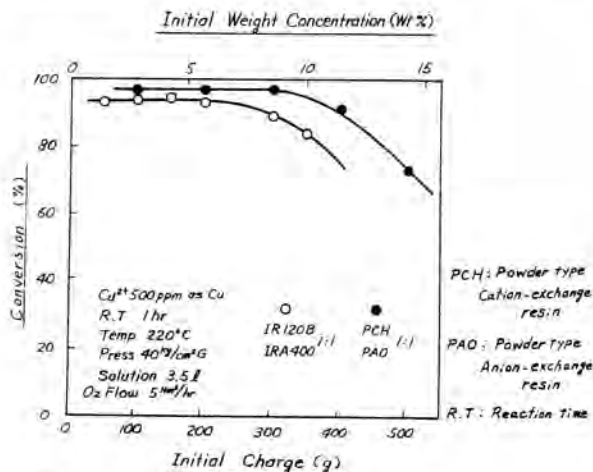


Fig. 4 Oxidation of IER Rate VS Initial Charge of Various Resins

With the small scale bubble tower, the reaction itself dominates the decomposition rate when initial charges are up to 7 wt.% for bead resins and up to 10 wt% for powder resins. On the other hand, when the percentage value exceeds the above figures the decomposition rate is dominated by the diffusion speeds of oxygen gas within the liquid phase. Consequently, the optimum initial charge per batch can be predicted.

Furthermore, the inter-relationships between the conversion and gas flow velocity were examined.

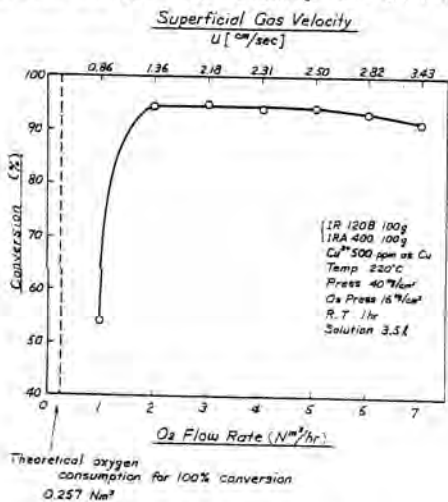


Fig. 5 Effect of Oz Flow Rate

Fig. 5 shows a relationship between the O_2 gas flow and conversion. From the curve it is found that a good conversion is attained for a gas flow velocity above 1.4 cm/S, with the rate decreasing for a lower gas flow velocity. The reason for the decrease in conversion is considered to be due to bad mixing of the test sample caused by low gas flow velocity.

Next, tests on possibilities of repeated use of catalyst liquid (one of the features of the process) were implemented. Fig. 6 indicates a relationship between numbers of resin charge cycle and the respective conversion. In the experiment, the deterioration of catalysts were examined with a catalyst liquid with Cu concentration of 500 ppm which treats resins of 200 gr per each cycle. No drop in conversion were observed up to around the 8th cycle i.e. it was demonstrated that the catalyst liquid could be repeatedly used until the weight of resin treated with 1/2 catalyst liquid reached at least 0.5 kq.

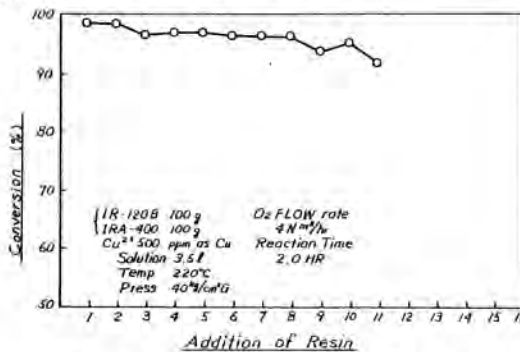


Fig. 6 Repeated Usage of Catalyst Solution

Finally, the result of off-gas analysis during the reaction period is given. Fig. 7 indicates relationship between gas concentrations and proceeded time.

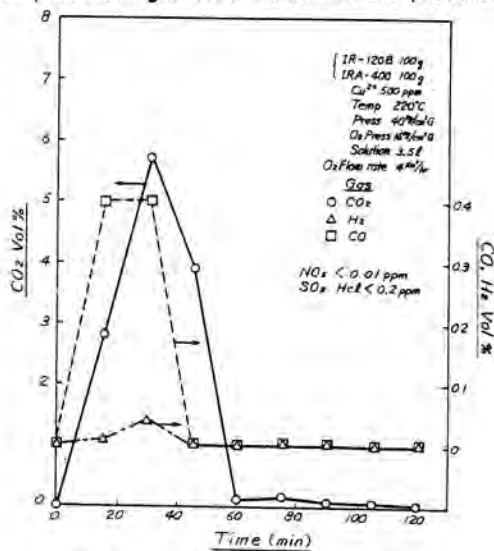


Fig. 7 Analysis of Exhaust Gas

Off-gas was quantitatively analysed by a gas chromatograph. The drawing shows that CO_2 gas content is around 6% at the maximum and that the reaction comes to an end in 1 hour. NO_x , usually a problem, was measured by using the Saltzman method and its concentration was found to be 0.01 ppm at max. and SO_x 0.2 ppm at max. It is evident that S and N contained in the resins were fixed within the liquid phase. Furthermore D.F. of the liquid and off-gas are shown

in Table 3 for cases where Co and Cs are used as indicator by a cold test. As evident in the table, for both Co and Cs, D.F. shows values of 10^6 or more, and therefore it is clear that the off-gas is extremely clean.

Table-3 D.F of reactant and off-gas

	Co D.F	Cs D.F
off-gas	$> 1.26 \times 10^7$	$> 5.06 \times 10^6$

$$D.F = \frac{\text{Co, Cs concentration in reactant (} \mu\text{g/l)}}{\text{Co, Cs concentration in off-gas (} \mu\text{g/l)}}$$

DF : Decontamination Factor

3.3 Pilot Plant Tests

On the basis of the aforementioned small scale bubble tower reactor tests, we were granted with subsidizes from the Science and Technology Agency in Japan for conducting pilot plant tests according to a 3 year terms program. The schedule of the program is shown in Table 4. Test results for the 1983 term year will be stated later. In the 1984 term year, hot tests in one of the authorized hot laboratories are scheduled. The objective of these tests is to obtain assurance that none or very few radio-active nuclides emigrate into the off-gas system.

Table-4 Experimental Schedule

	1983 Fiscal Year		1984 Fiscal Year		1985 Fiscal Year	
	First half	latter half	First half	latter half	First half	latter half
1. Pilot Plant Test plant design construction cold operation	—	—	—	—	—	—
2. Hot verification test	—	—	—	—	—	—
3. Modification, pilot plant	—	—	—	—	—	—
4. Automatic operation, pilot plant	—	—	—	—	—	—
5. Preliminary Design of Hot Demonstration Plant	—	—	—	—	—	—

In the final term year 1985, our research work will be oriented toward the automation of the pilot plant.

1) Test Results up to the present date.

The following is the outline of the status of our research work up to present date.

a) Manufacture of Pilot Plant

The core component of the pilot plant, a bubble tower reactor, as shown in Fig. 8 is a device which has around 60ℓ inside volume, i.e. 5 inch inner diameter x 5 m height, and made of Titanium metal highly resistant to chlorine and its derivatives.

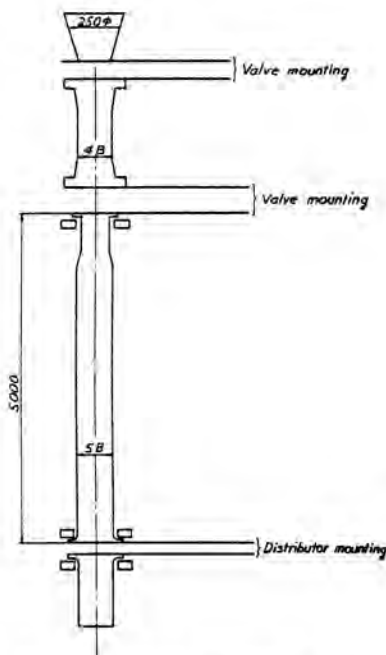


Fig.8 SKETCH OF BUBBLE TOWER

The pilot plant equipment are intended for a capacity for treating 3 kg waste per 1 batch reaction. Reactor height of 5 m is adopted with consideration to varied liquid levels. Although the present tests are conducted in a batch system, tests scheduled in the future will treat the raw material or the wastes fed semi-continuously and oxygen will be fed continuously.

b) Test Results with the Pilot Plant

In the pilot plant, initially various kinds of waste material were decomposed. The results are shown in Table 5. The table indicates good decompositions of the waste materials. Slight differences in conversion compared with autoclave test results, possibly due to inadequate fluid flow inside the reactor, were found.

The present operating conditions of around 200°C and 40 kg/cm²G are considered to be relatively high. We are considering future research for other catalysts capable of decomposing the waste materials at lower temperatures and pressures along with engineering analysis using further tests with pilot plants. Dispersion of solution and bubbles should also be improved furthermore.

Conclusions

Results from various tests verifies the capabilities of the wet oxidation process for treating various kinds of inflammable and flame-resisting wastes in a lumped form. It also provides a high weight-reduction of one-third compared with that of existing incinerators now used in most nuclear power plant. This is shown in the predicted results where this process is assumed for a BWR 1100 MW plant. Furthermore with this process, NO_x, SO_x, radioactive nuclide and etc. are retained within its liquid phase and therefore the process by no means demands for any large-scale off-gas treating facility. Accordingly we are confident that the present process will be an effective and promising technique for treatment and volume reduction of radioactive wastes.

References

1. T. Saida, "Wet oxidation of Ion-exchange resin", Proc. Fall meeting of the Atomic Energy Society of Japan, J29, Osaka (1982)
2. T. Saida and K. Obara, "Wet oxidation of organic radioactive wastes", Proc. Annual meeting of the Atomic Energy Society of Japan, F12, Tokyo (1983)

Table-5 Conversion of Wastes in Pilot Plant

Species	Conversion (%)
High density polyethylene	89.3
Ion-exchange resin	94.3
Natural Rubber	84.8

Reaction Condition

Temp 200°C
 Press 40 kg/cm²G
 R.T. 2.0 hr
 Solution 30L
 Catalyst 500 ppm as Cu
 O₂ Flow 20 N^m/hr
 Waste charged 1000g

The relations between O₂ gas flow velocities and charged waste volumes were then examined using polyvinyl chloride. As shown in Fig. 9 it is clear that the conversion varies with O₂ gas flow velocities. Up to roughly 2 cm/sec, increased gas flow velocities result in improved fluid flow, and thus conversion is increased. However, at higher velocities, conversion may drop due to channeling. The conversion of this experiment is low compared with that of autoclave tests. This conversion may be raised to a level equal to that of the autoclave test improving the fluid flow.

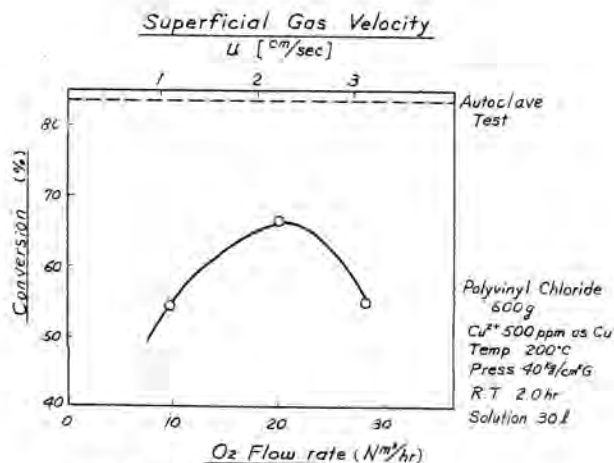


Fig. 9 Effect of O₂ Flow Rate