WET AIR OXIDATION STUDIES OF COAL GASIFICATION WASTEWATERS

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Summary

The kinetics of wet oxidation of coal gasification wastewater were studied. Experimental studies explored the effect of temperature and residence time on the extent of reaction by conducting constant volume batch tests in a 1-liter high pressure autoclave. The extent of reaction was determined by measuring the chemical oxygen demand (COD) and phenol concentrations of the wastewater at various times.

The effect of temperature was studied from 205 to 251°C with residence times from 30 to 90 minutes. The experimental data obtained were used to fit Arrhenius expressions of the reactions. A mathematical model consisted of two first-order reactions in series showing a maximum COD reduction of 60% and a maximum phenol reduction of 95%, both at 251°C and a 90 minute residence time. The activation energies for COD and phenol reduction were both found to be 8.0 kcal/mol.

Introduction

Coal gasification processes are capable of producing pipeline quality gas from coal. During the process, the raw gas evolved is usually quenched with water which results in an aqueous condensate stream characterized by high organic loading as well as high ammonia and hydrogen sulfide concentrations. This condensate stream is at high temperature and pressure in order to maintain the desired steam levels to the shift converters employed in the process. This condensate stream must be treated prior to its reuse and presents a formidable and costly problem.

Wastewater treatment technologies usually employed for gasifier condensate treatment have been biological oxidation, reverse osmosis, carbon absorption, coagulation and flocculation, solvent extraction, and dissolved gas stripping. For the coal gasification process, however, another method, wet oxidation, appears to be technically attractive due to the high temperature and pressure conditions of the coal gasification condensate.

Wet oxidation is a process in which dissolved or suspended organic material is oxidized in the aqueous phase at elevated temperature and pressure. The

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reaction proceeds at temperature ranges from about 177 to 315°C in the presence of water [2]. The pressure must be elevated to maintain a liquid phase and also to provide the appropriate partial pressure of oxygen for the reaction to proceed. Pressures typically range from 600 to 1200 psig [3]. Since the quench system of the coal gasification process is usually operated at temperatures between 210 and 320°C and pressures ranging from 600 to 1000 psig [4], it would seem that the wet oxidation process is ideally suited for treating this condensate without the heat exchangers and pressure equipment usually associated with the wet oxidation process.

The wet oxidation process is also attractive from the standpoint that it can provide energy as a by-product [5]. The oxidation reaction is self-sustaining and is a net producer of thermal energy in the form of saturated steam, which would help defray the costs of operating the treatment process.

Other advantages of wet oxidation stem from its liquid phase reaction. Expensive dewatering associated with most wastewater treatment processes is not necessary. Wet oxidation can proceed with less than 1% oxidizable organic materials in solution. The process is also air pollution free since the resulting "ash" remains in solution [6].

If the reaction kinetics are favorable, the wet oxidation process would seem to be an ideal treatment method for coal gasification wastewater. The object of this study was to evaluate the reaction kinetics involved in the wet oxidation of coal gasification wastewater.

Experimental

The experiment was carried out in an Autoclave Engineers 1-liter autoclave rated for temperatures up to 600°C and pressures up to 200 atm. Figure 1 is
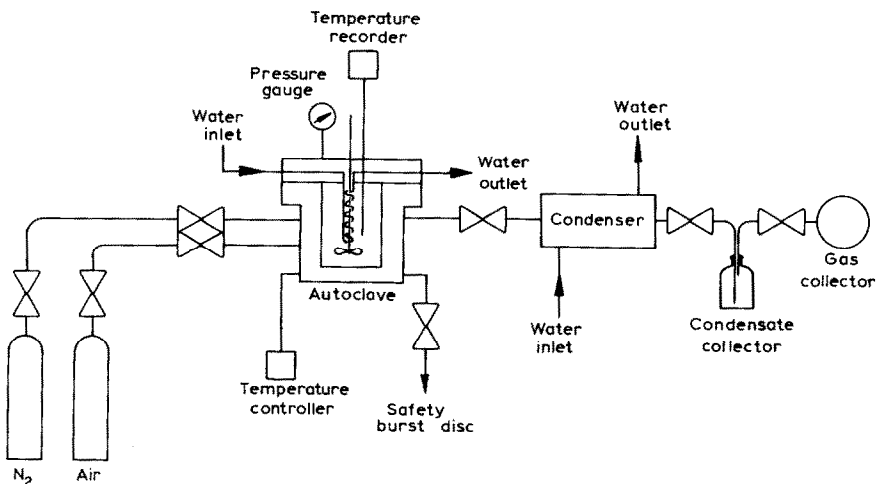

Fig. 1. Schematic diagram of the experimental reactor.

a schematic diagram of the experimental system. Air and nitrogen were supplied from pressurized gas bottles fitted with Matheson two-stage regulators. The reaction mixture was stirred by a magna-drive stirrer rotating at 1270 rpm. Heat was supplied to the reactor from electric heating elements surrounding the vessel, as required. A thermocouple in the reaction vessel was used to monitor and control the reaction temperature. Pressure was monitored by an Autoclave Engineers pressure gauge.

A predetermined volume of coal gasification wastewater was measured and added to the autoclave. The reactor was tested for leaks and purged with nitrogen to eliminate any oxygen. The desired temperature was set on the controller and the stirrer and heater were turned on. Once the desired temperature was reached, the reactor was pressurized with air to provide a partial pressure of oxygen of 100 psig, the introduction of the air was designated as time zero ($t = 0$). After a preset time, the heater was turned off and the reaction was quenched.

The liquid remaining in the reactor was preserved and stored for later analysis of chemical oxygen demand (COD) and phenol. COD analysis was determined using the Standard Ampule method [7]. Phenol concentration was determined in accordance with Standard Methods [8].

The wastewater used in this study was obtained from the University of North Dakota Energy Technology Center's slagging fixed bed gasifier. This wastewater was provided by the Pittsburgh Energy Technology Center where it was stored at 4°C. Prior to this study, the wastewater was stripped of hydrogen sulfide and ammonia by sparging with nitrogen in a steam heated vessel at 90°C for twelve hours prior to wet oxidation. After dissolved gas stripping, the feed to the wet oxidation reactor was determined to have a COD concentration of 39,200 mg/l and a phenol concentration of 5025 mg/l.

TABLE 1

Experimental data of temperature vs. time for wet air oxidation studies

Temperature (°C)	Time (min)	[COD]/[COD]^O	[phenol]/[phenol]^O
251	30	0.49	0.12
	60	0.49	0.06
	90	0.35	0.11
236	30	0.61	0.07
	60	0.53	0.10
	90	0.50	0.08
220	30	0.63	0.19
	60	0.56	0.12
	90	0.61	0.15
205	30	0.73	0.36
	60	0.65	0.24
	90	0.61	0.21

Results and discussion

The reaction parameters varied in this experiment were temperature and time. Twelve test runs were conducted at temperatures of 205, 220, 236, and 251°C and residence times of 30, 60, and 90 minutes. Each run was evaluated by following COD and phenol concentration. Table 1 summarizes the experimental data.

Plots of [COD]/[COD]^o versus time and [phenol]/[phenol]^o versus time are shown in Figs. 2 and 3, respectively. The curves are characterized by an initial rapid decrease in concentration lasting approximately 30 minutes; then the curves tend to level out for the remainder of the reaction time. The curves are consistent with the theory that wet oxidation involves heterogeneous oxidation which initially predominates and causes the rapid decrease in concentration. Once the solid surfaces are depleted, the slower homogeneous oxidation predomination is depicted by the leveling of the curves.

Maximum COD reduction was 60% at 251°C and a 90 minute residence time. The maximum phenol reduction of 95% was also at 251°C and a 90 minute residence time.
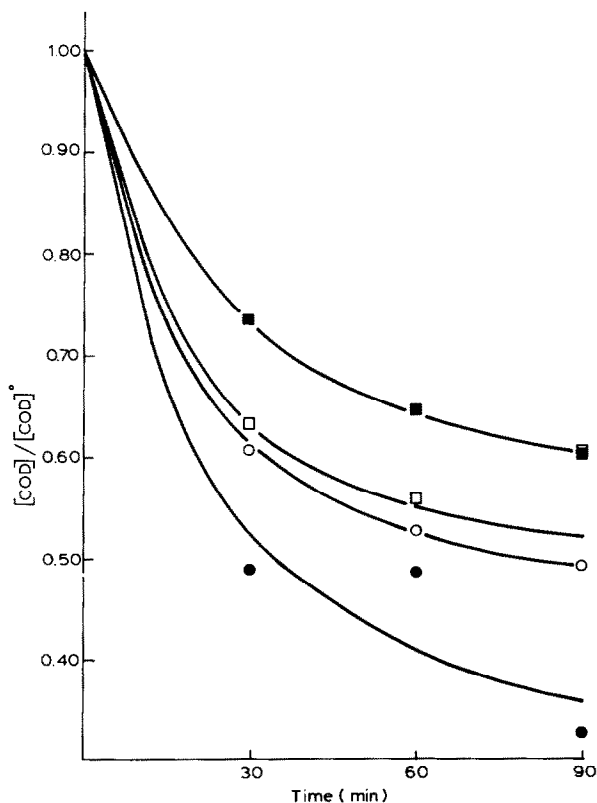

Fig. 2. Plot of [COD]/[COD]^o versus time for wet air oxidation. ■ = 205°C; □ = 220°C; o = 236°C; ● = 251°C.

Plots of log $[COD]/[COD]^O$ versus time and log $[phenol]/[phenol]^O$ versus time are shown in Figs. 4 and 5, respectively. The plots indicate an initial pseudo first-order reaction as O_2 is saturated followed by a slower pseudo first-order reaction. The reaction rates determined from the slopes of the semi-log plots are contained in Table 2.
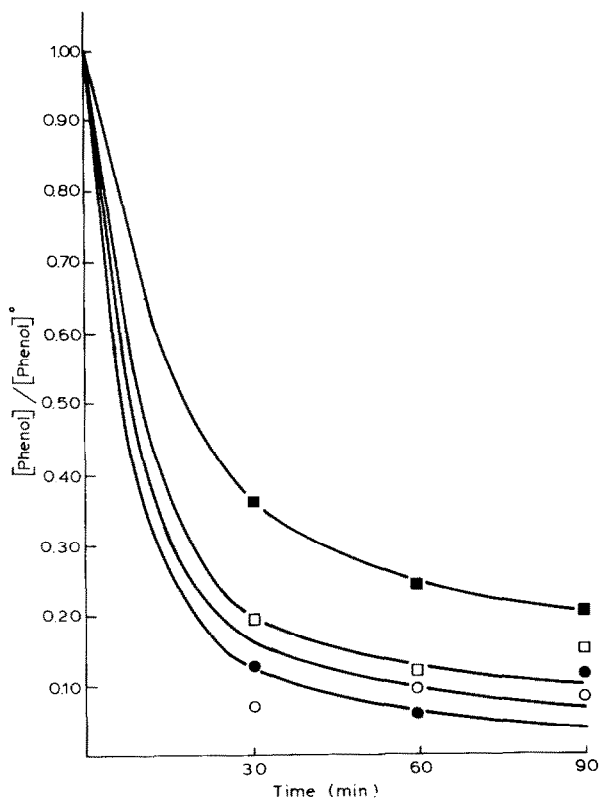

Fig. 3. Plot of $[phenol]/[phenol]^O$ versus time for wet oxidation. ■ $= 205°C$; □ $= 220°C$; ○ $= 236°C$; ● $= 251°C$.

The rate constants were correlated with temperature by Arrhenius plots. Figures 6 and 7 show the Arrhenius plots for COD and phenol, respectively. The activation energies were determined from the slopes of the Arrhenius plots. The activation energy for both phenol and COD oxidation was 8.0 kcal/mol. The equivalence of the activation energies suggests that the same rate-limiting step is involved for both COD and phenol reduction. This rate-limiting step is probably oxygen transport because of the low solubility of oxygen in water.

The activation energies obtained were a little lower than those reported in the literature, although the lack of similar kinetic studies makes comparison difficult. Bettinger et al. [10] reported an activation energy of 27 kcal/mol for copper oxide catalized wet oxidation of phenol solutions in water. Katzer
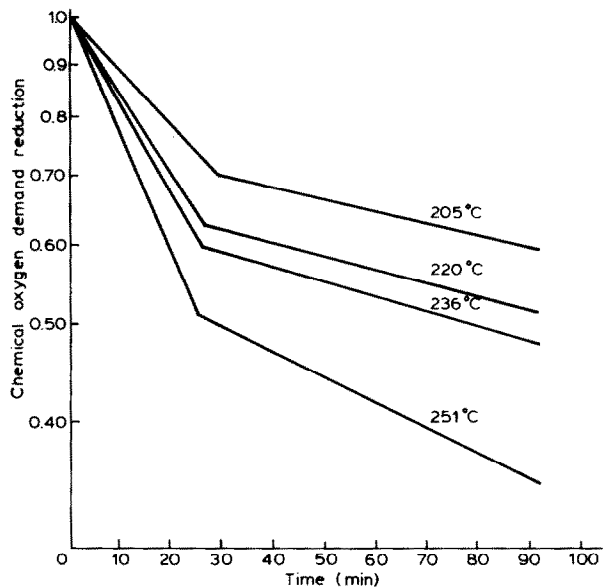
Fig. 4. Semi-log plots of chemical oxygen demand reduction for various temperatures.
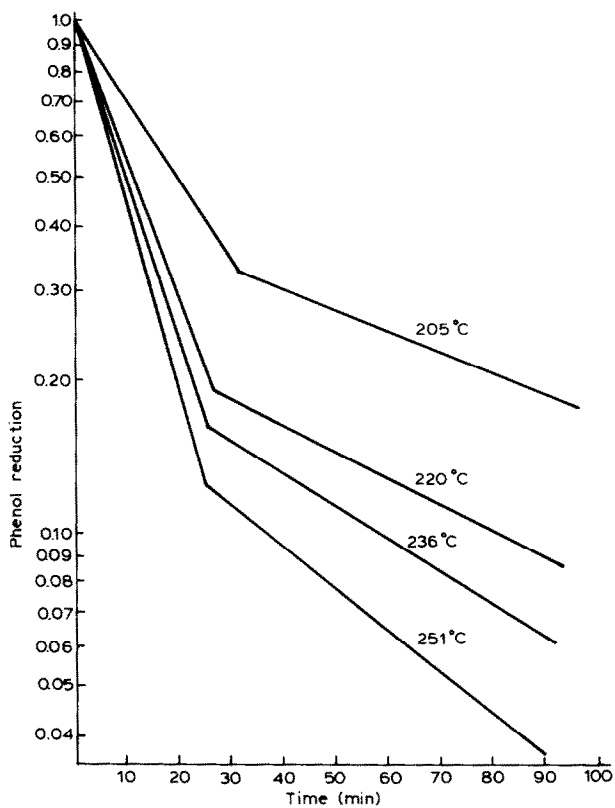

Fig. 5. Semi-log plots of phenol reduction for various temperatures.

TABLE 2

First-order reaction rate constants for wet air oxidation studies

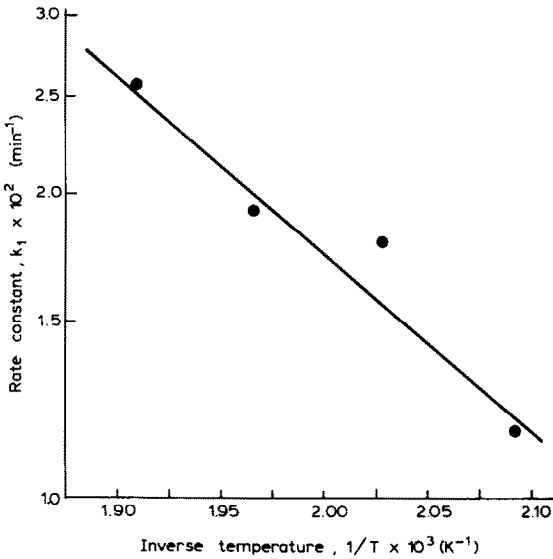|	Temperature (°C)	k_1 (min)	k_2 (min)
COD	205	0.0117	0.0025
	220	0.0180	0.0030
	236	0.0193	0.0032
	251	0.0256	0.0055
Phenol	205	0.0355	0.0099
	220	0.0613	0.0120
	236	0.0693	0.0145
	251	0.0824	0.0184

Fig. 6. Arrhenius plot for COD reduction.

[12] reported an acitivation energy of 17 kcal/mol for wet oxidation of glucose. The lower values obtained in these studies could be due to the formation of large quantities of intermediate complexes that hindered the reaction or poor mixing conditions which limited oxygen diffusion.
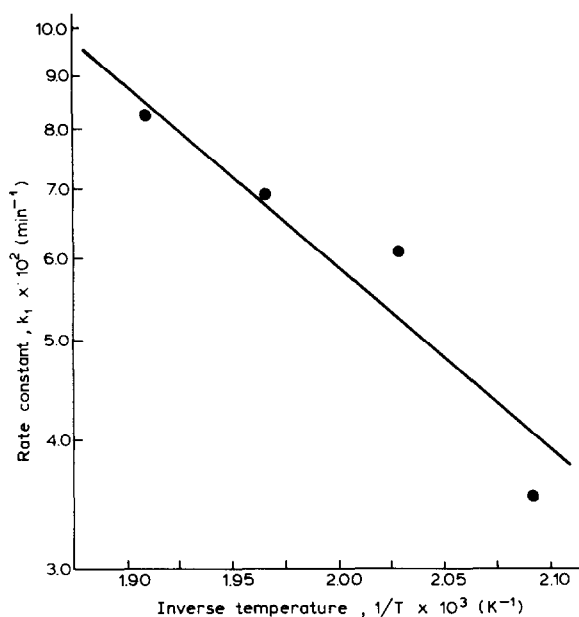
Fig. 7. Arrhenius plot for phenol reduction.

Conclusion

The reaction rate was found to increase as both the temperature and residence time were increased, although the residence time did not have as large an effect as temperature.

The experimental data were found to fit a model consisting of two first-order reactions in series. Maximum COD and phenol reduction were 60% and 95%, respectively, both at 251°C and 90 minute residence time.

The activation energies for COD and phenol reduction were both found to be 8.0 kcal/mol, suggesting a common rate-limiting step.

Acknowledgements

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