CATALYTIC WET OXIDATION OF PHENOLIC POLLUTANTS OF WATER

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To avoid spreading of refractory organic pollutants originating from the industrial wastewater into the environment appropriate measures are necessary. A sustainable chemical technology, the production with the minimum of the waste generation incorporates both cleaning separation technique and destructive processes of the waste. E.g., recycling of process water and regeneration of some chemicals call for needs of such technology.

Wet oxidation seems to be convenient process of destructive oxidation of toxic or refractory and/or bioresistant organic pollutants of the water streams, which are too dilute to incinerate and too concentrated for biological treatment. It can be defined as the oxidation of both organic and inorganic substances in aqueous solution or suspension by means of oxygen at elevated temperatures and pressures. Organic compounds can be converted to water and carbon dioxide without emissions of sulphur, nitrogen oxides or dioxins and fly ash, etc. As an intermediate products are formed biodegradable carboxylic acids, acetic, formic, maleic and oxalic acid. Therefore, the mentioned process is available as economy wastewater pre-treatment preceding biological stage.

The efficiency of aqueous phase oxidation can be largely improved by the use of catalyst and continual reactor unit. Overview of typical available processes and case study examples of an aqueous phenol and substituted phenols treatments are presented. Catalytic wet oxidation would, thus, provide an environmentally attractive option to manage the growing organic sludge and toxic wastewater treatment problems.

Introduction

Wet oxidation \([1]\) is an attractive treatment for waste streams, which are too dilute to incinerate and also too concentrated for biological treatment. It can be defined as the oxidation of organic and inorganic substances in an aqueous solution or suspension by means of oxygen or air at elevated temperatures and pressures. Typical conditions for wet oxidation range from 180 °C and 2 MPa to 315 °C and 15 MPa. Residence times may range from 15 to 120 min, and the chemical oxygen demand (COD) removal may typically be about 75–90%. Insoluble organic matter is converted to simpler soluble organic compounds which are in turn oxidized and eventually converted to carbon dioxide and water, without emissions of NOx, SO2, HCl, dioxins, furans, fly ash, etc. A complete mineralization of the waste stream is impossible by wet oxidation, since some low molecular weight oxygenated compounds (especially acetic and propionic acids, methanol, ethanol, and acetaldehyde) are resistant to oxidation. For instance, removal of acetic acid is usually negligible at temperatures lower than 300 °C. Organic nitrogen compounds are easily transformed into ammonia, which is also very stable. Therefore, wet oxidation is a typical pre-treatment of liquid wastes, which requires additional treatment of the process liquid and gas streams by conventional biological processes.

Wet oxidation reactions

The free radical chain mechanism involving the formation of hydroperoxides and oxyradicals allows to describe correctly the gaseous and liquid oxidation products. As first step hydrogen abstraction from the a, b and g-CH2 groups of carboxylic acids by O2 results in the formation of free radicals which react immediately with O2 to form per-oxy radicals. The peroxy radicals can lead to decarboxylation and formation of CO2 by H abstraction from the –COOH group of another molecule of carboxylic acid. The predominance of acetic acid as major byproduct is explained by the relative stability of the ethoxyl radical. A generalized kinetic model based on a simplified reaction scheme with acetic acid as the rate-limiting intermediate has been successfully used. Wet oxidation process involves two main steps, transfer of oxygen from gas phase to the liquid one, and chemical reaction between the organic substrate and dissolved oxygen. Concentration of oxygen in the liquid phase is defined by reaction rate and transfer phenomena on the interfacial area, influenced by wetting efficiency, and/or temperature dependent solubility of oxygen in water.

In the Fig. 1, constructed on basis of published data, is possible to distinguish particular temperature dependencies. At the total pressure of about 5 MPa, the oxygen concentration in the temperature range between 100 - 200 °C is almost constant, so the temperature influence on oxygen concentration in reaction mixture in this range is possible to neglect.

Continual heterogeneous catalytic oxidation

The challenging operating conditions of wet oxidation provided a strong driving force to investigate catalysts which would allow substantial gains on temperature, pressure and residence time. Another major
benefit of using catalysts in wet oxidation is the oxidation of the refractory compounds, namely acetic acid and ammonia, at much lower temperatures than in the absence of catalysts. Several crucial issues have to be solved related to chemical and physical stability of the heterogeneous oxidation catalysts during wet oxidation: leaching and sintering of the active phase and loss of surface area of the support. Leaching can be controlled to a large extent by a proper choice of the catalytic metal or metal oxide according to the available solubility data, and by pH control during wet oxidation. The same parameters are also of importance to control the hydrothermal stability of the catalyst carrier. Compared to standard wet oxidation, these processes are able to oxidize two refractory compounds, namely acetic acid and ammonia, thus allowing the treated water to be discharged directly or reused as process water.

Fig. 1. Temperature dependence of oxygen mole fraction in water at total pressure 1, 5 and 10 MPa respectively.

Fig. 2. Comparison of autoclave and trickle bed reactor phenol oxidation on powdered and extruded active black Chezacarb catalyst, reps. at 140 °C and 5 MPa of total pressure.
Comparison of results measured in autoclave and trickle bed reactor experiments are given in Fig. 2. A residence time of reaction mixture in TBR modified by catalyst concentration is taken as a common kinetic coordinate. The difference in reaction rate, measured in both reactors for the same value of conversion seems to be about three order of magnitude. This result appears to be reasonable as a product of the lower wetting efficiency (order of $10^{-1}$) in the TBR and internal effectiveness of catalyst extrudates (order of $10^{-3}$). But, the advantage of trickle bed operation consist in high catalyst to liquid ratio and the large interphase surface for oxygen transfer. High amount of concentrated waste waters demands continual process of treatment, i.e., to choice some of available continual reactors. To overcome a gas-liquid mass transfer limitation, the main disadvantage of slurry fluid bed bubble column and/or fixed bed upflow reactor, the extra investment and operational cost are needed. Trickle bed reactor offers low value of liquid holdup that implies only a thin liquid film for oxygen transport.

In contradiction to usual slurry operation, the trickle bed reactor have advantage of implicit catalyst separation, high amount catalyst to liquid ratio and high oxygen to liquid interfacial area. On the other hand, it was found that the hydrodynamics has a controlling role in the process operation.

The NS-LC process

The NS–LC process involves a Pt–Pd/TiO2–ZrO2 honeycomb catalyst. Two-phase flow in vertical monoliths gives in a broad range of G–L velocities a very beneficial flow pattern, the slug flow (segmented gas–liquid flow). Since each liquid plug is sandwiched between two gas plugs, a recirculation pattern is developed within each liquid plug, which improves mass transfer significantly [3] and prevents solids deposition. In addition, a thin liquid film is formed between the gas and the channel wall which, allows high mass-transfer rates while keeping the catalyst continuously wetted. Typical operating conditions of the NS–LC process are temperature 220 °C, pressure 4 MPa and SV 2/h. In these conditions the oxidation of compounds such as phenol, formaldehyde, acetic acid, glucose, etc. reaches or exceeds 99% [4]. In the absence of catalyst the removal efficiencies would be limited to 5–50%

The Osaka Gas process

The Osaka Gas CWO process is based on a mixture of precious and base metals on titania or titania–zirconia carriers (honeycomb or spheres). It has been demonstrated to work on several industrial and urban wastes: 1. a coal gasifier effluent in a pilot plant at British Gas’s London Research Station [5]; 2. wastewater from coke ovens; 3. concentrated cyanide wastewater of the Tufftride process (a soft nitriding process for steel); 4. sewage sludge and residential wastes some operational data on the treatment of wastewater from coke ovens; 5. zirconia carriers (honeycomb or spheres). It has been demonstrated to work on several industrial and urban wastes:

Continual process catalysed by active carbon

The reaction conditions used were following: total pressure 2 - 5 MPa, temperature 110-160°C, initial substrate concentration in water 5 g/l. The slurry experiments were carried out in stainless steel autoclave volume 1.25 l equipped with a magnetic agitator. Trickle bed operations were carried out in stainlessteel tube of 17.9 mm of inner diameter with 47 ml of catalyst fixed bed and LHSV ranged from 1 to 20 h⁻¹. A constant vent gas flow was set to 24 l/h at laboratory conditions.

The oxidation of different substituted phenolic compounds, i.e., 2-amino phenol, salicylic acid and 5- sulfo-salicylic acid was investigated [2]. The dependence of different substrate conversion on modified kinetic time coordinate is shown in Fig.3. The operation conditions are sufficient for high phenol and aminophenol conversion, but for aromatic acids the maximum conversion reached in experiments was only about 40%. During the oxidation of salicylic and sulfo-salicylic acids the same intermediates including phenol were detected in reaction mixture as in the phenol oxidation experiments.

The conversion versus kinetic coordinate dependencies shown in Fig. 3 exhibit the maximum at almost the same W/F coordinate. Probably the pure contacting (wetting) efficiency for low reaction mixture feed rates (high value of W/F coordinate), is responsible for these extremes. Surprised decrease of phenol conversion for the higher residence time value is caused by decreasing catalyst wetting owing to the formation of liquid rivulets and pockets fluctuating in the bed of catalyst.
Conclusions

Compared to conventional wet air oxidation, catalytic wet air oxidation offers lower energy requirements and much higher oxidation efficiencies. Commercial catalytic wet oxidation processes rely either on supported precious metal and/or base metal oxide catalysts or on homogeneous catalysts such as Fe or Cu. In some cases, the overall performance of wet oxidation can be close to that of supercritical water oxidation operating typically at pressures around 25 MPa and temperatures around 550 °C. The practical applications of heterogeneous catalysts are likely to be restricted to processes which treat industrial wastewater’s presenting well-defined compositions, to minimize the challenge linked to the variability of wastewater characteristics in terms of pH and presence of poisons. The risk of hydrothermal sintering of the catalytic phase or support should also be considered carefully. Thanks to catalysis, wet air oxidation is today a cost-effective solution for the treatment of organic sludge and refractory industrial wastewater. The charcoal catalysts exhibit less activity, in comparison to the usual metallic ones, but they are environmentally acceptable. The higher amount of the catalyst in the reaction mixture promotes overall oxidation rate. Influence of different aromatic ring substituents on phenolic derivates conversion rate depends on their nature, the negative role of carboxylic group decreases both the oxidation rate and the overall conversion. Trickle bed operation seems to be promising variant due to high catalyst to waste water ratio. The main problem of trickle bed reactor is low wetting efficiency of the catalyst bed and low catalyst effectiveness. The intrinsic residence time of organic species in the bed and amount of available wetted catalyst surface imply that there is an optimal value of the feed to reach maximal reactor productivity.

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References