Calcium Carbonate Catalysis of Alcohol Oxidation in Near-Critical Water

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The near-critical water oxidations (NCWO) of phenol, methanol, ethanol, n-propanol and n-butanol were evaluated at temperatures between 200 and 374°C and pressures between 2 and 220 bar. Reactions were conducted in packed-bed flow reactors with ZrO_2 and $CaCO_3$ packings with a stoichiometric amount of HOOH. The effectiveness of $CaCO_3$ as an oxidation catalyst increased markedly between 200 and 374°C enhancing oxidation rates $> 100\times$ at 374°C for phenol. Hydrolysis was observed for phenol, ethanol, and methanol over $CaCO_3$ at 374°C and was largely nondetectable in the absence of $CaCO_3$. Despite being inexpensive and environmentally benign, $CaCO_3$ exhibited catalytic abilities equal to or better than many of the best published performance of NCWO catalysts containing noble or transition metals.

Introduction

As an alternative to incineration, low-temperature oxidation processes provide more-compact and less-energy-intensive methods for destroying organic wastes. Low-temperature oxidation processes are particularly attractive for wastewater where the net sensible heat and latent heat intake of water can be reduced or eliminated by wet-air oxidation, near-critical water oxidation, and supercritical water oxidation. Mishra et al. (1995) report low-temperature water-phase oxidation processes to be self-sustaining when the wastewater has a chemical oxygen demand (COD) of at least 20,000 mg/L, while incineration requires a COD of at least 30,000 mg/L.

This article summarizes the near-critical water oxidation of methanol, ethanol, *n*-propanol, *n*-butanol, and phenol using hydrogen peroxide. Emphasis is placed on evaluating the catalytic abilities of calcium carbonate ($CaCO_3$), which was identified as a potentially environmentally benign catalyst toward these oxidations. In near-critical water, $CaCO_3$ is an inexpensive heterogeneous catalyst that poses little if any environmental risk.

Background

Wet-air oxidation, near-critical water oxidation (NCWO), and supercritical water oxidation (SCWO) are nonmicrobial waste oxidation alternatives primarily defined by their oxidation temperatures relative to the critical temperature of water (374°C). Wet-air oxidation requires the lowest energy input due to lower oxidation temperature (<320°C). NCWO processes (300 to 400°C) operate near the critical point of water, while SCWO processes operate above the critical point of water (>370°C).

Water oxidation technologies have great potential for providing organic-waste-destruction technologies that are compact, inexpensive, and of low environmental impact. The inherent advantages embedded in this technology include:

1. Water can rapidly neutralize several hazardous chemicals prior to destruction.
2. Oxidation rates are increased by the presence of water.
3. Strict regulations on incinerators do not apply to the SCWO process.
4. Ninety-nine and one-half percent of nonhazardous wastes and 99.7% of hazardous wastes are in the form of wastewater.
5. For SCWO the decomposition is fast, since there is minimal transport resistance at and near critical conditions.

Unlike most industrial processes where catalysts are used to promote selectivity, for water oxidation processes, the primary purpose of catalysts is to reduce reactor size. Most substrates will oxidize completely to carbon dioxide and water if given sufficient time to react, albeit some dimers and intermediates may have half-lives orders of magnitudes greater than the original substrate.

At higher-temperature supercritical conditions homogeneous rate constants can be quite high; advantages gained by

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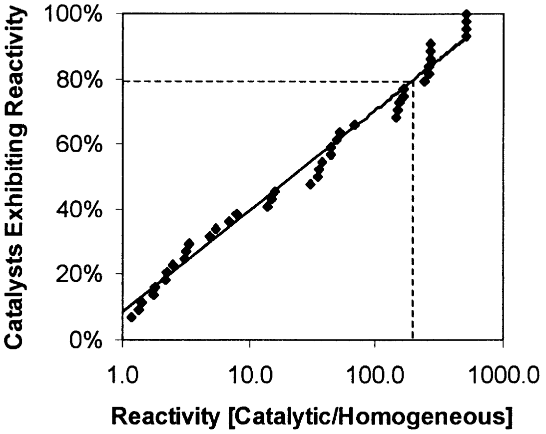

Figure 1. Distribution of observed catalytic activities (relative to noncatalytic reaction) for oxidation catalysts in supercritical water at temperatures between 390 and 450°C.

further reducing already-small reactor volumes are often minimal. However, at near-critical and subcritical conditions large reactor volumes can dominate equipment cost and catalysts may improve process viability.

The combination of effective catalysts and recuperative heating provide an essentially boundless opportunity for water oxidation processes to expand into areas currently dominated by incineration or biological treatment options. Today, most applications of wet-air oxidation are for process wastes prior to biological treatment.

Typical catalysts evaluated in SCWO include V_2O_5, MnO_2, Cr_2O_3, Inconel beads, $ZnCl_2$, CuO/ZnO, TiO_2, MnO_2, and $KmnO_4$ (Yu and Savage, 2000; Ding et al., 1995; Yang and Eckert, 1988; Jin et al., 1990, 1992; Webley et al., 1991; Li and Houser, 1992; Krajnc and Levec, 1994; Chang et al., 1993; Frisch, 1992, Frisch et al., 1994). Supports used for water oxidation include titanium oxide, zirconium oxide, hafnium oxide, magnesium aluminum oxide, y-aluminum, α-aluminum, vanadium pentoxide, nickel oxide, zinc oxide, copper oxide, cobalt oxide (Gloyna and Li, 1995; Krajnc and Levec, 1997). As is typical in catalysis, most efforts are on applications of noble and transition metals and their oxides. More recently, Ross et al. (2000) inferred that calcium carbonate is catalytic toward the oxidation of wastes, but no data were presented.

Ding et al. (1996) reviewed catalytic SCWO summarizing most of the catalysts just cited. Of particular interest is Ding et al.'s summary of rate constants for noncatalytic heterogeneous catalytic oxidation at similar conditions. Figure 1 summarizes the ratio of reactivities in the presence of catalyst to noncatalytic reactivities. Only about 20% of these catalysts increased reactivities greater than 200-fold at temperatures ranging from 380°C to 450°C, with most of the greater catalytic impacts at temperatures > 410°C.

Many of the catalysts in Figure 1 would provide reasonable reductions in reactor volumes; however, additional costs and operational constraints could also be incurred, including:

1. High catalyst costs
2. Increased costs of a catalytic reactor vs. a homogeneous reactor of similar volume
3. Downtime and operational costs associated with changing catalysts
4. Potential release of toxic metals due to corrosion or leaching of the noble and transition metals of the catalysts.

Depending on the nature of the catalyst, considerable increases in reactivity would have to be realized to overcome these problems. Due to the combination of these problems and the limited availability of catalysts that provide significant increases in oxidation rates, the use of catalysts in SCWO is not a common practice.

The substrates of Figure 1 include acetic acid, pyridine, chlorophenol derivatives, benzene, phenol, 2-*n*-propanol, and several other compounds. Overlap of the present study and the summary of Ding et al. (1996) includes investigation of phenol and 2-propanol substrates; 1-*n*-propanol was evaluated in the present study.

Phenol was evaluated by Ding et al. (1995). The catalytic activity with Cr_2O_3 catalyst was observed to be lower than the homogeneous reaction. A 1.5X increase in reactivity was observed with MnO_2/CeO_2 catalyst, and a 5X increase in reactivity was observed with V_2O_5 catalyst. Krajnc and Levec (1994) also evaluated the phenol oxidation with an 8X increase in reactivity using a CuO/ZnO catalyst. More recently, Krajnc and Levec (1997) obtained 100X increases in reactivity (with phenol) using a mixture of CuO, ZnO, and CoO on porous cement at 400°C.

For the total oxidation of phenol to carbon dioxide and water, Imamura et al. (1988, 1986) reported a Ru/Ce catalyst to have an activity similar to homogeneous $Cu(NO_3)_2$ (Japanese Patent 75106862) at 200°C with 1-MPa partial pressure of O_2. The homogeneous $Cu(NO_3)_2$ had reactivities 1.6X to 10X as compared to homogeneous reactions when oxidizing acetic acid, *n*-butylamine, PEG, pyridine, and ammonia—a comparison to the homogeneous oxidation of phenol was not provided. An extrapolation of these data suggests that Ru/Ce is 10X more effective than the homogeneous noncatalytic oxidation of phenol at 200°C.

More recently, Krajnc et al. (1997) and Thornton et al. (1990a,b) evaluated transition metal catalysts. A combination of supported copper, zinc, and cobalt oxide were used by Krajnc et al., which resulted in a decrease in residence time by two orders of magnitude for over 90% conversion at supercritical conditions. The overall reaction rate was shown to be well described by Langmuir-Hinshelwood kinetic formulation, which accounted for both phenol and dissociative oxygen adsorption as well as the surface process that controls the overall reaction rate. HOOH was used as the oxidant. One interesting feature of this catalyst was the high selectivity for end product CO_2 and H_2O. Considerably fewer intermediate products were observed as compared to noncatalytic reaction at the same reactor conditions.

Gloyna and Li (1993) evaluated the oxidation of both methanol and *n*-propanol with O_2. At supercritical conditions, oxidation rates were generally first order in the substrate concentrations. Dietrich et al. (1985) evaluated the oxidation of 2-*n*-propanol and ethanol at 280°C. Krajnc and Levec (1994) also evaluated 2-*n*-propanol where the reactivity increased from 0.0 s^{-1} to 3.0 s^{-1}, which is interpreted as a > 60X increase in reactivity. Taylor and Weygandt (1974) evaluated 1-*n*-butanol oxidation at temperatures between 160 and 200°C.

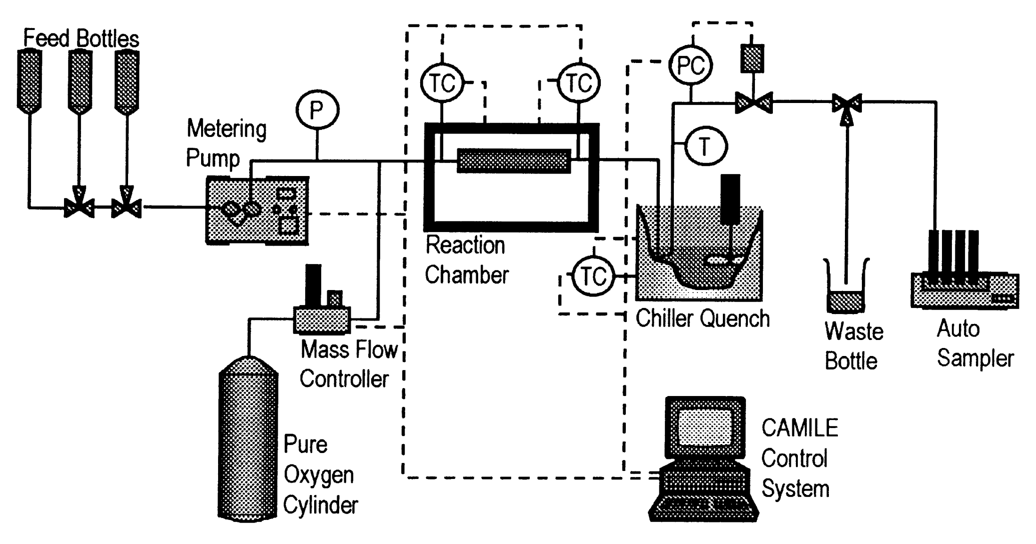

Figure 2. Packed-bed reactor system.

Other catalytic studies evaluated popular oxidation catalysts on similar molecular structures. Yang and Eckert (1988) used copper and magnesium as catalysts for supercritical and subcritical oxidation of *p*-chlorophenol in water with modest success. Vanadium oxide was used as catalyst for oxidation of 1,4-dichlorobenzene in water with significant improvement in total conversion of the model compound. Platinum on alumina proved to be very effective for chloroform destruction, even at atmospheric pressure between 300 and 400°C (Rossin and Farris, 1993). The catalyst worked for over 72 h of continuous run with little deactivation. Kinetic expressions were developed taking into account the inhibition of reaction rate by the product HCl.

Experimental Procedure

The study of oxidation of alcohol substrates at near-critical conditions was conducted in a packed-bed reactor. The packed-bed reactor was a 6-in. Hastelloy tube with an internal diameter of 1/4 in. located in a crucible furnace with a lid containing a fan to cause convective heating. The tube was normally packed with either an inert material (zirconium oxide) or heterogeneous catalyst (14-20 mesh crushed limestone). The reactor was provided with an inlet and an outlet thermocouple. The temperature of the reactor was controlled by a PID controller through a Camile control system. The whole reactor system is shown in Figure 2, with an expanded view of the furnace and reactor in Figure 3.

The premixed reactant feed solution was stored in inverted PVC bottles (three PVC bottles for three different reactants) and were pumped to the reactor using an HPLC/ELDEX pump. Solenoid valves and a manifold system were used to switch between the PVC feed tanks in either a Camile-automated or interactive mode.

When HOOH was used as an oxidant it was premixed with the aqueous stock solution in the feed tank. When pure oxygen was used it was fed on-line to the aqueous solution after the HPLC pump and prior to the reactor using a Brooks mass-flow controller (Model 5850TR). The reaction products were immediately quenched in a constant-temperature quench pot. A Retriever 500 liquid autosampler from ISCO collected samples at preprogrammed time intervals. The pressure of the reactor system was maintained using a Vexta steeping motor-operated Autoclave micrometering valve within a PID control loop.

The entire system was automated insomuch as 48 h of continuous run can be performed at one stretch. The automated actions were carried out by a sequential function chart (SFC) program in the Camile software. Isothermal conditions of the reactor were maintained by providing coiling of the 1/16-in. tube inside the crucible furnace prior to the reactor. It has been seen that the maximum temperature difference between inlet and outlet temperatures at steady state was approximately 10°C, which was within the acceptable limit, considering the fact that the reactor was operated up to 374°C. The pressure controller with a maximum deviation of 10% from setpoint was satisfactory--no commercial high-pressure

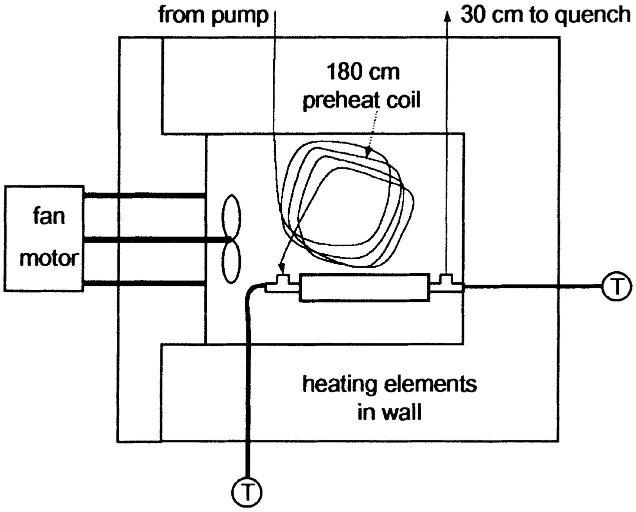

Figure 3. Reactor and furnace.

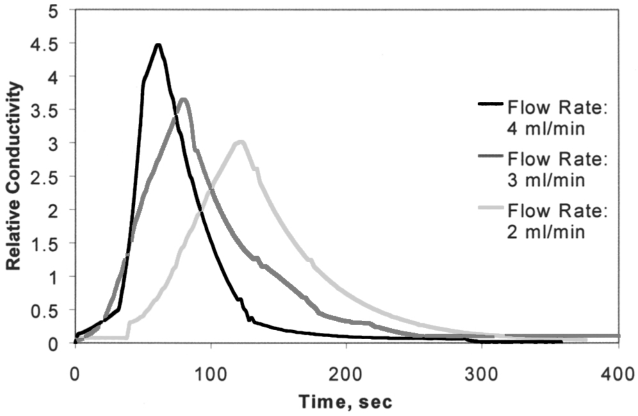

Figure 4. Residence time distributions in packed reactors.

Inert packing was similar to calcium carbonate packing. Higher flow rates lead to shorter average residence times.

controllers are available for liquid flowing at 0.5 mL/min. Samples were collected when the temperature and pressure conditions in the reactor were within 2°C and 10%, respectively, for more than three reactor volumes.

Analysis of the reactor residence time distribution was performed periodically to determine the reactor volume and dispersion characteristics of the reactor. Typically, a 0.01-g/mL solution of NaOH was employed for such analysis. The outlet concentration of NaOH was determined indirectly using an on-line conductivity meter and Camile. The free reactor volume (total volume less packing material) was calculated to be 4.2 mL. Attempts were made to use a volatile traceer compound instead of NaOH solution to characterize vapor-phase reactions/processes; however, these attempts were without success due to very low conductivity of the volatile tracers. Figure 4 shows a typical residence-time curve at three different flow rates.

Each experiment was preceded by a control experiment wherein pure feed without oxidant (typically 1,000 ppm model compound solution) was passed through the reactor at different flow, temperature, and pressure conditions to check for loss of compound due to reaction with dissolved oxygen, decomposition, leaks, and evaporation. To prevent such leakage from occurring, several steps have been taken, including: (1) the quench pot was always maintained between 0 and 15°C; (2) whenever the reactor setup was opened (say, for catalyst changeover), a thorough pressure test was conducted.

Typical packed-bed reaction studies included specification of temperature, pressure (reported in bars of gauge pressure), model compound, packing, and oxidant (or lack thereof) for investigation. Based on specifying these degrees of freedom, the rate constants for the multiple elementary reactions involved in oxidation and hydrolysis/reforming have unique values. In order to evaluate either overall apparent reaction rates or elementary rate constants, conversion vs. reaction time data are needed. Product samples (with Retriever 500 autosampler) were collected at multiple reactant influent feed rates as specified by the Camile-controlled metering pump feeding the premixed reactant feed.

After generating the concentration vs. flow-rate data, reaction orders and rate constants were evaluated by a least-squares method (in some instance, a relatively constant reaction order was observed and held as a constant, only optimizing the rate constants). Based on these least-squares values, half-lives were calculated and reported as a consistent basis for comparing reaction rates.

Stainless steel (ss) tubing for the experimental system was manufactured by Alltech (Cat#3005) with 0.01 in. ID, 1/16 in. OD. Glass-lined tubing was used as a control and was purchased from Restek (Cat#20592). The glass-lined tubing was deactivated fused-silica-lined SS tubing with a maximum temperature range of 400°C, minimum bend radius of 2 in. and incompatibility with acids having a 0.01 in. ID and 1/16 in. OD.

Zirconium oxide (ZrO_2) was obtained from TAM Ceramics Inc. (item ZIROX CS, $-6+20$ mesh, product number 51722) of Niagara Falls, NY. Approximate $-16+20$ mesh $CaCO_3$ was obtained from Iowa Limestone Company of Des Moines, Iowa.

GC and HPLC analysis of the product samples provided reactant (and in some cases intermediate) concentrations as a function of metering pump setting. Tabulated density data for water (at reaction conditions) were used to convert the metering pump setpoints to reactor residence times.

Methanol, ethanol, *n*-butanol, *n*-propanol, chloroethanol, chloropropane, chloropropane, and a limited number of phenol samples were analyzed by direct aqueous injection using a Hewlett-Packard (HP) 6890 GC equipped with an HP 7683 injector and a flame ionization detector. A Restek stabiliwax-DA (30 m, 0.53 mm ID, 1.0-μm film thickness) column was used for the analysis. Standard curves of at least 4 points were used for linearity, and a midrange standard was analyzed periodically. Percent deviations of the repeated standards were $<5\%$. Injection amounts were 1 μL for phenol and 2 μL for the other compounds. The split/splitless injection chamber was set at a 2.5 split and 210°C for Phenol and 160°C for the other compounds. Oven temperatures for phenol were initially at 80°C for 1 min, then ramped at 15 degree/min to 160°C and held for 2 min, then ramped at 30 deg/min to a 210°C and held for 4 min. Oven temperatures for methanol, ethanol, *n*-butanol, and *n*-propanol were initially 40°C for 1 min, then ramped at 20°C/min to 180°C. With the helium carrier gas flowing at 5.4 mL/min, typical retention times were 3.57, 3.83, 4.46, 4.58, and 11.58 for methanol, ethanol, *n*-butanol, *n*-propanol, and phenol respectively.

Samples evaluated in both the GC and HPLC were analyzed directly as aqueous samples and without removal of soluble ions.

Phenol compositions were analyzed primarily in a Hewlett-Packard 1100 series isocratic HPLC. A mobile phase made up of 40:60 ratio of acetonitrile–water at a flow rate of 1.0 mL/min and a Syncropak RPP column (250×4.6 mm ID) from Micra Scientific Inc. were used for this purpose. The wavelength of the variable-wavelength detector was kept at 254 nm for best resolution. Typical residence time for the phenol peak was 3.2 min. Concentrations down to 5 ppm with a maximum standard deviation of 2% were detectable with this setting.

Any remaining nonvalatile organic material was analyzed using a Dormann Carbon Analyzer for material balance purpose. The sample was first acidified to pH 4 using *o*-phosphoric acid to drive out any inorganic carbon. The samples were then refrigerated and purged with nitrogen before carrying out TOC analysis. The catalyst for this purpose was prepared by dissolving 60 gm of $K_2S_2O_8$ and 4 mL of H_3PO_4 in 2 L of distilled water. An IR-I detector detected the reacted CO_2 from the analyzer.

All the organic compounds used as model compounds were purchased from Aldrich. Loose crystals of phenol with 99.99% purity were used. All other chemicals were HPLC grade with 99.5%+ purity. Twenty-nine percent HOOH from Fischer scientific with a maximum impurity of 0.01% sulfate was used as oxidant. All samples, substrate mixtures, and standards were stored in a refrigerator at 4°C when not in use.

Results

Based on preliminary liquid-phase studies, $CaCO_3$ was chosen for further investigation as a fixed-bed oxidation catalyst. Calcium carbonate was selected since (1) initial phenol and methanol reactions showed $CaCO_3$ to have good catalytic activity; (2) $CaCO_3$ is one of the most prevalent compounds found in nature, thus being considered benign, safe to handle, and easy to dispose; and (3) $CaCO_3$ has extremely low solubility in water (~ 15 ppm in cold water, ~ 20 ppm in hot water and $\ll 20$ ppm in water phases having densities < 0.5 g/mL).

Most packed-bed reactions were conducted with phenol, methanol, and ethanol substrates. Two controls were commonly used. Zirconium oxide (assumed to be inert) packing was used as a packed-bed control intended to provide similar reactor dynamics without catalytic activity. In addition, control reactions were conducted without the HOOH oxidant to determine if the reactions were true oxidation or, alternatively, hydrolysis or reforming. Additional reactions were also conducted in a glass-lined reactor for comparison to both the zirconium oxide packing and the steel surface of the reactor and tubing.

Figure 5 compares the phenol oxidation results at 300 and 374°C and 2 bar in the presence and absence of $CaCO_3$ packing in a reactor of volume 4.2 mL. Unless otherwise indicated, a 1× stoichiometric amount of HOOH was used as the oxidant. Clearly $CaCO_3$ has significant impact on the reaction rate at higher temperature. For example, at 374°C, > 99.5% conversion of phenol was observed at all flow rates. Similar results were found for methanol, ethanol, *n*-propanol, and *n*-butanol as well. Table 1 summarizes the half-lives of methanol, ethanol, *n*-propanol, *n*-butanol, and phenol at 300°C and at 100-bar pressure.

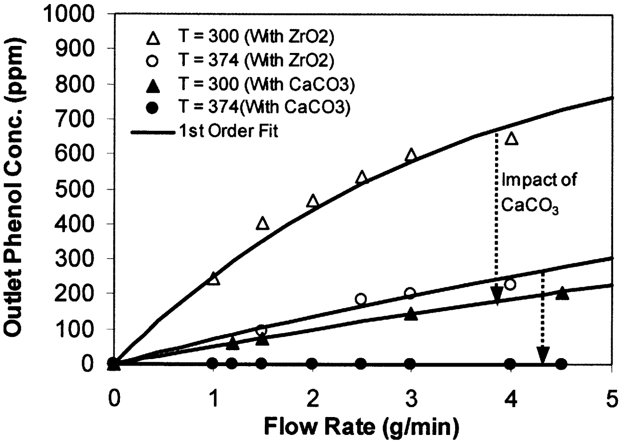

Figure 5. Effect of $CaCO_3$ on phenol oxidation in a flow reactor.

Table 1. Half-Lives (in Seconds) of Different Model Compounds in the Presence and Absence of $CaCO_3$ in a Packed-Bed Reactor at 300°C

Alcohols	With $CaCO_3$	Without $CaCO_3$	With $CaCO_3$	Without $CaCO_3$
Half-lives(s)	100 bar		2 bar	
Methanol	190	480	0.63	> 1.66
Ethanol	162	285	0.31	> 1.75
Propanol*	< 1	30	0.08	0.13
Butanol*	< 1	22	0.08	0.14
Phenol	18	35	0.04	0.10
Order of reaction				
Methanol	1.0	0	1.24	0
Ethanol	0.75	2.0	0.5	0
Propanol		1.1	~ 0.5	~ 0.5
Butanol		1.0	~ 0.5	~ 0.5
Phenol	0.9	1.0	~ 0.5	~ 0.5

*Rate too fast to evaluate, estimate at < 0.56 s.

As indicated by Table 1, for phenol, methanol, and ethanol, the half-lives decrease by approximately 50% when $CaCO_3$ was used as catalyst in liquid water at 300°C, but for *n*-propanol and *n*-butanol, the decrease is over two orders of magnitude. As discussed later, the catalytic activity of $CaCO_3$ is a a strong function of temperature.

Phenol, ethanol, and methanol were evaluated over temperatures and pressures covering gas, liquid, and near-critical fluid phases to evaluate the activity of $CaCO_3$ Tables 2 through 5 summarize the reactivities. The conversion vs. time data for these reactions are available elsewhere (Roy, 2000).

Table 2. Ethanol Oxidation over Inert Packing and $CaCO_3$ Packing at Different Temperatures and Pressures in Packed-Bed Reactor

T (°C)	Pressure (bar) 2	100	220
Inert packing		Half Lives (s)	
300	> 1.75	285	135
350	> 0.92	8.9	55
374	> 0.60	7.3	29
		Reaction Order	
300	0	2.00	0.35
350	0	1.24	0.98
374	0	1.15	1.66
Calcium carbonate packing		Half Lives (s)	
300	0.31	162	98
350	0.21	5.2	30
374	0.18	3.4	9.2
		Reaction Order	
300	0.5	0.75	1.41
350	0.5	1.74	1.01
374	0.5	1.90	1.53

Table 3. Phenol Oxidation over Inert Packing and $CaCO_3$ Packing at Different Temperatures and Pressures in a Flow Reactor

Phenol−Oxidation Over Inert Packing

T (°C)	Pressure (bar) 2	50	100	200
	Half Lives (s)			
200	—	—	—	—
250	0.15	—	38	—
300	0.10	—	35	—
374	0.04	—	1.71	7.5
	Reaction Order			
200	—	—	—	—
250	0.53	—	1.02	—
300	0.52	—	1.01	—
374	0.43	—	0.72	0.91

Phenol−Oxidation Over Calcium Carbonate

T (°C)	Pressure (bar) 2	50	100	200
	Half Lives (s)			
200	0.08	—	37	—
250	0.06	—	24	—
300	0.04	—	18	—
374	< 0.002	< 0.05	< 0.10	< 0.61
	Reaction Order			
200	0.34	—	1.02	—
250	0.47	—	0.95	—
300	0.44	—	0.94	—
374	—	—	—	—

Phenol−Reforming

T (°C)	Pressure (bar) Inert Packing 2	Inert Packing 220	Calcium Carbonate 2	Calcium Carbonate 100
	Half Lives (s)			
374	> 5.0	> 7,000	1.6	2,300
	Reaction Order			
374	—	—	0.80	1.37

Table 4. High-Pressure Flow Reactor Studies for Methanol Oxidation

T (°C)	Pressure (bar) 2	100	220
Inert packing			
	Half Lives Evaluated as 0 Order (s)		
300	> 1.66	480	480
350	> 1.42	25	310
374	> 1.02	17	190
Calcium carbonate packing			
	Half Lives (s)		
300	0.63	190	183.7
350	0.39	13	114.5
374	0.30	9	44.5
	Reaction Order		
300	1.24	0.99	0.66
350	1.07	0.80	1.03
374	0.92	0.74	0.90

At low pressures (2 bar), the density of water is more than two orders of magnitude lower than that of liquid water. This was reflected on the calculation of half-lives in gas, liquid, and supercritical phase. The half-lives of gas-phase reactions are considerably lower than in liquid phases even though the conversion increased with increases in pressure at the same temperature (and constant reactor volume).

Tables 2 through 5 include oxidation rates as well as hydrolysis rates (without HOOH). For ethanol oxidation, the half-life at 200°C decreased by about 20% when the packing was changed from inert (ZrO_2) to $CaCO_3$. At 374°C and 100 bar, the half-life decreased by more than two orders of magnitude. The catalytic effect of $CaCO_3$ increased with increasing temperature resulting in half-lives considerably less than one second. The ethanol and phenol substrate reaction orders changed from ~ 0.5 to ~ 1.0 when the fluid changed from gas phase to liquid phase, suggesting a shift in reaction mechanism.

The rather chaotic changes in the least-squares reaction order of methanol can be explained by a reaction mechanism that is more autocatalytic than ethanol or phenol (at least in regard to partial oxidations of these substrates); such an autocatalytic mechanism was reported by Dagaut et al. (1996). If an autocatalytic mechanism is followed, the least-squares order of reaction has little meaning; however, the half-lives retain value as characterizing the oxidation of the methanol.

No significant hydrolysis/reforming was observed for ethanol in the presence of inert packing, but some conversion did take place when the inert packing was replaced with $CaCO_3$ packing. The half-life for inert hydrolysis/reforming at supercritical condition was more than 200 s, whereas it was approximately 6 s at 374°C and 100 bar in the presence of $CaCO_3$. The calcium carbonate increased hydrolysis/reforming rates by at least an order of magnitude, with higher pressures leading to longer half-lives. Hydrolysis half-lives were $> 2\times$ more than oxidation rates over $CaCO_3$, and so oxidation dominated the reaction rates when HOOH was present.

Table 5. High-Pressure Flow Reactor Studies for Methanol Reforming

T (°C)	Pressure (bar) 2	50	100	220
Inert packing				
	Half Lives Evaluated as 0 Order (s)			
300	> 1.9	> 39	> 1030	> 1120
350	> 1.5	> 28	> 51	> 850
374	> 1.3	> 24	> 44	> 530
425	> 0.73	> 12	> 24	> 98
Calcium carbonate packing				
	Half Lives (s)			
300	0.86	8.9	285	304
350	0.44	6.3	14	246
374	0.25	4.3	9.8	79
425	0.09	2.5	4.9	11.7
	Reaction Order			
300	0	0	0.00	0.59
350	0	0	0.43	0.94
374	0	0	0.38	1.58
425	0	0	0.27	0.70

Table 6. Gas Chromatography and TOC Analysis for Phenol Conversion in Packed-Bed Reactor at High Conversions

Phenol–Oxidation at 1× HOOH, 300°C, and 100 bar				
Flow Rate (mL/min)	Concentration (ppm)			
	Packing	Phenol	TOC	Intermediates
1	ZrO_2	87	176	89
4.5	ZrO_2	257	386	129
1	$CaCO_3$	53	110	57
4.5	$CaCO_3$	171	293	122

$CaCO_3$ also showed similar catalytic activity for phenol oxidation. For example, at 250°C and 100 bar, the half-life decreased by $\sim 40\%$ when the reactor packing was changed from inert to $CaCO_3$. With increasing temperature, the catalytic activity increased, and at 374°C and 100 bar the increase was > 17X. Unlike ethanol, for phenol no significant conversion was noticed in the reforming reaction either in the presence of ZrO_2 or $CaCO_3$ where the half-life was ~ 1 h.

Although some of the samples showed nearly complete substrate conversion, a number of intermediates were detected while performing the GC analysis, most notably acetaldehyde (analyses were not tuned to detect organic acids). To estimate the extent of oxidation plug-flow studies were repeated with TOC analysis of oxidation products. Tables 6 and 7 summarize conversion data with TOC analysis.

According to Table 6 (300°C data), at $\sim 95\%$ conversion the TOC tends to be dominated by phenol with the intermediates being present at about the same total concentration as phenol. The TOC values of Table 6 are lower than those reported by Gopalan and Savage (1995)—this is likely due to the improved oxidation ability of HOOH as compared to diatomic oxygen.

Savage et al. (Thornton and Savage, 1990a,b; Gopalan and Savage, 1995) performed a more detailed study on the types of intermediates formed during phenol oxidation. More than 13 different intermediates were identified during the oxidation process, which included dimers like 4-phenoxy phenol, 2-phenoxy-phenol, dibenzofuran, and 2,2-biphenol as well as mono- and di-carboxylic acid and carbon monoxide. According to Gopalan and Savage (1995), as much as 50% of the phenol could transform to dimers before degrading to lower molecular products at high residence time. Oxidation seemed to be more complete using HOOH and especially with $CaCO_3$ catalysis.

Table 7. Gas Chromatography and TOC Analysis for Ethanol and Ethanol Conversion in Packed-Bed Reactor at High Conversions

Ethanol–Oxidation at 1× HOOH, 300°C and 100 bar					
Flow Rate (mL/min)	Concentration (ppm)				
	Packing	Ethanol	TOC	Acetaldehyde	Other
1	ZrO_2	137	256	91	28
4.5	ZrO_2	378	576	78	120
1	$CaCO_3$	81	197	59	57
4.5	$CaCO_3$	157	253	45	51

Table 8. Conversion of Ethanol Over Zirconium Oxide Packing with 3× Stoichiometry at Diatomic Oxygen

	$T = 300°C$		$T = 374°C$	
RT	$P = 2$ bar	$P = 100$ bar	$P = 2$ bar	$P = 100$ bar
1.00	786	892	715	755
1.50	805	912	751	800
2.00	821	939	779	832
3.00	864	953	816	908
4.50	901	965	859	939
Init.	1,000	1,000	1,000	1,000

During ethanol oxidation at 300°C, the nonethanol TOC was present at about the same concentration as ethanol at $\sim 90\%$ conversion. The predominant intermediate was acetaldehyde.

The low byproduct TOC values are encouraged, since refractory byproducts could be formed that would persist at levels much higher than phenol or ethanol; these data indicate that these refractory byproducts are not being formed in high concentrations. However, more data are needed, since the byproduct TOC values likely represent several byproducts, some of which may be refractory in nature. The nonreactive nature of these refractory byproducts would only be detectable at higher conversions.

A few studies were performed on the oxidation of phenol and ethanol with diatomic oxygen. These reactions were conducted in the packed-bed reactor with compressed oxygen flow controlled by a mass flowmeter. The oxygen was mixed with the aqueous feed prior to the reactor. For these studies the maximum oxygen pressure was restricted to < 200 bar by the oxygen pressure in the feed tank. Three times stoichiometric oxygen was used. Tables 8 and 9 summarize these oxidation studies for ethanol over ZrO_2 and phenol over $CaCO_3$.

Oxidation rates using diatomic oxygen were substantially less than those with HOOH; however, conversion was detected even at the lower temperatures. Unlike trends exhibited by HOOH-driven oxidation, for diatomic oxygen-driven oxidation the increasing pressures resulted in lower conversions at the same reactor volume. As indicated by the data, these performance trends were consistently observed. Possible explanations for the changing impact of pressure on reactivity include (1) possible side reactions leading to the de-

Table 9. Conversion of Phenol Over Calcium Carbonate Packing with 3× Stoichiometry of Diatomic Oxygen

Flow Rate (g/min)	$T = 200°C$		$T = 250°C$	
	$P = 2$ bar	$P = 100$ bar	$P = 2$ bar	$P = 100$ bar
1	786	892	618	773
1.5	791	912	673	818
3	830	963	760	927
4.5	900	1022	863	889
Init.	1000	1000	1000	1000
Flow Rate (g/min)	$T = 300°C$		$T = 374°C$	
	$P = 2$ bar	$P = 100$ bar	$P = 2$ bar	$P = 100$ bar
1	545	673	450	580
1.5	609	700		768
3	709	691	580	690
4.5	851		688	800
Init.	1000	1000	1000	1000

struction of HOOH (formation of O_2) in the gas phase, and (2) increased solubilities of oxygen in gas phase as compared to liquid phases.

To determine if the reactor surface had catalytic properties, reaction profiles in SS tubing were compared to reaction profiles in a deactivated fused silica-lined SS tubing, both 12 feet in length and having 0.01 in. ID (0.18 mL). The reactions were conducted at 300°C and 100 bar. One stoichiometric amount of HOOH was used as oxidant. The reaction profiles were quite similar with zirconium oxide system exhibiting about 15% greater conversion. Except for the silica lining, the tubing reactors had essentially identical configurations. These results indicate that zirconium oxide is not catalytic toward this reaction as compared to glass-lined tubes at liquid-like densities.

Discussion

At temperatures $> 200°C$ over a range of pressures, $CaCO_3$ showed increasing catalytic activity with increasing temperatures for methanol, ethanol, *n*-propanol, and *n*-butanol oxidation—it served as a heterogeneous catalyst. For ethanol, the half-lives decreased by 20% at 200°C in liquid phase to $> 50\%$ at supercritical conditions. For phenol, the decrease in half-lives was from 35% at 250°C in liquid phase to more than two orders of magnitude (estimate, reaction too fast to measure) at supercritical conditions. The impact of $CaCO_3$ on the reactions in gas phase (2 bar) were mainly observed at the supercritical condition; at $< 300°C$ some data suggested that $CaCO_3$ actually inhibited reaction, while at 374°C reaction rates increased by more than two orders of magnitude.

Reaction rates were much greater in the gas phase (2 bar) as compared to liquid phases at the same temperature. On a more practical basis, however, the densities and respective contact times in the gas phase are a few orders of magnitude lower than in the liquid phase. Due to these density differences, higher conversions were typically achieved for liquid phases at similar reaction volumes.

From the perspective of minimizing reactor volumes, liquid-phase reactions are preferred to gas-phase reactions when using HOOH as the oxidant. For gas-phase reactions, the limited data indicated that gas-phase reactions achieved higher conversions at the same reactor volumes, indicating that gas-phase reactions had considerably higher reaction rates.

Methanol displayed the most resistance to oxidation, and the ease of oxidation increased with increasing molecular weight. Phenol had both the greatest reactivity and greatest selectivity to organic intermediate formation alternative to complete oxidation to carbon dioxide and water. However, the formation of stable intermediates at temperatures $>$ 250°C over $CaCO_3$ was considerably less than previously reported.

Based on data of Thornton and Savage (1992), the half-life for phenol oxidation at 380°C, 278 bar, and $8\times$ stoichiometric oxygen is 15 s. This combined with their reported Arrhenius energy of activation (12.4 kcal/mol) allows a direct comparison of the data of this study (Table 3) as presented by Figure 6. Based on this comparison, the improved ability of HOOH over O_2 as an oxidant is obvious. Also, the catalytic ability of $CaCO_3$ is particularly exemplified with significant increases in oxidation rates at the critical point. The fact the data are at different pressures and that the 374°C data over $CaCO_3$ are the maximum value (essentially complete conversion only allowed reporting of a range of half-lives instead of a value) complicates interpretation; however, $> 100\times$ decreases in half-lives are apparent.

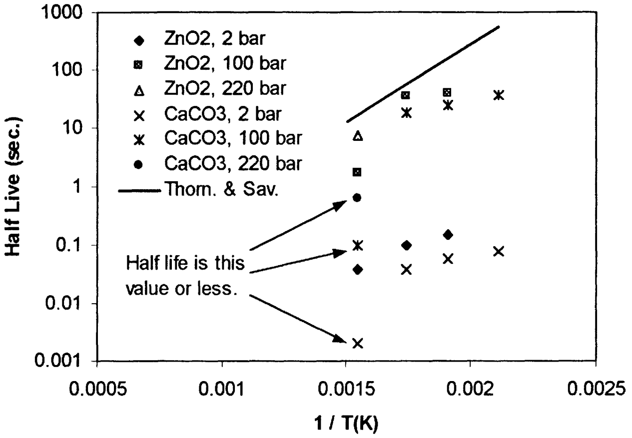

Figure 6. Comparison of reaction half-lives to Thornton and Savage (1992).

Dietrich et al. (1985) reported data indicating a half-life for methanol and ethanol at 280°C to be 2,900 and 770 s. This is substantially larger than the methanol half-lives reported in Tables 3 and 4 (300°C) that range from about 0.6 to about 184 s. for methanol and 0.3 to about 98 s for ethanol. Both HOOH oxidation and $CaCO_3$ catalysis reduce oxidation half-lives. In general, the data of Dietrich et al. corroborated current findings that oxidation rates increase with increasing chain lengths of alcohols.

In general, previously reported data on oxidation of these substrates substantiates that HOOH promotes oxidation better than O_2, and the $CaCO_3$ catalyzed oxidation with HOOH offers a substantial increase in reactivity and decrease in half-lives.

Conclusions

The most significant findings of this research from the practical perspective were the utility of $CaCO_3$ to improve wastewater oxidation process and the utility of $CaCO_3$ for hydrolyzing/reforming organic compounds. Furthermore, at temperatures $> 350°C$, $CaCO_3$ enhances oxidation rates equal to or better than the best reported performance of catalysts based on noble and transition metals. This performance is achieved without toxicity concerns related to catalyst leaching, corrosion, or erosion, and for applications with low pH or halogenated hydrocarbons the calcium can buffer the pH and convert halogens to benign salts; during these latter interactions the calcium will be consumed.

In the absence of HOOH, conversion of alcohols was promoted by $CaCO_3$ at the critical point of water. No attempts were made to determine if conversion was due to hydrolysis/reforming or reforming. The hydrolysis/reforming rates were less than oxidation rates for phenol and ethanol, and so hydrolysis/reforming reactions were not the predominant driving force for alcohol destruction in the presence of HOOH. However, the rate of methanol disappearance was similar for methanol hydrolysis/reforming and oxidation reactions, and so, hydrolysis/reforming (water–gas shift) was a major driving force during methanol oxidation. This explains the different reaction orders of the methanol reactions.

Hydrogen peroxide is a better oxidant than diatomic oxygen; therefore, the transformation of HOOH to diatomic oxygen is not considered to be a mechanism through which HOOH affects oxidation. Wall intiation of the reaction due to the SS surface was negligible, as seen from the comparison of data from SS tube reactor and glass-lined SS tube reactor. Acetaldehyde was identified as an important refractory material that formed during the oxidation and reforming of several of the alcohols.

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