Development of the Monolith Froth Reactor for Catalytic Wet Oxidation of CELSS Model Wastes

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Martin Abraham[*]
Department of Chemical Engineering
The University of Toledo
Toledo, OH 43606

John W. Fisher
MS 239-11
NASA – Ames Research Center
Moffett Field, CA 94035

The aqueous phase oxidation of acetic acid, used as a model compound for the treatment of CELSS (Controlled Ecological Life Support System) waste, was carried out in the monolith froth reactor which utilizes two-phase flow in the monolith channels. The catalytic oxidation of acetic acid was carried out over a Pt/Al_2O_3 catalyst, prepared at The University of Tulsa, at temperatures and pressures below the critical point of water. The effect of externally controllable parameters (temperature, liquid flow rate, distributor plate orifice size, pitch, and catalyst distance from the distributor plate) on the rate of acetic acid oxidation was investigated. Results indicate reaction rate increased with increasing temperature and exhibited a maximum with respect to liquid flow rate. The apparent activation energy calculated from reaction rate data was 99.7 kJ/mol. This value is similar to values reported for the oxidation of acetic acid in other systems and is comparable to intrinsic values calculated for oxidation reactions. The kinetic data were modeled using simple power law kinetics.

The effect of "froth" feed system characteristics was also investigated. Results indicate that the reaction rate exhibits a maximum with respect to distributor plate orifice size, pitch, and catalyst distance from the distributor plate. Fundamental results obtained were used to extrapolate where the complete removal of acetic acid would be obtained and for the design and operation of a full scale CELSS treatment system.

Introduction

The need for recycling and recovery of usable materials is very important in a Controlled Ecological Life Support System (CELSS), defined as a life support system that relies heavily on biological subsystems for recycling (Wydeven, et al., 1992). For example, recycled carbon

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[*] Formerly at Department of Chemical Engineering, The University of Tulsa, Tulsa, OK 74104

dioxide, water, and inorganic nutrients can be supplied to a crop growth chamber to grow food in a closed environment. There are also several physical/chemical methods that have been considered for recycling and waste treatment in a CELSS including thermal processes such as incineration, wet air oxidation, and supercritical water oxidation, and nonthermal processes such as electrochemical oxidation and ultraviolet (UV) radiation (Wydeven, Upadhye, and Wignarajah, 1993). One of the most promising and effective methods of waste treatment and recycling is wet air oxidation (Oguchi and Nitta, 1992).

Wet air oxidation (WAO) is defined as the liquid phase oxidation of organic compounds at temperatures (125-320°C) and pressures (0.5-20 MPa) below the critical point of water using a gaseous source of oxygen (Mishra, Mahajani, and Joshi, 1995). The main advantages of wet air oxidation as part of a CELSS are the recovery of useful water and the reduction of solid wastes to a very small weight and volume of sterile, nondegradable ash (Johnson and Wydeven, 1985). Other advantages include the possibility of using carbon dioxide and inorganic matter as plant food and the energy savings associated with not evaporating large quantities of water.

Wet air oxidation is a well-established technique for the treatment of highly organic and toxic wastewater. Researchers have investigated the oxidation of a wide variety of compounds and wastes, including low molecular weight carboxylic acids (formic, acetic, propionic), cyanides, nitriles, and waste streams from municipal sewage sludge, alcohol distillery waste, and effluent streams from pulp and paper mills (Mishra et al, 1995). Pollutant molecules of these various waste streams are oxidized to low molecular weight carboxylic acids, mainly acetic acid, which in turn, are oxidized to carbon dioxide and water if the reaction conditions are severe enough [Imamura et al (1979, 1980a, 1980b, 1981)]. Because of the slow rate of oxidation of acetic acid, it presents a major limitation to the wet air oxidation process. Therefore, the complete oxidation of acetic acid is an important problem.

Because of the slow oxidation rate for acetic acid, the use of both homogeneous and heterogeneous catalysts has become standard practice. Homogeneous catalysts are more effective for the oxidation of acetic acid [Tagashira et al (1975), Goto et al (1977), and Imamura et al (1982c)] but the separation of the catalyst from the effluent provides a major drawback. Therefore, heterogeneous catalysts are the preferred method for acetic acid oxidation.

Previously, three-phase reactions have been carried out in slurry and trickle bed reactors. In these three-phase reactors, gas and liquid are fed into the reactor separately (as is the case with slurry reactor) or flowed cocurrently down through the bed (trickle bed reactor). Although there are several advantages to these reactors (intrinsic rates measured, good temperature control), there are also many disadvantages. The major disadvantages are the costly catalyst recovery steps and the slow gas-liquid mass transfer rates in the case of slurry reactors, while there could be significant channeling of the gas and liquid feeds in the trickle bed reactor.

Satterfield and Ozel (1977) have discussed the potential use of catalysts supported on monoliths for use in three-phase reactors, as an alternative to conventional packed beds. Monoliths consist of uniform, parallel, non-connecting capillary channels that have a honeycomb structure. The channels can have varying geometry, but the most common are square and cylindrical channels. Monolith supports have been studied extensively and are widely used in the field of automotive emission control and the treatment of industrial waste gases. The main advantages of these supports over conventional packed beds are high external surface area to volume ratio, low pressure drop, very low axial dispersion, uniform flow characteristics through the monolith, and excellent mechanical strength.

Recently, a novel monolith froth reactor, utilizing two-phase bubble train flow within the channels of the monolith, was developed at The University of Tulsa. Bubble train flow consists of alternating gas bubbles and liquid slugs within the channels of the monolith. This type of flow is characterized by gas bubbles that have a diameter close to the diameter of the channel and a length that is greater than the diameter of the channel. The two-phase flow is formed as a froth, produced below the monolith, is forced upwards into the monolith channels. Reaction occurs at the catalyst, on the walls of the monolith. Investigators at The University of Tulsa, working with bubble train flow, have generated very thin liquid films (Chellppannair et al., 1993). Therefore, diffusion of reactant and oxygen through the liquid to the catalyst is very rapid and measured rates should be close to intrinsic values.

The primary objective of the current study was to assess the viability of the novel monolith froth reactor for waste treatment and recycling as part of a CELSS. The reactor was operated as a recycle reactor to increase the conversion that could be achieved in the system. The reactor performance was evaluated using the oxidation of acetic acid over a Pt/Al_2O_3 monolith oxidation catalyst prepared at The University of Tulsa. The model reaction was chosen because of its appearance as a by-product in many wet air oxidation processes [Bailloud et al (1982, 1985), Fisher (1971), Foussard et al (1989)] and because it is difficult to oxidize [Imamura et al (1979, 1980a, 1980b, 1981)]. It was felt that if the monolith froth reactor could oxidize acetic acid effectively, then all other organic compounds would be relatively easy to oxidize. Simple power law kinetics were used to assess the performance of the reactor and to explain the results in terms of theory. The effect of several operating parameters (temperature, liquid flow rate, distributor plate orifice diameter, pitch, and catalyst distance from the distributor plate) on the rate of acetic acid oxidation was also investigated. The apparent reaction rate was calculated by measuring the conversion as a function of time-on-stream and was compared to intrinsic rates reported in the literature by activation energies. Concerns from the previous study were also addressed. It was hoped that the information obtained in this study could be used in the design and operation of a full-scale system for the wet air oxidation of CELSS waste.

Experimental Results

All experiments were conducted in the monolith froth reactor that is described elsewhere [Klinghoffer, *et al.*, 1998a, 1998b]. The reactor was operated in semi-batch mode: air was fed through the reactor in a single pass while the liquid was recirculated through the system. All analysis of the products was conducted on a gas chromatograph. The initial concentration of acetic acid was 1000 ppm (v/v) for all experiments.

The complete catalytic oxidation of acetic acid can be described by the following equation:

$$CH_3CO_2H + 2\ O_2 \rightarrow 2\ CO_2 + 2\ H_2O$$

The only reaction product detected from the monolith froth reactor was CO_2. No partial oxidation products of acetic acid (formic and oxalic acid or formaldehyde) were detected in this study. No carbon monoxide was detected during the course of this study, indicating that the catalyst maintained its activity for the duration of the study. These results are consistent with those of previous researchers, who have investigated the oxidation of acetic acid (Levec and Smith, 1976; Imamura et al., 1982). Levec and Smith (1976) used a trickle-bed reactor operating in downflow mode, with a ferric oxide catalyst and observed no gas-phase acetic acid or carbon monoxide or liquid-phase formic acid or formaldehyde.

Imamura et al. (1982a) studied the wet oxidation of acetic acid in a batch reactor, employing several different cobalt-bismuth complex oxide catalysts. Similarly, they found no liquid-phase formic or oxalic acid because of the highly reactive nature of these compounds. Because of unreliability in the measurement of CO_2 in the gas phase, the stoichiometry of the reaction was not examined. They concluded that over 80% of the acetic acid reacted was transformed into carbon dioxide.

The reaction was adequately modeled by second order kinetics, namely $-r_A = k\, C_A^2$, where C_A is the concentration of acetic acid. This is in contrast with previous researchers investigating the oxidation of acetic acid. Levec and Smith (1976), studying the oxidation of acetic acid using a ferric oxide catalyst in a trickle-bed reactor, reported that the reaction was first order in acetic acid concentration. However, the second order fit was used because it gave the best correlation coefficients, based on linear regression, for all rate expressions examined.

Rate constants at each reaction temperature were calculated at conditions of constant gas and liquid flow rates, and are provided in Table 1. Although the oxygen concentration varied in each experiment due to the effect of temperature and pressure on the solubility of oxygen in the liquid, the model assumes the reaction rate was not a function of oxygen concentration. Using normal Arrhenius analysis, the rate constant is related to the temperature through the apparent activation energy. The apparent activation energy calculated from values of the rate constants was 99.7 kJ/mol. This value is comparable to apparent activation energies reported for the oxidation of acetic acid over ferric oxide catalysts in a trickle-bed reactor, 87.9 kJ/mol (Levec

Table 1
Estimated First Order Rate Constants

Temperature (°C)	Liquid Flowrate (cm^3/min)	Distributor	Froth Height (cm)	k (s^{-1})
220	64.47	1 mm x 2 mm	5.9	0.0827 ± 0.0018
220	63.46	1 mm x 4 mm	5.9	0.0393 ± 0.0031
220	63.77	1 mm x 6 mm	5.9	0.0367 ± 0.0031
220	64.45	2 mm x 4 mm	5.9	0.0779 ± 0.0070
220	64.66	3 mm x 4 mm	5.9	0.0483 ± 0.0060
220	65.34	2 mm x 4 mm	4.0	0.1175 ± 0.0108
220	64.73	2 mm x 4 mm	2.4	0.0739 ± 0.0085
200	57.76	Fritted plate	5.9	0.0366 ± 0.0030
220	62.59	Fritted plate	5.9	0.0720 ± 0.0096
220	28.47	Fritted plate	5.9	0.1080 ± 0.0126
220	107.44	Fritted plate	5.9	0.0840 ± 0.0144
240	62.47	Fritted plate	5.9	0.1860 ± 0.0096

and Smith, 1976), and 71.2 kJ/mol for Cu:Mn:lanthanum oxides on Al_2O_3 and ZnO (Levec et al., 1976). The reported apparent activation energy is also consistent with activation energies of intrinsic kinetics for oxidation reactions. This result suggests, as also observed by other researchers (Crynes, 1993) that the observed rate in the monolith froth reactor is close to the intrinsic kinetic rate and is only slightly inhibited by mass transfer.

Scale-up and Design Issues

One of the major goals of any reactor design or reaction rate study is to use the intrinsic reaction rate data obtained at the bench scale in the design and operation of a commercial scale system. This is important because it is not feasible, from a practical as well as economic viewpoint, to build a large-scale unit and test all possible scenarios. Another important concept, especially for waste treatment applications, is the concept of the design limiting compound. The design limiting compound is defined as the compound that is most difficult to destroy (oxidize). The basic idea is that if the system is designed and operated at conditions where the design limiting compound is destroyed, then the system should be able to effectively destroy all other compounds. These two basic ideas were applied in this study.

The current study focused on the viability of wet air oxidation as a treatment method for CELSS wastes. Acetic acid was chosen as the model compound because pollutant molecules of various waste streams (municipal sewage sludge, alcohol distillery waste, and effluent streams from pulp and paper mills) are oxidized to low molecular weight carboxylic acids, and in particular, to acetic acid. Moreover, acetic acid has been found to have a slow rate of oxidation (Mishra et al. 1995). Therefore, the complete oxidation of acetic acid presents a major limitation to the wet air oxidation process.

Many waste treatment applications require very high levels of destruction of the pollutant molecules to such benign species as CO_2 and water. For CELSS waste treatment, a process needs to be able to achieve destruction levels that approach 100% to be a suitable process (Takahashi, Wydeven, and Koo, 1989) because the water has to be reused by living organisms.

Any system deemed suitable for CELSS waste treatment would have to meet or exceed these levels of destruction.

The first step into verifying that the monolith froth reactor is suitable for CELSS waste treatment is to measure reaction rates for the oxidation of acetic acid. The monolith froth rector was operated as a recycle reactor and the data was measured as cumulative conversion as a function of run time. A rate expression, second order in acetic acid concentration, was used to describe the data.

$$-r_A = -\frac{dC_A}{dt} = kC_A^2$$

Using simple linear regression, rate constants, k, were calculated for three different temperatures, 200, 220, and 240°C. The rate constants can be used to calculate the time required to achieve the desired level of conversion in the monolith froth rector.

Using the available data (second order reaction rate constant measured at 240°C), the time required to achieve 99.99% conversion is over 3000 hours. The time to convert 99.99% of acetic acid is extremely long. Therefore, there is a need to increase the reaction rate using available parameters. One obvious way to do this would be to increase the reaction temperature. Since no data were measured above 240°C, the reaction rate constant must be extrapolated using the Arrhenius expression. Unfortunately, this could lead to erroneous results because the true reaction rate might be smaller than the calculated reaction rate if external mass transfer resistance would be important at elevated temperatures. Other reactor parameters would then be adjusted to increase the reaction rate to achieve the desired level of conversion. Again, data was measured as $-r_A = -dC_A/dt$ where reaction rate was expressed as $-r_A$ = mol acetic acid/cm^3 liq sec. For a catalytic reaction an alternate second order rate expression can be written as:

$$-r_A = k'\left(\frac{\tau_{\text{reactor}}\rho_{cat}}{\tau_{\text{system}}}\right)C_A^2$$

where τ_{system} is the residence time in the reactor system and τ_{reactor} is the residence time the fluid is in contact with the catalyst.

The rate expression, in this form, has many variables that can be optimized to increase reaction rate that lead directly to scale-up. For example, increasing the catalyst loading, and thus increasing the catalyst density, increases the overall reaction rate. Also, by increasing the ratio between the reactor volume to the volume of liquid in the system, the reaction rate should also increase. Therefore, there are many different ways to increase the reaction rate to achieve the desired level of conversion.

As previously discussed, the monolith froth reactor utilizes bubble-train flow within the channels of the monolith to reduce mass transfer resistance and produce reaction rates that are near intrinsic values. The key to achieving bubble-train flow in the channels is the "froth" feed that is generated at the entrance of the monolith. The "froth" can be described as a collection of a large distribution of bubbles of differing sizes dispersed randomly in a liquid phase. If the characteristics of the "froth" could be described, quantified, and related to reactor performance, the feed system could then be designed to give the optimal reaction conditions. Previous researchers have investigated certain fundamental aspects of the "froth" (bubble size distribution) and how a single bubble enters a single capillary, but no work has been done on relating the generation of the "froth" to reactor performance. A second set of experiments was performed to relate certain previously outlined feed system characteristics to reactor performance.

Results indicated that by changing feed system design parameters such as the perforated plate hole size, pitch (distance between the centers of adjacent holes), and catalyst distance from the perforated plate, the conversion, and hence, the reactor performance was affected. Therefore, in theory, this information could also be used in conjunction with the reaction rate data to design an optimum feed system for the monolith froth reactor. Also, in theory, the dimensions of the feed system parameters are easily scaled-up for commercial applications. For example, it should make no difference whether the perforated plate is 54 mm or 540 mm in diameter, the hole size and pitch that gives the best results can still be constructed. Unfortunately, the results that relate feed system design parameters to reactor performance are much more difficult to understand and use in a practical situation. It would be very difficult to model or produce a practical correlation to design the feed system. The flow patterns in the monolith channels are extremely complex and there is very little available literature that is relevant that relates "froth" characteristics to flow patterns inside the monolith. The only available studies are for idealized situations that are not representative of the conditions encountered in the operation of the monolith froth reactor.

In comparison to other published literature on the oxidation of acetic acid, the monolith froth reactor appears to compare very favorably. For example, Levec and Smith (1976) report 10 - 20% conversion of acetic acid using a trickle-bed reactor with a ferric oxide catalyst for temperatures between 250 and 286°C. Imamura et al (1982a) report a total organic carbon removal of 67% at a temperature of 248°C using a Co:Bi (5:1) complex oxides as the catalyst. Imamura et al (1988) also reports total organic carbon removal of 19.4% at a temperature of

200°C using Ru/Ce, $Cu(NO_3)_2$, and Mn/Ce catalysts in a batch reactor. The monolith froth reactor compares very favorably with other published studies on the oxidation of acetic acid. Lower operating temperatures were used in the present study to obtain, in some cases, higher conversions and, by using a flow system, there is the added benefit of not having to separate the treated liquid and the catalyst. The monolith froth reactor also utilizes the added advantages of the monolith catalyst (lower pressure drop, high surface area to volume ratio, excellent mechanical stability) for the oxidation of acetic acid. Now that such issues as acetic acid destruction and catalyst stability have been addressed, the monolith froth reactor should be considered as a viable alternative for three-phase catalytic reactions, and in particular, for use in wet oxidation for the destruction of CELSS wastes.

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