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THE WET-AIR OXIDATION OF RUM DISTILLERY WASTES

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THE WET-AIR OXIDATION  
Of  
RUM DISTILLERY WASTES

I - Introduction

The disposal of rum distillery wastes is one of the major problems facing the rum industry in Puerto Rico. At present these wastes are disposed of by diluting them with water and dumping the mixture into the sea. One local distillery uses a sizable fraction of the diluted wastes for irrigation of its sugar cane plantations, and only the excess portion reaches the ocean. The industry is now seeking proper ways to manage its wastes, since water pollution control regulations make it mandatory to treat them before discharge.

Conventional biological treatment methods have been considered as likely candidates for treatment of the wastes. Their cost, however, has been found to be very high, mainly because of the high contents of organic matter of the material being handled.

This study was aimed at determining the feasibility of oxidizing rum distillery wastes using a wet-air oxidation process, with and without catalysts. In wet-air oxidation organic matter dissolved in water is oxidized with air directly in the aqueous phase. High temperatures and pressures are used to achieve fast reaction rates. The optimum operating conditions for oxidizing the wastes under consideration were to be defined in this work, and the use of catalysts to improve the reaction kinetics was to be evaluated.

the rum wastes with tap water in a 1 to 6 ratio before anaerobic digestion, and obtained a 53 per cent removal of BOD<sub>5</sub> and a final effluent concentration of 1800 mg BOD<sub>5</sub> per liter.

Sen et al<sup>2</sup> conducted laboratory studies on the anaerobic digestion of molasses distillery wastes using cow manure as seed. For a BOD<sub>5</sub> loading of 0.189 lb/day/cu ft and a detention time of 10 days, it was possible to obtain BOD<sub>5</sub> removals of about 90 per cent and a final effluent concentration of 1000 mg. BOD<sub>5</sub> per liter.

The use of activated sludge to treat rum distillery wastes diluted with domestic wastes has been reported unsatisfactory for dilutions equal or greater than 10 per cent.<sup>1</sup>

Trickling filters have been used successfully in Great Britain to treat whiskey distillery wastes and brewery wastes.<sup>4</sup> BOD<sub>5</sub> removals of 98 per cent have been reported for a plant processing whiskey distillery wastes.<sup>4</sup>

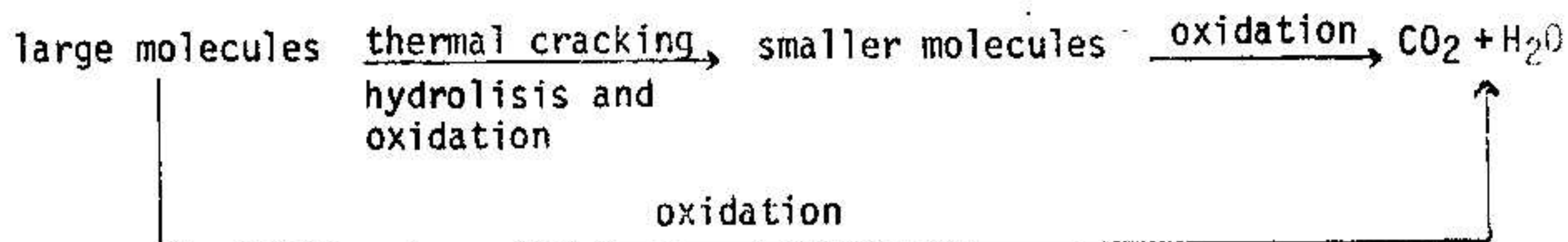
The use of trickling filters for the treatment of undiluted distillery wastes has been reported as impractical because of the large filter area required to process large quantities of wastes.<sup>2</sup>

Burnett<sup>3</sup> studied the treatment of diluted rum distillery wastes using both activated sludge and trickling filters. The rum wastes were diluted to 10 per cent concentration and neutralized to pH 7.2 to 7.5. Under these conditions a COD removal efficiency of 33 per cent was obtained with a retention time of only 4.5 hours.

The major disadvantages of the biological treatment of rum wastes is the large retention time necessary to obtain a high removal efficiency.

D - MECHANISM OF WET-AIR OXIDATION REACTION

The overall aqueous phase oxidation reaction is probably a multi-step process of the form<sup>13</sup>:



Both the thermal and the oxidation reaction convert solid matter to soluble matter and/or CO<sub>2</sub>. Any substance capable of burning that remains dissolved or suspended can theoretically be oxidized<sup>14</sup>.

The relative rates of thermal cracking and hydrolysis compared with that of oxidation, and their dependence upon reaction conditions are not known nor has the importance of mass transfer been completely defined for wet oxidation. Information on the overall reaction network and the rate of the individual steps is needed to define the rate controlling step, if one exists.

Iwai found that the rate of oxidation was not influenced by oxygen pressure nor stirring rate between 300-1000 rpm<sup>15</sup>. Schatzberg et al proposed that wet oxidation involves two first-order reactions in series, the first being the hydrolysis and oxidation of large molecules to water, carbon dioxide, and low molecular weight organic compounds<sup>16</sup>. The second step suggested was a lower one in which intermediates are oxidized to carbon dioxide and water. Between 250-300°C the reaction rate constants varied from 0.1 to 0.2 minutes<sup>-1</sup> for the fast reaction step and from 0.003 to 0.008 minutes<sup>-1</sup> for the slower reaction. COD reductions of 80% were obtained after 15 minutes at 260°C.

The reaction was deemed zero order in oxygen at these and higher oxygen concentrations. The first order rate constant for the thermal reaction was found to be  $0.052 \text{ minutes}^{-1}$  at  $175^\circ\text{C}$ , while that for the combined reaction was  $0.086 \text{ minutes}^{-1}$ . The thermal reaction contribution was therefore, larger than that of the oxidation reaction at these conditions.

### III- EXPERIMENTAL PROCEDURES

#### A - EQUIPMENT USED

The experimental runs were all made in a high-pressure autoclave rated 1-gallon, 3000 psig, and  $650^\circ\text{F}$ . All wetted components were constructed of type 316-stainless steel. The pressure vessel was provided with a variable-speed agitator, a cooling coil, a thermowell, and an external 3.5 K. W. electric heater. Figure 1 shows a schematic diagram of the autoclave with its most significant mechanical features described.

The vessel had a bolted cover, also constructed of 316 stainless steel, which was closed tight using eight socket head cap screws. The cover was provided with the following openings: a) two for the cooling coil,  $1/8"$  N. P. T. with quick-disconnects; b) one  $1/8"$  opening for a sampling tube which allowed drawing samples from the inside of the autoclave; c) one  $0.1285"$  diameter drill for the thermowell; d) a  $3/8"$  diameter port for charging the unit; e) one for a valve which connected to vent and to a pressure gauge; f) one for a valve which led to a blow pipe; and, g) a  $1/8"$  N. P. T. lantern connecting to the oil cylinder of the rotor assembly.

The openings in the body of the autoclave were two 1/4" tube connections for inlet and outlet of gas from the chamber and one 1/2" safety head connection. This was fitted with an Inconel safety head rupture disc which was rated at 3,750 psi at 72°F.

The turbine-type agitator which fitted into the chamber had a 2 1/2" diameter impeller. Two vertical baffles inside the chamber helped increase the turbulence levels for any setting of the variable-speed motor which drove the agitator.

The strip heaters which surrounded the chamber were wired in three lapped circuits for 110-volt service. The degree of heating was controlled by varying the number of circuits in operation at any time. Additionally, voltage regulators were used in each circuit to permit reaching temperature levels intermediate to those corresponding to full 110-volts operation.

The autoclave was fitted with a pressure gauge having a range from 0 to 5,000 psi. Its dial was 3 1/2" in diameter, and its Bourdon tube was made of type 403 stainless steel.

#### B - OPERATING PROCEDURE

The high-pressure autoclave was operated only in batch fashion: feeding to it known amounts of liquid and of air and allowing the mixture to react during a desired period of time. Continuous operation, with both gas and liquid being removed continuously from the vessel at the same rate at which they were fed, would have required more complex equipments than those available.

A typical experimental run involved essentially the following sequence of steps:

- k) Cleaning of the pressure chamber and of all tubes and parts which came into contact with the liquid.

Most runs were made as per this mode of operation. Temperatures were varied from 350°F to 550°F, pressures from 500 psig to 2000 psig, and reaction times from a minimum of 2 hours to a maximum of 10.

Four runs (numbers 28, 29, 29b, and 30) were also made in which samples were drawn from the chamber at various times throughout the course of the reaction rather than at the conclusion of the run. In one of these (no. 29) a fresh charge of air was fed to the autoclave after 8 hours reaction time, and the oxidation was allowed to proceed during 7 additional hours. In run no. 29b the rate of agitation was about twice as that used in all the other runs. In this group of runs samples were taken of the fresh feed to the reaction as well as of the liquid once the operating temperature had been reached but immediately before oxidation began. This was done to determine if thermal cracking occurred during the initial heating period.

The most common problem met in operating the autoclave was that of leakage of gases through the cover. This was corrected by tightening the bolts until the leakage ceased. Another drawback inherent to the autoclave properly was that the times required to bring the system to operating temperatures were excessively long, ranging from 1 to 3 hours. This was so because the power to the electric heaters was increased gradually to values such that overshooting of the temperature was avoided, thereby minimizing localized charring of the liquid inside the chamber.



- a) Biochemical oxygen demand - The 5-day BOD was determined following the standard procedures described in "Standard Methods for the Examination of Water and Sewage"<sup>19</sup>.
- b) Chemical oxygen demand - The standard test which uses potassium dichromate as oxidant was employed for this analysis<sup>19</sup>.
- c) Total organic carbon and total carbon - A Model DC 50 Dohrman Analyzer was used in these determinations. The instrument had a precision of 2%.
- d) Suspended solids, total solids, and volatile solids - These three parameters were evaluated using the analytical procedures which the Rum Pilot Plant of the University of Puerto Rico has developed for the analysis of rum and of rum distillery wastes<sup>20</sup>.
- e) pH - An electric meter accurate to the second decimal place was used to measure the pH of all the samples.

As previously mentioned, attempts were made in the early parts of this study to determine the composition of the gaseous mixture finally present in the autoclave at the conclusion of an experimental run. A Model 900 Perkin Elmer gas chromatograph was used for these analyses. The carrier gas employed was helium, and the separations were effected in stainless steel columns packed with Porapak Q molecular sieve packing. The failure to gather gas samples from the high pressure chamber without contamination by air made meaningless the results of the analyses, and the use of the chromatograph was therefore discontinued.

TABLE 1  
SUMMARY OF DATA FOR RUNS SAMPLED AT THE CONCLUSION OF THE REACTION

Run Number	Pressure, psig	Temperature of	Duration, hours	RESULTS OF ANALYSES										
				Reaction time, hrs	BOD ppm	COD ppm	TOC ppm	C total, ppm	pH	Suspended solids, ppm	Total solids, ppm	Volatiles		
2	500	350	4	0	21,239	63,598	-	-	-	-	-	-	-	-
				4	12,955	31,398	-	-	-	-	-	-	-	-
3	500	350	4	0	22,349	85,690	26,550	27,450	-	-	-	-	-	-
				4	15,231	57,323	16,608	16,608	-	-	-	-	-	-
4	500	350	8	0	28,200	93,218	34,400	37,650	-	-	-	-	-	-
				8	19,969	49,294	18,734	18,734	-	-	-	-	-	-
5	500	350	2	0	30,552	101,513	-	-	-	-	-	-	-	-
				2	21,690	68,485	-	-	-	-	-	-	-	-
6	500	350	4	0	28,575	97,941	36,100	38,000	3.95	21,800	86,710	64,79	-	
				4	23,688	75,096	24,000	25,344	4.10	8,736	66,720	46,64	-	
7	500	350	2	0	32,000	98,857	38,600	39,700	3.90	34,500	88,280	67,61	-	
				2	27,119	75,154	29,046	29,798	4.04	11,468	67,840	48,84	-	
8	500	350	6	0	29,300	98,395	34,500	37,500	3.91	34,500	88,290	67,61	-	
				6	22,992	72,260	19,200	22,560	4.20	12,144	65,933	45,30	-	
9	500	350	8	0	30,480	100,426	38,000	38,000	4.28	18,200	94,250	68,42	-	
				8	18,903	45,775	15,664	16,198	4.41	5,340	42,591	25,33	-	
10	1000	350	2	0	66,963	145,360	45,650	49,800	4.45	14,600	82,650	64,18	-	
				2	46,957	116,368	25,062	25,943	4.39	10,146	55,420	39,48	-	

SAMPLING AND ANALYSIS RESULTS AT THE END OF THE PERIOD OF THE REACTION

Run Number	Pressure, psig	Temperature, °F	Duration, hours	RESULTS OF ANALYSES										
				Reaction time, hrs	BOD, ppm	COD, ppm	TOC, ppm	C total, ppm	pH	Suspended solids, ppm	Total solids, ppm	Volatile solids, ppm		
19	1500	350	2	0	40,602	105,013	30,700	32,500	3.82	18,600	88,965	67,365		
				2	26,069	61,618	15,876	17,337	4.15	5,242	51,822	34,300		
20	1500	550	2	0	35,866	105,013	30,558	33,403	3.99	27,075	93,572	72,729		
				2	22,210	72,924	17,027	17,611	4.78	18,195	54,488	34,575		
21	1500	550	3.5	0	35,334	104,284	25,711	30,980	3.94	22,761	89,831	64,117		
				2.5	20,834	72,231	16,541	18,876	4.79	17,319	-	72,790		
22	1500	550	6	0	21,373	80,864	24,481	27,884	4.04	9,336	74,066	62,303		
				6	11,429	60,576	17,751	19,050	4.86	12,005	38,474	29,589		
23	1500	550	8	0	25,897	82,053	30,435	32,174	4.06	-	77,146	62,176		
				8	9,726	50,409	14,734	15,042	4.95	6,934	35,525	27,811		
24	1500	550	10	0	23,291	86,405	26,724	30,991	4.03	22,521	65,571	50,582		
				10	9,962	56,415	13,828	14,602	4.94	7,156	36,484	27,472		

TABLE III

## EFFECT OF THE OXIDATION PROCESS ON RUM DISTILLERY WASTES

(Runs 2 to 24, all conducted batchwise)

Run No.	PER CENT REDUCTIONS						
	BOD	COD	TOC	C total	Suspended Solids	Total Solids	Volatile Solids
2	39.0	50.6	-	-	-	-	-
3	31.8	33.1	31.4	39.5	-	-	-
4	29.2	47.1	45.5	50.2	-	-	-
5	29.0	32.5	-	-	-	-	-
6	17.1	23.3	33.5	33.3	59.9	23.0	28.0
7	15.2	24.0	24.7	24.9	64.6	23.1	27.7
8	21.5	26.6	44.3	39.8	64.8	25.3	33.0
9	37.9	54.4	58.8	57.4	70.7	54.8	63.0
10	29.8	19.9	45.1	47.9	30.5	32.9	38.5
11	32.3	25.7	44.8	43.4	41.6	39.2	45.1
12	32.9	35.0	41.7	41.5	28.2	37.6	44.7
13	29.1	34.6	45.6	47.3	37.9	41.6	51.3
14	27.8	32.6	36.9	28.4	-	37.3	46.2
15	30.8	37.9	55.4	37.7	41.8	42.0	50.6
16	40.5	51.8	57.2	59.9	76.5	45.3	54.6
17	36.7	30.9	53.8	60.8	20.4	32.4	38.1
18	21.8	30.2	43.4	36.6	45.5	36.8	43.9
19	35.8	41.3	48.3	46.6	69.9	41.7	49.1
20	38.1	30.6	44.3	47.3	32.8	41.7	62.5
21	41.0	30.7	35.7	39.1	23.4	-	-
22	46.5	25.1	27.5	31.7	28.5	48.1	52.5
23	62.4	38.6	51.6	53.2	-	53.9	55.6
24	67.2	34.7	48.2	52.9	68.2	44.3	45.7

B - DISCUSSION OF RESULTS

The data reported in Tables I and II were used to determine the percent decrease in BOD, COD, TOC, total carbon, and solids for each experimental run. The results thereby obtained appear summarized in Tables III and IV.

The maximum percent reductions obtained are seen in Table III to be 67.2% in BOD, 54.4% in COD, 58.8% in total organic carbon (TOC), 60.8% in total carbon, 76.5% in suspended solids, 54.8% in total solids, and 63.0% in volatile solids. These values were obtained in different runs, and therefore they do not define the optimum conditions for carrying out the oxidation process. They do provide, however, an index of the efficiency to be expected of the process under the ranges of pressures and temperatures which were considered.

A discussion of the removal efficiencies for the various parameters assessed in this work is pertinent at this point. Considering first the suspended, total, and volatile solids, the results in Table III show the following:

- a) At 500 psig and 350°F, the average percent removals of suspended solids, total solids, and volatile solids were 56, 35, and 42% respectively.
- b) For 1000 psig and 450°F, the corresponding figures for the same parameters were 37, 40, and 48 per cent respectively.
- c) At 1500 psig and 550°F, the corresponding average reductions were 38, 47, and 54 per cent.

Increases in temperature therefore cause increases in the removal efficiency for volatile solids and for total solids, as expected from the principles of reaction kinetics. However, the percent removal of

data obtained. The COD test was also established to be more reproducible than the BOD one, and it would therefore provide the most reliable result among all those parameters considered.

The BOD data are useful in that they provide estimates of the biodegradability to be expected if the distillery wastes were managed via the conventional biological treatment processes.

#### C - REACTION KINETICS

The effect of pressure on the rate of oxidation was determined by carrying out four batch runs at 350°F during two hours, at pressures of 500, 1000, 15000, and 2000 psig respectively (runs number 5, 10, 18, and 19). The results show considerable variation, and they fail to demonstrate with confidence any effect of pressure on reaction rate. The kinetics of the process will therefore be established independent of pressure. This is in agreement with the results obtained by Iwai<sup>15</sup> and Dávila<sup>18</sup> as described previously in this report.

The data obtained in batch runs made at 350°F, 450°F, and 550°F are shown in Figures 2, 3, and 4 respectively, using a first-order reaction model. This model is the one which best fits the results of previous workers for the kinetics of the wet combustion process<sup>13,16,18</sup>. The present study confirms this mechanism. Attempts at correlating the data assuming a second-order reaction mechanism yielded equations with much larger deviations than those corresponding to the first-order kinetics.

The reaction rate constants were determined by fitting the data with an equation of the type

$$C = C_0 e^{-k t}$$

in which

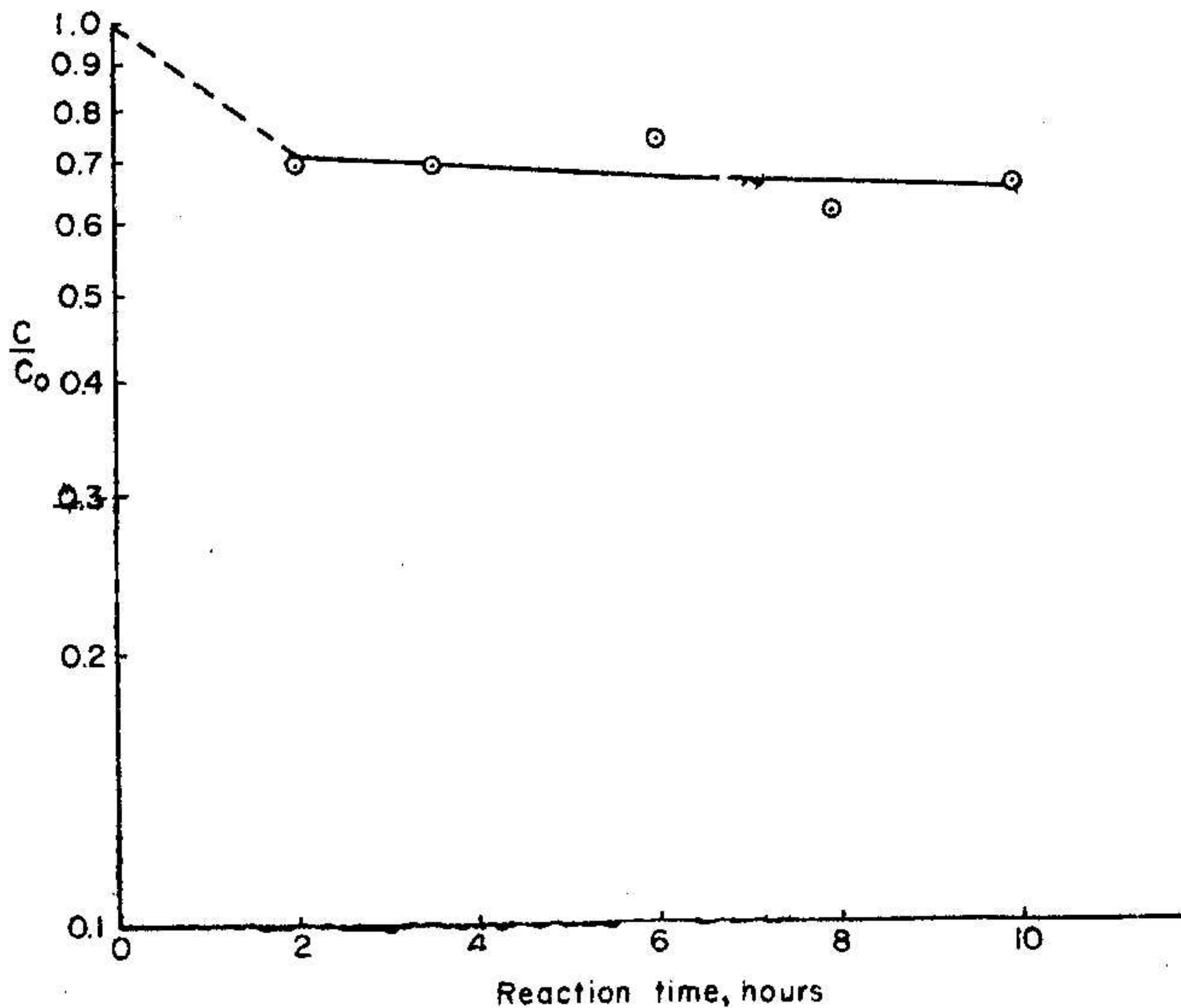
$$C = \text{chemical oxygen demand of the wastes at time } t$$

FIGURE 3

VARIATION IN CHEMICAL OXYGEN DEMAND  
WITH REACTION TIME AT 550°F AND 1,500 PSIG

Notes

- 1-  $C$  = COD value at time  $t$
- 2-  $C_0$  = COD value at start of run ( $t=0$ )
- 3- Includes runs 20, 21, 22, 23, and 24
- 4- First order reaction rate constant is 0.01175 hours<sup>-1</sup>



$C_0$  = chemical oxygen demand of the wastes at time zero

$k$  = reaction rate constant, hours<sup>-1</sup>

$t$  = time of reaction, hours

The least-square regressions applied to the three groups of data gave the following results:

a) At 350°F (Figure 2),  $k = 0.02665$  hours<sup>-1</sup>, with a variance of 0.0060.

b) At 450°F (Figure 3),  $k = 0.01572$  hours<sup>-1</sup>, with a variance of 0.0043.

c) At 550°F (Figure 4),  $K = 0.01175$  hours<sup>-1</sup>, with a variance of 0.0055.

The results indicate an anomalous decrease in reaction rate with increasing temperature. This, however, is consistent with the observed decrease in removal of suspended solids with increases in temperature which was presented previously in Section B. Theoretical considerations give support to the decrease in reaction rate with temperature if charring of the reacting organic compounds occurs, since charring produces solid compounds which react much more slowly than the dissolved ones. Again, the fact that charring did occur is substantiated by the observed increases in suspended solids with temperature.

The values of the reaction rate constants reported by Iwai<sup>15</sup> and by Dávila<sup>18</sup> do not agree with each other, nor do they agree with those found in this study. This is in accordance with the general principle that chemical substances vary in their reactivity as their molecular



## V - CONCLUSIONS

The aqueous-phase oxidation of rum distillery wastes was done batchwise at temperatures ranging from 350°F to 550°F and at air pressures from 500 psig to 2000 psig. The maximum percent conversions obtained were 67.2% in BOD, 54.4% in COD, 58.8% in total organic carbon, and 60.8% in total carbon. The reaction times required to achieve these reductions varied from 8 to 10 hours, smaller values being obtained at shorter reaction times.

As per these results, the wet-oxidation of rum distillery wastes does not appear to be an adequate treatment process for the management of these wastes. The required operating conditions are severely high, and the resulting products would still have to be submitted to a posterior treatment before they could be discharged safely into receiving bodies of water.

Limitations in the equipment used in this study did not allow carrying out the process under continuous conditions. The case could be that this mode of operation could improve the overall efficiency of the process to an extent such as to render it acceptable for industrial applications. Such work remains yet to be done.

The experimental results show that the rate of reaction is independent of pressure, that the oxidation is essentially a first-order reaction, and that thermal cracking occurs concurrently with the oxidation process. These findings are in agreement with those reported in the literature for the aqueous phase combustion of other substances.

The use of catalysts to determine their effectiveness in producing higher reductions in organic load at less severe conditions was also considered in this study. The results obtained are presented in the next part of this report.

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