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CATALYTIC OXIDATION
OF RADIOACTIVELY CONTAMINATED
ORGANIC WASTES

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Page 7, Third Paragraph.

The first sentence should read:

The other three catalysts were prepared in the laboratory by loading the molecular sieve with the metal by repeated washings with a solution of a salt of the metal, and then washing with distilled water until no more of the metal ion came off.

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and Processing

CATALYTIC OXIDATION
OF RADIOACTIVELY CONTAMINATED
ORGANIC WASTES

By

K. C. Knoll

Water and Waste Management Department
Environmental and Life Sciences Division

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CATALYTIC OXIDATION
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K. C. Knoll

ABSTRACT

A method for oxidizing liquid organic wastes from a nuclear fuel separations plant using a catalytic bed as a method of disposal was investigated. Wastes were fed either as a liquid or vapor, together with a flow of air, through the catalyst bed. Oxidation took place with the generation of heat. Off-gases were contained and could be monitored. A list of some catalysts used as well as the organics oxidized by this method are presented.

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CATALYTIC OXIDATION OF RADIOACTIVELY CONTAMINATED ORGANIC WASTES

K. C. Knoll

INTRODUCTION

Disposal of radioactively contaminated liquid organic wastes poses a difficult problem for nuclear separations plants. The wastes may not only be contaminated with radionuclides but also the very property which dictates their use in the plant, the ability to extract certain metallic ions from other ion exchangers, makes their disposal to the environment potentially hazardous.

Several organic waste disposal methods should be considered. The first, soil disposal of these organics must be carefully controlled and evaluated for each disposal circumstance. The presence of organics in the soil apparently does not inhibit the removal of radionuclides from subsequent aqueous wastes by ion exchange; however, the organics may contain ions which will not be removed by exchange in the soil. Also, some of the organic wastes will readily remove previously deposited radionuclides as they migrate through the soil. These radionuclides may be carried by the organics and may eventually reach ground water.⁽¹⁾

Biodegradation is a second method of organic disposal. It would be a simple, inexpensive process requiring little equipment and supervision. To date, this method has not been demonstrated, but there is some promise that with the acclimation of certain strains of bacteria these wastes may prove to be degradable.

A third method of disposal is burning. The problem here is the likelihood of polluting the atmosphere by the resultant off-gases, but what is more hazardous is the possible dispersal

of radioactivity in the gases released by burning. Tests conducted in the laboratory show that open-pan burning gives rise to large amounts of incomplete combustion products, although the bulk of the radioactivity tends to remain in the burning pan.⁽²⁾ When the fuel was atomized and burned in an air stream, only 75% of the radioactivity could be recovered from the combustion tube and downstream HNO_3 scrubbers, cold traps and filters which suggests that a portion of the radioactivity passed into the atmosphere.⁽³⁾

In an effort to develop a disposal method which would retain the benefits of burning but insure complete control of off-gases as well as low temperature operation, the use of a catalyst to promote oxidation was investigated. This report describes the experimentation which led to the successful laboratory demonstration of a novel catalytic oxidation technique.

SUMMARY AND CONCLUSIONS

The disposal by catalytic oxidation of organic wastes from the nuclear fuels separations plants at Hanford has been investigated and found to be feasible. When organic wastes were fed to a catalyst bed, either as a liquid or vapor together with air, oxidation took place at controlled temperatures in a contained system. Initiating temperatures were 200 to 250 °C and oxidation temperatures were 400 °C or greater. Several organic wastes were oxidized successfully. Seven different catalysts were tried; the ones generally used were metal-loaded molecular sieves. One sample of organic contaminated with ^{137}Cs was oxidized with no release of activity to the atmosphere.

The catalytic oxidation technique holds much promise as a method for destroying organic wastes without contaminating the atmosphere. To provide a basis for pilot plant studies, additional research on optimal operating conditions needs to be performed. Research on the requirements for disposal of spent catalytic beds will also be necessary.

DISCUSSION

EXPERIMENTAL METHODS

Two methods for the catalytic oxidation process have been developed. In one method, fuel is fed to a heated lower chamber where it is vaporized. The vapors are swept out with an air stream through a porous plate into an upper chamber which is also heated and contains the catalyst. The oxidation reaction takes place in this upper chamber. The off-gases are swept from this second chamber either for recycle or disposal. In the second method, the liquid fuel is fed directly into the heated catalyst bed through which air is being blown. The oxidation reaction takes place at the catalytic bed and the off-gases are swept out with the air stream, again either for recycle or disposal.

In both cases, there is a minimum temperature to which the catalyst must be raised to start the reaction. This temperature varies with the catalyst, but is generally in the region of 200 to 250 °C. The reaction will begin in 3 to 5 min and the temperature will rise to 350 °C or above. To prevent the catalyst from being damaged, the temperature should be controlled to less than 600 °C.

The choice of which method to use depends upon the fuel to be oxidized. Under the conditions used in this work, a fuel such as tributyl phosphate leaves a residue of phosphoric acid when it is vaporized. If this fuel is fed directly to the catalyst bed, this residue will cement the catalyst particles together and reduce their efficiency. Such fuels should be vaporized in a chamber that does not contain the catalyst. If the fuel vaporizes completely, it can be fed directly to the catalyst bed and thus eliminate one chamber.

The equipment used is shown in Figure 1. It is constructed of stainless steel in sections that can be bolted together. The

thermocouples are connected to a multipoint recording potentiometer. Air flow is measured by a rotameter and the air is heated before being fed to the reactor. Off-gases pass through a condenser to remove water and any unburned fuel. To determine the completeness of oxidation, a gas chromatograph is used to measure the amounts of CO and CO₂ produced.

FIGURE 1. Catalytic Oxidation Reactor

ORGANICS

Many of the organics used at the Hanford chemical processing plants and combinations of them which appear as wastes have been tried as fuels for catalytic oxidation. Some have been used rather extensively to study the process itself; others have been merely tried several times to determine if the process was broadly applicable to a wide number of organic wastes and thus warrant extensive study as a full scale plant process.

Dodecane; NPH, a commercial mixture of normal paraffin hydrocarbons (C_{10} - C_{14}); water saturated NPH; and an NPH-tributyl phosphate mixture (70-30 vol%) were used as fuels for most of the experimental work and all oxidized readily. A water saturated organic waste consisting of 0.4M di-(2-ethylhexyl) phosphoric acid and 0.2M tributyl phosphate in NPH was oxidized successfully several times. With Linde SK 410 as a catalyst, a 30-70 vol% mixture of dibutylbutyl phosphonate in CCl_4 was oxidized. The reaction occurred at a lower temperature than with other fuels, probably because of the diluting effect of the carbon tetrachloride. The off-gases were not analyzed. The possibility of oxidizing "Fab oil", which is a 25-75% mixture of lard oil in carbon tetrachloride, was examined. A nickel-based Type A catalyst was used. The reaction was started with NPH and the fuel was then changed to "Fab oil." The reaction temperature dropped about 50 °C. About 6 ml were oxidized directly from the liquid phase.

CATALYSTS

Commercial Types

The following catalysts were used in the course of this study.

- W. R. Grace and Company No. 908
- Union Carbide Corporation Linde Division SK 400
- Union Carbide Corporation Linde Division SK 410

The composition of the Grace No. 908 is unknown. It apparently is nickel-based and is pelletized. The binder does not retain integrity during use, especially when used in the liquid phase mode of operation where the pellets break apart.

The two Linde products are Type Y molecular sieves; the 400 being nickel-based and the 410, copper-based. Both of these are good catalysts, but the binder is soft and the pellets tend to breakup to powder.

Figure 2 shows a comparison of the behavior of the three commercial catalysts. The air flow in each case was the same, but the fuel feed varied slightly as shown. The decreasing temperature of the reaction of the Grace No. 908 catalyst with time indicates a lowering of the efficiency of the reaction.

FIGURE 2. Comparison of Three Commercial Catalysts

Laboratory Produced

The following catalysts were produced in the laboratory.

- Ni-based Type A Molecular Sieve
- Na-based 13X Molecular Sieve
- Cu-based 13X Molecular Sieve
- Raney nickel

The Raney nickel was a very fine powder. While its catalytic properties were good, its physical form made it difficult to work with.

The other three catalysts were prepared in the laboratory by loading the molecular sieve with the metal~~x~~ by repeated washings with a solution of a salt of the metal, and then washing with distilled water until no more of the metal ion came off. They were then oven-dried at about 200 °C. The physical characteristics of the molecular sieve catalysts were very good with little tendency to break or powder. There is no comparison available at present for the laboratory produced catalysts, but all function very well in oxidizing the organics.

OPERATING CONDITIONS

The effect of changing the feed rate of the fuel is shown in Figure 3. With the same catalyst on two successive days, the air flow was kept the same but the fuel feed rate was more than doubled with a resulting rise in the reaction temperature.

The effect of changing the air flow is shown in Figure 4, where the temperature of a bed of Grace No. 908 catalyst is plotted against time. The fuel feed was the same, but as the air flow was changed from 525 to 1250 ml/min, the temperature rose from 400 to 650 °C. No study has been made of the interrelation between fuel feed and air flow changes.

No catalyst bed has yet been run to exhaustion. However, a 5 g (7.5 cm³) bed of Na-based 13X was used on five successive

FIGURE 3. Effect of Feed Rate Change on Reaction Temperature

FIGURE 4. Effect of Air Flow Change on Reaction Temperature

days, stopping and restarting each day until 310 ml of TBP-NPH (30-70%) had been burned. This amounts to 41 bed volumes through-put. There was no evidence of catalyst exhaustion at the end of this experiment.

The off-gas composition from most of the wastes is very complex, thus a material balance has not been achieved with anything but the simplest fuel compositions. A volume of 9.9 ml of dodecane was oxidized using a Cu-based 13X and the off-gases were passed through a NaOH scrubber. Incoming air was also scrubbed with NaOH to remove the CO₂ present. Titration of the scrubbing liquid against standard HCl showed that 21.01 g of CO₂ had been produced, containing 5.74 g of carbon. The fuel burned contained 6.4 g of carbon which gave a recovery of 90%. A very small weight percent of the gas, probably about 0.1%, would be CO judging from previous analysis of the off-gas on a gas chromatograph.

A sample of TBP-NPH (30-70%) was spiked with ¹³⁷Cs and vaporized in a catalytic reactor. The vapors were passed through a bed of crushed Grace No. 908 catalyst. The off-gases were passed through a condenser, a trap, a filter* and another trap. After 20.4 ml of the fuel had been vaporized, the equipment was disassembled. The liquid in the trap, the acetone wash of the vaporizing crucible, the filter, and one gram of the catalyst were measured for gamma activity with a scintillation counter.** The acetone wash of the vaporizer contained 85% of the radio-activity that had been in the fuel. No activity was measurable in the filter or traps. The fact that no activity was found in the other parts of the system would indicate that the 15% unaccounted for might have been present on the crucible and had not been taken off with the wash.

* Millipore MAWG 037A0.

** Auto-gamma Spectrometer. Packard Instrument Company, LaGrange, Illinois.

REFERENCES

1. K. C. Knoll. *Unpublished Data. Pacific Northwest Laboratory, Richland, Washington. 1968. ("Reactions of Organic Wastes and Soils," BNWL-860, in press)*
2. K. C. Knoll. *Unpublished data. Pacific Northwest Laboratory, Richland, Washington. 1968. (Notebook BNW 888, p. 51.)*
3. K. C. Knoll. *Unpublished Data. Pacific Northwest Laboratory, Richland, Washington. 1968. (Notebook BNW 888, pp. 62-3)*

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