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Catalytic Destruction of Hazardous Organics in Aqueous Solutions

**E. G. Baker
L. J. Sealock, Jr.**

April 1988

**Prepared for the U.S. Department of Energy
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**Pacific Northwest Laboratory
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ORGANICS IN AQUEOUS SOLUTIONS

E. G. Baker
L. J. Sealock, Jr.

April 1988

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U.S. Department of Energy
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Richland, Washington 99352

SUMMARY

Pacific Northwest Laboratory (PNL) is developing a process for destroying hazardous organics and chlorinated organics in aqueous solutions. The process is targeted at liquid waste streams that are difficult and costly to treat with conventional or developing technologies. Examples of these waste streams include contaminated groundwater and surface water and industrial wastewater.

In the PNL process, aqueous solutions are treated with a transition metal catalyst at 300°C to 460°C and 2000 to 5000 psig pressure to convert the wastes to innocuous gases. During proof-of-principle tests conducted in a 1-L batch reactor, destruction of over 99% (in most cases approaching 99.9%) of the organic material was achieved. Hexone (methyl isobutyl ketone, MIBK), p-cresol, hexane, benzene, and naphthalene were used as model waste materials. The only major product with all of the organic compounds was a gas containing 50% to 75% methane, 25% to 45% carbon dioxide, and 0% to 5% hydrogen.

A variety of catalysts and experimental conditions were used in the proof-of-principle tests. These tests showed that reduced nickel was the only effective catalyst and that the optimal operating conditions for destroying nonchlorinated organics were 350°C to 400°C, 2000 to 4000 psig, and 30- to 60-min residence time. These tests also indicated that catalyst deactivation or fouling would not be a problem at these conditions.

Two chlorinated hydrocarbons, chlorobenzene and trichloroethylene (TCE), were also tested. Destruction of both compounds was 99% or greater, but the products were different from those obtained from hydrocarbons. With TCE, the major product was carbon dioxide; with chlorobenzene the major product identified was benzene. In the tests with the chlorinated hydrocarbons, the chlorine was converted to HCl and the reduced nickel was converted to nickel hydroxide, which may be detrimental to long-term catalyst activity.

The first 6 months of testing in the batch reactor have indicated that the concept has significant promise as a commercial process for destroying hazardous organics and chlorinated organics in aqueous streams. The major

benefit of catalytic destruction, compared with conventional treatment technology such as carbon adsorption or air stripping, is that the process removes and destroys the organic materials. No hazardous residuals are produced. A gas, which can be burned for process heat, and a clean water stream are the only products. The process is adaptable to modular construction for mobile units, and can be used to treat a wide range of organic compositions and concentrations. An invention report on the concept has been filed, and a review of the relevant literature completed. A patent application was filed in March 1988.

Additional testing with a continuous flow reactor is needed to determine the effect of pressure and flow rate (residence time) on destruction. In addition, better analytical techniques are required to study more dilute solutions and provide improved material balances with the chlorinated hydrocarbons. When this information is obtained, a preliminary design and economic feasibility study can be completed. Based on favorable results, a transportable demonstration unit could be built, and the concept could be field tested as early as 1989.

ACKNOWLEDGMENTS

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INTRODUCTION

The Northwest Hazardous Waste Research, Development, and Demonstration Center was established at Pacific Northwest Laboratory (PNL)(a) in accordance with the provisions of the Superfund Amendments and Reauthorization Act (SARA) that was signed into law by the President in October 1986. The purpose of the Center is to carry out a program of research to adapt and develop innovative technologies for assessing the impacts of inactive hazardous and radioactive mixed-waste sites and remediating the effects of these wastes.

A multiyear research program was developed by the Center specifically to suit the needs of both the Northwest region and the Hanford Site. As part of this research program, PNL is developing a proprietary process for the catalytic destruction of hazardous organics in aqueous solutions. The process is targeted at liquid waste streams that are difficult or costly to treat with conventional or developing technologies. Specific examples of these waste streams are contaminated groundwater and surface water and industrial wastewater.

Contaminated groundwater is a problem associated with nearly all Northwest National Priorities List sites, and is an issue at most Comprehensive Environmental Response, Compensation, and Liability Information System (CERCLIS) sites in the four Northwest states and at the Hanford Site. Typical organic contaminants in groundwater include chlorinated and nonchlorinated aliphatics and aromatics.

Current technologies for treating groundwater contaminated with organics rely on separation processes, which do not destroy the hazardous material. A cost-effective method for destroying mixtures of organic compounds present at dilute concentrations in aqueous streams is needed to permanently protect human health and natural resources, as encouraged by the SARA legislation.

This report presents the results of proof-of-principle tests conducted in a 1-L batch reactor to evaluate the catalytic destruction process. The

(a) Operated for the U.S. Department of Energy by Battelle Memorial Institute.

objectives of the proof-of-principle tests were to determine what types of organic materials could be destroyed and to identify the optimal operating conditions and catalysts. Model compounds were used to represent organic and chlorinated organic wastes. The results of these proof-of-principle tests can be used as a basis for further development of the process. Summaries of the experimental results are included in the appendix.

BACKGROUND AND OBJECTIVE

The increasing need for cost-effective, environmentally acceptable methods for hazardous waste treatment requires that new and improved technologies be developed. A proprietary concept has been defined at PNL that has significant potential for catalytically converting organics (including chlorinated hydrocarbons) in aqueous solutions to innocuous gases. The concept was formulated from past experience at PNL regarding high-moisture biomass gasification and catalyst research. The objective of the research project described in this report was to adapt the concept to catalytic destruction of aqueous organic hazardous waste.

Many hazardous wastes can be chemically converted to less hazardous products. Examples of some of the technologies that can be used for some types of hazardous waste include wet air oxidation, ozonation, molten salt combustion, electrochemical oxidation, neutralization, catalytic hydrogenation, and incineration. Each technology has advantages and drawbacks based on the type of waste to be treated, the concentration of the waste, specific costs, and environmental issues. Treatment of aqueous streams for organic removal is already practiced commercially, and similar processes may likely be applicable to hazardous organic waste streams.

Liquid waste streams with high organic content can be incinerated or treated with techniques using solvent extraction. Liquid streams of intermediate organic content (0.1% to 10%) and sludges typically release much of the emissions at hazardous waste management facilities and are the most difficult wastes to treat (Allen and Blaney 1985). Aqueous streams having low organic content (<1000 ppm) can be treated with techniques used in purifying drinking water (Love et al. 1984) or in municipal wastewater treatment (Shukla and Hicks 1984). The technologies already being used to clean leachate at large disposal sites (O'Brian and Bright 1983; Parmele and Allen 1983) rely on separation processes, such as air stripping or carbon adsorption. However, organics removed by these processes are not destroyed and are ultimately released back to the environment from off gas during air stripping and from solid wastes generated by activated carbon.

Figure 1 shows organic concentration ranges over which various treatment technologies are applicable (Allen and Blaney 1985) and the range of treatment expected for the process being developed at PNL. The concept employs a metal catalyst to convert aqueous waste at 300°C to 460°C and high pressures up to 5000 psig. The organics are converted to innocuous gases, primarily CH₄, H₂, and CO₂. The large water content of aqueous organic wastes dictates that the system operate at conditions where the water remains a liquid to prevent large expenditures of energy for water evaporation.

FIGURE 1. Approximate Range of Organic Concentrations Over Which Various Treatment Technologies are Applicable

A somewhat similar process (Elliott and Sealock 1982; Sealock and Elliott 1984) has been demonstrated successfully at PNL with high-moisture biomass feedstocks (up to 90% water, 10% biomass). Very high conversion of biomass to gas has been achieved at 400°C with nickel and nickel/alkali catalysts. Typically, 95% carbon conversions (or higher) have been obtained for several different high-moisture feedstocks. The high pressure prevents excessive vaporization of water, which minimizes the energy requirements of the process. In many cases, the heat for catalytic destruction using this process could be supplied by burning the off gas from the system.

The purpose of the research project discussed here was to conduct proof-of-principle tests with aqueous organic wastes. The objectives were to determine what types of hydrocarbons and chlorinated hydrocarbons could be destroyed and to identify the best operating conditions, i.e., type of catalyst, temperature, residence time. The information gained in the research on this process has been used to define patentable concepts for not only the catalytic destruction of aqueous organic wastes but for other destruction/conversion applications as well. A patent application was filed in March 1988.

EXPERIMENTAL SYSTEM AND PROCEDURES

The system being used for experiments to develop concepts for the catalytic destruction of hazardous organic waste is centered around a 1-L, Inconel®, bolted-closure autoclave (reactor). This section describes the system and the procedures used in the experiments.

REACTOR SYSTEM

In the reactor system, aqueous waste is converted at low temperatures (300°C to 460°C) and high pressures (up to 5000 psig) to innocuous gases consisting primarily of CH₄, CO₂, and H₂. The system is equipped with a sampling system that allows several samples to be taken throughout the period of the experiment while the reactor is maintained at reaction temperature and pressure. A drawing of the 1-L reactor is presented in Figure 2. The reactor is an autoclave, manufactured by Autoclave Engineers, and is operated with standard heating, cooling, and stirring equipment provided with the unit. The stirring baffle is not used so that a stainless steel liner can fit into the reactor. The use of the liner facilitates product recovery and reactor cleanup, and provides containment of alkali, chlorides, or other potential corrosive compounds.

The autoclave is heated by a 1.7-kW heater, which has the capability to heat the reaction environment up to ~500°C. Typical heatup time required to heat 300 mL of aqueous solution and catalyst to 400°C is about 90 min. The aqueous fluid, reaction gases, and catalyst are rapidly mixed inside the autoclave by a magnetic-coupled stirrer. The reactor has a cooling coil that is used to cool down the reactor contents at the end of each experiment. The reactor and the majority of the experimental equipment under pressure are contained inside a 1/4-in. steel barricade (see Figure 3, a schematic of the entire system). Pressure indicators, temperature and stirrer controllers, and pressure and temperature alarms are held outside the barricade.

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Gas samples are taken through a body wall port in the top of the reactor. The reactor and sample removal system are operated remotely after the reactor has been batch charged. The sampling system, shown in Figure 3, employs a combination of a manually operated sampling valve and a pressure transducer on the sample loop to collect carefully controlled sample volumes. Typically, the sample loop is filled to a pressure of 50 psig.

FIGURE 2. One-liter Autoclave Reactor

FIGURE 3. Reactor System

The volume of the sampling system is about 3.9 mL (2.6 mL sample holding loop, 1.3 mL dead space prior to the sampling valve). The sampling system allows the entire sample loop to be evacuated prior to taking a sample, avoiding contamination of the sample by previous samples. The system is equipped with an adsorbent column to collect any water and other liquids in the samples. This column is weighed before and after experiments for a quantitative determination of the mass of water collected.

EXPERIMENTAL PROCEDURES

The organic compounds used in this study and their properties are described in Table 1. Table 2 lists the physical data for the various catalysts that were evaluated to determine their effectiveness in converting the organic wastes to innocuous products.

Catalytic destruction experiments were conducted batchwise in the presence and absence of catalysts. The experimental parameters are listed below:

Temperature	300°C - 460°C
Pressure	2000 - 5500 psig
Organic Concentration	2 wt% and 10 wt% in water
Organic Compounds	(see Table 1)
Catalyst Concentration	0.4, 1.2, and 3.6 g/g organic
Catalysts	(see Table 2)

In a typical catalytic experiment, the desired amounts of organic material, water, and catalyst were weighed and charged to a stainless steel liner. The mixed-waste catalyst slurry in the liner was placed in the 1-L reactor under ambient conditions. The reactor was sealed, purged with nitrogen, tested for leaks at 1000 psig with nitrogen, and vented until the pressure was approximately 100 psig. The nitrogen that remained in the reactor was used as a reference to monitor the accumulation of gaseous products produced during the destruction of the organic. This was accomplished by measuring the dilution of the nitrogen in gas samples taken at regular intervals once the reactor reached temperature.

TABLE 1. Properties of Organic Compounds Used in the Investigation

Material	Chemical Formula	Elemental Analysis, wt%				Liquid Density, g/mL	Boiling Point at 760 mm, C	Solubility in H ₂ O at 25 C, wt%	Grade Purity
		C	H	O	Cl				
Benzene	C ₆ H ₆	92.3	7.7	--	--	0.88	80	0.07	99+% (ACS), spec. gr.
p-Cresol	C ₇ H ₈ O	77.8	7.5	14.8	--	1.03	202	1.8	99+%
n-Hexane	C ₆ H ₁₄	83.7	16.3	--	--	0.66	69	0.014	99+%
Hexone (MIBK, isopropyl acetone, 4-methyl 2-pentanone)	C ₆ H ₁₂ O	72.0	12.0	16.0	--	0.80	117	1.9	98% tech. gr.
Naphthalene	C ₁₀ H ₈	93.8	6.2	--	--	1.15	218	0.003	reagent grade
Chlorobenzene	C ₆ H ₅ Cl	64.0	4.4	--	31.4	1.11	132	0.049	99+% spec. gr.
Trichloroethylene (tri-clene, TCE, trichloroethene)	C ₂ HCl ₃	18.3	0.8	--	81.0	1.47	87	0.1	99+% spec. gr.

TABLE 2. Physical Data for Catalysts Tested for the Destruction of Organics in Aqueous Solutions

Catalyst ID	Supplier	Composition: Active Metals	Support	Surface Area, m ² /g	Form	Comments
Ni 1404	Harshaw	64% Ni	P	125	1/8-in. E	reduced and stabilized version of Ni 3263
Ni 3263	Harshaw	64% Ni	P	125	1/8-in. E	unreduced
G-65RS	United Catalysts	27% Ni	refractory	--	1/4-in. T	reduced and stabilized version of G-65
G-65	United Catalysts	25% Ni	refractory	--	1/4-in. T	unreduced
Ni 3288	Harshaw	60% Ni	P	155	1/16-in. E	reduced and stabilized
G-90C	United Catalysts	15% Ni	70% Al ₂ O ₃ 8% CaO	3-15	5/8-in. x 5/8-in. R	unreduced
KAT 479	Katalco	19.0% MoO ₃ 4.0% CoO	Al ₂ O ₃	180	1/8-in. E	unreduced
LZY82	Union Carbide	--	65.6% SiO ₂	625	1/8-in. E	--
G-47	United Catalysts	3% Fe ₂ O ₃	SiO ₂ -Al ₂ O ₃	--	1/4-in. S	unreduced
C-73	United Catalysts	95% Fe ₂ O ₃	2% Al ₂ O ₃ 1% K ₂ O 2% CaO	--	1/4-in. x 1/2-in. G	unreduced
C-73 RS	United Catalysts	--	--	--	1/4-in. x 1/2-in. G	reduced and stabilized version of C-73
G-62RS	United Catalysts	34.5% Co	refractory	--	3/16-in. E	reduced
--	Aldrich	99+% K ₂ CO ₃	--	--	--	in solution

P = Proprietary; E = Extrudates; T = Tablets; S = Spheres; G = Granules; R = Rings.

Under normal conditions, 60 to 90 min were required to heat the reactor to the desired temperature (300°C to 460°C). Gas samples were taken at regular intervals once the reactor reached the desired temperature (sampling procedure was described in the Experimental System section), and the reactor was held at the designated reaction temperature for approximately 1 h. Pressures in the system ranged from about 2000 to 5500 psig depending on the reaction temperature selected and the amount of gas produced.

At the end of each experiment, cooling water was flushed through the internal cooling coil of the reactor and the contents brought to a temperature of 200°C within 5 min. After the autoclave had cooled completely, the gas product was vented and analyzed. The liquid contents of the reactor were removed and measured, and saved for later analysis.

Gaseous products were analyzed by gas chromatography using a Carle AGC-S gas chromatograph equipped for refinery gas analysis. This system analyzes for H₂, N₂, O₂, CO₂, CO, CH₄, and C₂ hydrocarbons. Larger hydrocarbons and water are rejected in a backflush. When a large backflush was detected, the sample was also analyzed for C₃-C₆ hydrocarbons with a Carle AGC-S gas chromatograph with a flame ionization detector (FID). Both chromatographs were calibrated using standard gases.

The aqueous phase of the liquid product was analyzed directly by a gas chromatograph. The entire liquid contents of the reactor were extracted with methylene chloride and the resulting extract analyzed. In some instances where conversion was low, an organic layer could be separated and analyzed. The liquid products and the extracts were analyzed with a Hewlett Packard 5830A gas chromatograph with an FID and a Hewlett Packard 18850A integrator. Standard solutions were used for calibration.

Solids, which were primarily catalyst, were filtered from the liquid contents of the reactor after the liquids were extracted with methylene chloride. The filtered solids were dried and weighed. A Perkin Elmer 240 Analyzer was used to determine the carbon content of the catalysts.

Waste conversion was determined by subtracting the weight of original organic still present in the reactor liquid product from the weight of organic material charged to the reactor. Carbon conversions to gas were

calculated using a computer program written for the high-moisture biomass project. The amount of gas produced was based on the gas analysis using the inert nitrogen added as a tracer gas. Because of inaccuracies in this analysis procedure, carbon conversions to gas exceeded 100% in some cases. Carbon balance was based on the carbon in the organic feed material compared with the carbon in the gas, in the liquid, and on the solid catalyst. Overall material balance was based on the weight of organic, water, and catalyst charged to the reactor compared with the weight of the liquid and catalyst removed from the reactor plus the weight of the gas produced.

In the experiments with chlorinated hydrocarbons, the vent gas was scrubbed in an 8% NaOH solution to remove any chlorine that might have been produced. The scrubber solution and the water remaining in the reactor liner were analyzed for Cl^- by the specific ion electrode method using an Orion Model 94-17B chloride electrode and a Corning 130 pH meter.

EXPERIMENTAL RESULTS

Tests were completed with a variety of organic compounds and several different types of catalysts. The organic compounds and catalysts investigated were shown previously in Tables 1 and 2. Complete results for all of the tests are included as the appendix of this report. Over 50 tests were completed as part of this investigation, and for the purpose of this discussion the runs will be referred to by number as they are in the appendix. The majority of the tests were made with hexone (methyl isobutyl ketone, MIBK), which was used as the organic material to investigate the effect of temperature, catalyst, and catalyst loading. Tests with other organic compounds were made at a standard set of conditions so they could be compared with each other and with hexone.

RESULTS WITH HEXONE

The objective of the initial testing was to define the optimal processing conditions, specifically, temperature, catalyst type, and catalyst concentration. In the previous tests with high-moisture biomass feedstocks, a combination of a reduced nickel catalyst, Ni 1404, and sodium carbonate was found to be the best catalyst system. In tests with these catalysts at 400°C, 430°C, and 460°C (Runs 2 to 4), conversion of hexone was significantly lower than anticipated, 30% to 84%, respectively. Conversion was much higher when Ni 1404 was used alone, 99.9% and 99.7% at 460°C and 400°C (Runs 5 and 6). For comparison, with no catalyst in the reactor, conversion of hexone was only 6.0% at 400°C.

With Ni 1404, hexone was converted almost entirely to gas (>99%). Typical gas concentrations are shown in Table 3. In some of the runs with other catalysts, acetone was a significant byproduct.

Catalyst Effect

Once Ni 1404 was established to be effective for converting hexone, several other types of catalysts were tested at 400°C and the same hexone concentration (10 wt% in water) and catalyst concentration (1.2 g catalyst/g

TABLE 3. Typical Composition of Gas Produced from Hexone with Reduced Nickel Catalysts at 400°C

<u>Component</u>	<u>Vol%</u>
H ₂	5-13
CO ₂	24-32
CO	---
CH ₄	54-58
C ₂ H ₆	<1
C ₃ H ₈	1-2
C ₄ H ₁₀	1-3

of hexone). These results are shown in Table 4. With reduced nickel catalysts, Ni 1404, Ni 3288, and G-65 RS, hexone conversion was over 99%. With the other catalysts the highest conversion was 23%, and the results with most of the catalysts were basically the same as with no catalysts (6% conversion). The other catalysts tested included three nickel oxide catalysts.

TABLE 4. Hexone Conversion With Different Catalysts (400°C, 1.2 g catalyst/g hexone, 10% hexone in water)

<u>Run No.</u>	<u>Catalyst</u>	<u>Catalyst Composition</u>	<u>Hexone Conversion, wt%</u>
6	Ni 1404	Ni/Al ₂ O ₃	99.7
23	Ni 3288	Ni/Al ₂ O ₃	99.6
32	G-65 RS	Ni/refractory	99.4
16	KAT 479	CoMo/Al ₂ O ₃	23.1
51	G-62 RS	Co/refractory	14.9
18	G-90C	Ni/Al ₂ O ₃	14.6
17	LZY82	Y-Zeolite	13.4
35	G-65	Ni/refractory	12.2
38	Ni 3263	Ni/Al ₂ O ₃	10.0
11	--	Na ₂ CO ₃	7.9
34	C-73	Fe ₂ O ₃	6.9
25	G-47	Fe ₂ O ₃ /Al ₂ O ₃	6.4
36	C-73 RS	Fe ₂ O ₃	5.5
10	None	--	6.0

Hexone conversion with these three unreduced catalysts was 10.0% to 14.6%. Two other reduced and stabilized transition metal catalysts, C-73 RS containing iron and G-62 RS containing cobalt, were also ineffective.

Three different catalyst concentrations were tested with Ni 1404: 0.4, 1.2, and 3.6 g catalyst/g hexone. With 1.2 and 3.6 g/g, hexone conversion was over 99% at 400°C (Runs 6 and 20). With 0.4 g/g, conversion fell to 89%. Figure 4 shows carbon conversions to gas as a function of time at temperature for the three different catalyst loadings. There is little difference between 1.2 g/g and 3.6 g/g, but the rate of conversion is significantly slower with 0.4 g/g.

A test was also conducted with G-65 RS, which contains only 27% nickel compared with 64% for Ni 1404. Over 99% destruction was achieved in this

FIGURE 4. Effect of Catalyst Loading on Carbon Conversion to Gas

test despite the lower nickel loading. These results indicate that the poor conversion with 0.4 g Ni 1404/g hexone is not due to the reduced amount of nickel in the reactor but is more likely due to poor catalyst contacting at the reduced loading.

Effect of Temperature

The effect of temperature on hexone conversion with Ni 1404 was evaluated over the range of 300°C to 460°C (Runs 5, 6, 21, and 54). Conversion was high at the three highest temperatures tested: 99.5% at 350°C, 99.7% at 400°C, and 99.9% at 460°C but fell to 96.6% at 300°C. The results at 400°C and 460°C were very similar, but some differences were noted at 350°C and 300°C. At 400°C and 460°C, gas was the only product from hexone destruction. At 350°C, conversion to gas was only 84% and at 300°C only 50%. At 350°C, the remainder of the carbon from the hexone was present as a solid on the catalyst. At 300°C, there was no additional carbon on the catalyst. About 46% of the carbon was unaccounted for in this test. Table 5 shows the weight of carbon on the catalyst after each of the three runs. At 400°C and 460°C, the weight of carbon on the catalyst is the same before and after the run, indicating little or no deposition of carbon from the hexone. At 350°C, 4.0 to 5.8 wt% carbon was detected on the catalyst compared with 2 to 3 wt% for the fresh catalyst. At 300°C, the catalyst had only 3 wt% carbon on it.

The buildup of carbon on the catalyst at 350°C may be due to operation below the critical point of water (374°C). A similar phenomenon has been

TABLE 5. Carbon on Ni 1404 Used in Tests with Hexone

<u>Run No.</u>	<u>Temperature, °C</u>	<u>Carbon on Catalyst, wt%</u>
5	460	2.1
6	400	2.5
21	350	5.0
54	300	3.0
Fresh Ni 1404		3.0

noted by Modell, Reid, and Amin (1978). Another explanation for carbon on the catalyst is a reduced rate of conversion at 300°C to 350°C. Figure 5 shows carbon conversion to gas for the four temperatures as a function of time.

This figure indicates that given enough time all of the carbon would have been converted to gas at 350°C and there would have been no carbon on the catalyst. However, the lack of carbon on the catalyst at 300°C and the poor material balance for this run do not completely substantiate this conclusion.

In the long term, carbon, if it does collect on the catalyst, may have deleterious effects on the catalyst. Long-term tests in a continuous operating unit are necessary to determine if carbon buildup on the catalyst will be a factor. The concentration of waste (10 wt% in water) was high in these tests, probably higher than typically would be found. With more dilute organic solutions, carbon buildup, if it occurred at all, would not be a

FIGURE 5. Effect of Temperature on Carbon Conversion to Gas

serious problem. In any event, at temperatures above 400°C, carbon buildup on the catalyst does not appear to be a problem.

Effect of Organic Concentration

Most of the tests were made at 10 wt% organic in water. This level, which is probably higher than typically would be encountered in an aqueous waste stream, allowed for better mass balances. Tests were made with hexone and p-cresol at 2 wt% (Runs 14 and 15) for comparison. Catalyst concentration was kept at 1.2 g/g of organic. Conversions were 99.9% with both compounds at the 2 wt% level. Figure 6 shows carbon conversion to gas as a function of time. With p-cresol the 2 wt% solution converted more rapidly than the 10 wt% solution, but the hexone converted more slowly at the 2 wt% level. The results on the effect of organic concentration are inconclusive.

FIGURE 6. Effect of Organic Concentration on Carbon Conversion to Gas

Tests at lower concentrations are necessary to fully define the capabilities of the concept. However, these tests will require development of improved analytical techniques.

TESTS WITH OTHER HYDROCARBONS

In addition to hexone, tests were made with four other hydrocarbons: hexane (Run 27), benzene (Run 53), p-cresol (Run 52), and naphthalene (Run 26). All of these tests were conducted at 400°C with 10 wt% organic/water mixtures. The catalyst used was Ni 1404 at 1.2 g/g organic. Conversion of all of the model compounds was over 99% and in most cases approached 99.9% as shown in Table 6.

Gas was the only product from catalytic destruction of these organics except from p-cresol and benzene, where small amounts of other aromatics (0.4% to 0.8% yield) were identified in the water. The composition of the gas was similar to that produced from hexone, except little or no C₃-C₄ hydrocarbons were present in the gas. Figure 7 shows carbon conversion to gas for all four hydrocarbons and hexone. Hexone and hexane are converted most rapidly. Benzene, p-cresol, and naphthalene were slightly slower.

A mixed organic waste containing 2.5 wt% each of hexone, hexane, benzene, and naphthalene was tested at 400°C and 1.2 g Ni 1404/g waste (Run 50). Conversion was over 99.6% for all of the components.

TABLE 6. Conversion of Other Hydrocarbons (400°C, 1.2 g Ni 1404/g organic)

<u>Run No.</u>	<u>Compound</u>	<u>Conversion, wt%</u>
6	hexone	99.7
52	p-cresol	99.7
26	naphthalene	99+(a)
27	hexane	99.7
53	benzene	99.9
50	hexane, hexone, benzene, naphthalene mixture	99.7

(a) No naphthalene was detected by the gas chromatograph (GC), but the detection limit for naphthalene is high so conversion is given as 99+%.

FIGURE 7. Carbon Conversion to Gas for Other Hydrocarbons

RESULTS WITH CHLORINATED HYDROCARBONS

Two chlorinated compounds, trichloroethylene (TCE) and chlorobenzene, were tested. The TCE is representative of a wide number of chlorinated solvents that are often a problem in groundwater. Chlorobenzene was used as a model compound for chlorinated aromatics such as polychlorinated biphenyls (PCBs).

Conversion of both compounds was high, typically 99% for chlorobenzene (Runs 28 to 30,33) and 99.9% for TCE (Run 37), at 400°C and about 4500 psig, but the products were much different from those obtained from hydrocarbons. With chlorobenzene, very little gas was produced and it consisted mostly of CO₂ compared with the large amount of CH₄ produced from hydrocarbons. Benzene was the major product identified. With TCE, conversion to gas was higher, but because TCE is predominantly chlorine on a weight basis there is still not much gas produced. In the two tests with TCE, 38% of the carbon

was converted to gas at 350°C (Run 47) and 62% at 400°C (Run 37). The gas was primarily CO₂ with a little CH₄ and C₂H₆.

The initial tests with the chlorinated hydrocarbons were made using 2 wt% solutions to limit the amount of chlorine in the reactor. With the 2 wt% solutions, the carbon balances for both the chlorinated hydrocarbons tested were poor. With chlorobenzene, only 10% to 20% of the carbon was recovered as liquids or gases, primarily benzene. The catalyst had a large weight gain, but elemental analysis of the spent catalyst showed only 1.9% to 2.8% carbon content, which is similar to the fresh catalyst charged to the reactor (see Table 6), indicating no carbon formation on the catalyst.

Carbon recovery with TCE was better with 92% to 105% of the carbon being in the gases, liquids, or on the catalyst. About 30% of the carbon in the TCE ended up on the catalyst. Again a large weight gain was noted on the catalyst, much more than was due to the carbon.

Infrared (IR) analysis of the spent catalysts indicated the presence of Ni(OH)₂. The formation of NiCl₂, which is water soluble, was a concern but apparently did not occur. The following reaction represents what appears to occur:

Analysis of the liquid remaining in the reactor liner and the vent gas scrub solution indicated that all of the chlorine ends up in the water remaining in the liner and is most likely HCl. No chlorine could be detected in the vent gas scrubber, indicating little or no formation of chlorine gas. The IR analysis of the catalyst indicated the possibility of a small amount of chlorine on the catalyst, but primarily the chlorine remained in solution.

The reactor is constructed of Inconel 600, which has excellent resistance to chlorides at high temperatures and pressures, but corrosion is still a concern. Increased pitting was noted in the reactor body itself but is not considered a serious problem to the integrity of the reactor. In four tests (Runs 40 to 42, 45) with high concentrations of TCE (5 to 10 wt%), the Inconel rupture disk failed prematurely at pressures ranging from 3200 to

4200 psig. These failures were apparently due to corrosion of the disk, which indicates corrosion could be a serious problem with large quantities of chlorine in the reactor. We were able to run a 5 wt% TCE mixture at 350°C (Run 47) without blowing the rupture disk. Because of the reduced temperature, the pressure was only 2900 psig.

These tests indicate that Inconel may not be the appropriate material of construction for use with chlorinated hydrocarbons in the PNL process. Processes for dechlorination (LaPierre et al. 1977) and wet air oxidation of chlorinated hydrocarbons (Sworzyn and Ackerman 1982) have used a Teflon[®]-lined reactor and a titanium reactor, respectively, to avoid corrosion.

The PNL catalytic destruction concept shows promise for destroying chlorinated hydrocarbons at low concentrations; however, analytical techniques need to be improved to develop a better understanding of the reaction chemistry as well as to obtain improved elemental balances. Better analytical methods are also required to operate with dilute solutions similar to actual aqueous waste streams. Furthermore, the effect the chlorinated compounds on catalyst activity needs to be understood. Obviously, chlorinated compounds have a major effect on the conversion chemistry as little or no methane is produced. In several tests with hydrocarbons made after tests with chlorinated hydrocarbons, catalyst effectiveness was lower than in previous tests. The residual chlorine in the reactor and liner apparently affected catalyst activity. Refluxing an 8% Na₂CO₃ solution in the reactor for 48 h effectively decontaminated the reactor.

REACTION MECHANISM

Tests with pure organic compounds provide some information for speculation on the mechanism of conversion. One possible mechanism is complete gasification of the organics to carbon monoxide and hydrogen followed by establishment of the methanation and the water gas shift equilibrium as shown below. This equation is the accepted mechanism for high-temperature naphtha steam reforming (Rostrup-Nielsen 1984):

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The hydrocarbons chemisorb on the catalyst and a carbon-carbon bond ruptures producing a surface radical. With normal paraffins, a stepwise degradation has been found in the temperature range of 250°C to 450°C with the nickel selectively attacking the ends of the chain until all of the carbon-carbon bonds are broken (Rostrup-Nielsen 1975; Phillips, Mulhall, and Turner 1969). The surface radicals, which are formed when the carbon-carbon bond ruptures, react with adsorbed water to produce CO and H₂. If this mechanism occurs in the PNL system, the CO must be rapidly hydrogenated to methane, as no CO has been observed in the gas at any time.

Another possibility is the direct hydrogenation of the surface radical to methane without formation of CO. This is similar to the mechanism for hydrogenolysis (cleavage by hydrogen) of hydrocarbons (Sinfelt 1969; Sinfelt 1974). It is possible that both mechanisms contribute.

In the test with hexane, no other hydrocarbons were observed except methane, which suggests the nickel does selectively attack the ends of the chain. If the nickel attacked in the middle of the chain, C₂-C₄ hydrocarbons would be expected in the gas. With hexone, C₃-C₄ hydrocarbons and acetone were found in significant quantities, which suggests the nickel also attacks at the locations indicated below:

In tests at 350°C to 450°C, Phillips, Mulhall, and Turner (1969) found normal paraffins to be the most reactive for steam reforming, followed by

branched hydrocarbons and cycloparaffins, with benzene being the least reactive. As previously indicated, a similar trend was noted in the PNL studies as hexane was converted most rapidly and benzene was the slowest.

In the tests with the chlorinated compounds, TCE and chlorobenzene, dechlorination appears to take place rapidly, as little or no chlorinated compounds are detected in the products. Nickel is known to catalyze dechlorination of chlorinated hydrocarbons in the presence of hydrogen at temperatures as low as 100°C (LaPierre et al. 1977). Based on the results here with hydrocarbons, the dechlorinated hydrocarbons should convert to methane, but do not. Instead, the primary product with the chlorinated hydrocarbons is CO₂. Very little methane is formed, which indicates that the chlorine affects the chemistry that takes place on the nickel catalyst.

CONCLUSIONS AND PLAN FOR FUTURE DEVELOPMENT

The first 6 months of testing using a 1-L batch reactor demonstrated that catalytic destruction has significant promise as a commercial method for destroying organics and chlorinated organics in aqueous streams. With hydrocarbons, conversions were 99% and often approached 99.9% at 350°C to 400°C in the presence of a reduced nickel catalyst.

In all of the tests, the reactor was held at temperature for about 1 h. Over 90% conversion was often achieved in 15 to 20 min, based on monitoring the gas production. Catalyst loading and contacting affected the rate of reaction. Tests in a continuous feed reactor are necessary to more precisely determine the residence time requirements. Based on the batch tests, 30 min or less appears to be sufficient in most cases.

Reduced nickel catalysts were the only catalysts found to be effective. Two other transition metals (cobalt, iron), with catalytic properties similar to nickel, were both ineffective in the reduced state and as oxides.

Most of the batch testing was conducted at pressures greater than 4000 psig because the gas produced could not be vented. In a continuous system, where the gas can be vented as it is produced, the pressure can be reduced. To minimize the process energy requirements, the pressure must be high enough to minimize the amount of water converted to steam. The pressure also reduces the size of the reactor. Table 7 shows the enthalpy and specific volume of water at various conditions. Based on these results, optimal operating conditions appear to be 350°C to 400°C and 2000 to 4000 psig. The effect of pressure on reaction rate and conversion needs to be evaluated in a continuous processing unit where the gas can be vented.

Figure 8 is a flow schematic for a conceptual process based on the results to date. The aqueous organic waste is pumped to 2000 to 4000 psig and then passed through heat exchange equipment to heat the waste stream to 350°C to 400°C. Most of the preheat can be provided by heat exchange with the reactor effluent. Some auxiliary heat will be necessary and may be supplied by burning the product gases. If the organic content of the waste stream is 1% or more, it will provide sufficient fuel gas to heat the

TABLE 7. Effect of Operating Conditions on the Enthalpy and Specific Volume of Water

Temperature, °C °F		Pressure, psig	Phase	Enthalpy, Btu/lb	Specific Volume, ft ³ /lb
350	662	3000	liquid	700	0.030
350	662	2000	vapor	1200	0.210
400	752	4000	supercritical fluid	1000	0.060
400	752	3000	vapor	1200	0.150
400	752	2000	vapor	1290	0.300

FIGURE 8. Flow Schematic of Conceptual Process

process. For concentrated organic streams, such as sludges, production of energy from the process either as natural gas, electricity, or shaft power is possible.

Two chlorinated hydrocarbons, trichloroethylene and chlorobenzene were tested, and both were destroyed or converted to nonchlorinated organics (99+% conversion). However, the HCl produced appears to have a detrimental effect on catalyst activity. One possibility for chlorinated hydrocarbons is a two-step process, catalytic hydrodechlorination (LaPierre et al. 1977) followed by catalytic destruction of the resulting dechlorinated hydrocarbon. Additional laboratory-scale studies are necessary to apply catalytic destruction to chlorinated hydrocarbons.

A 1-L continuous flow reactor is currently under construction in the Chemical Process Development Laboratory at PNL. This reactor will be ideal for additional development of the concept. Factors that need to be studied include the effect of pressure and residence time (space velocity) on conversion. There was no indication in the batch tests that catalyst deactivation would be a problem with hydrocarbons; however, this needs to be confirmed in longer tests in the continuous reactor.

Following development in the 1-L continuous unit, the concept should be ready for field demonstration with hydrocarbon wastes in a small transportable unit during 1989. Development of the concept for chlorinated hydrocarbons will require further testing with the batch and continuous reactors prior to field demonstration.

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APPENDIX

RUN SUMMARIES

APPENDIX

RUN SUMMARIES

No data were obtained for the following runs:

<u>Run No.</u>	<u>Cause</u>
1	blank, pressure check
8	leaking gasket
40	rupture disk failure
41	rupture disk failure
42	rupture disk failure
45	rupture disk failure

NOTES

- (a) Filtration prior to analysis resulted in large loss of organic phase. Carbon balance is poor and conversions are based on estimated losses.
- (b) Sample weathered in a hood after GC analysis but before measurement of organic layer.
- (c) GC showed no naphthalene remaining; however, accuracy is limited for these high boiling compounds.
- (d) Sample was ruined and could not be analyzed.
- (e) 50 psig H₂ added initially.
- (f) No chlorobenzene was detected; this represents the limit of detection for the gas chromatograph.
- (g) H₂ generated from the catalyst (Fe + H₂O + Fe₂O₃ + H₂).
- (h) No TCE was detected; this represents the limit of detection.
- (j) Autoclave was contaminated with chlorine from previous runs; these results are not true results with hydrocarbons.
- (k) 2.5% hexone, 2.5% hexane, 2.5% benzene, 2.5% naphthalene in water.

CATALYTIC DESTRUCTION OF HAZARDOUS WASTE

Run #	2	3	4	5	6	7
Date	3/23	3/25	3/27	4/4	4/8	4/9
Catalyst	Ni 1404+ Na ₂ CO ₃	Ni 1404+ Na ₂ CO ₃	Ni 1404+ Na ₂ /CO ₃	Ni 1404	Ni 1404	Ni 1404+ Na ₂ CO ₃
Catalyst Loading, g/g waste	1.2/0.33	1.2/0.33	1.2/0.33	1.2	1.2	1.2/0.33
Temp, °C	400	430	460	460	400	400
Final Press, PSIG	5050	5470	4870	5240	5360	4740
Waste Feed	hexone	hexone	hexone	hexone	hexone	p-cresol
Concentrations, wt%	10.0	10.0	10.0	10.0	10.0	10.0
Waste Conversion, wt%	29.9(a)	74.4(a)	84.0(a)	99.9	99.7	24.0(a)
Carbon Conversion to Gas, wt%	10.2	38.4	42.6	99.1	104	20.5
Gas Yield, mL/g waste	231	726	1011	1626	1416	458
Gas Composition, vol%						
H ₂	41.0	39.5	41.8	12.7	5.1	31.5
CO ₂	44.7	26.9	25.4	30.8	29.6	36.0
CH ₄	12.0	27.9	27.1	54.3	57.8	29.7
C ₂	0.2	0.7	1.0	0.2	0.4	0.4
CO	--	--	--	0.5	--	0.5
Backflush	2.0	5.1	4.5	1.5	7.0	1.4
Other Products, yield, wt%						
Acetone	3.9	9.2	15.1	--	--	
Other Liquids	2.0	--	--			2.9
Wt% Carbon on Catalyst	5.2	5.2	3.6	2.0 2.3 2.6	2.2 2.9	6.7
Mass Balance, wt%	99	100	98	96	100	97
Carbon Balance, wt%	43(a)	58(a)	63(a)	99	104	46(a)

CATALYTIC DESTRUCTION OF HAZARDOUS WASTE

Run #	9	10	11	12	13
Date	4/14	4/21	4/22	4/23	5/6
Catalyst	Ni 1404	--	Na ₂ CO ₃	--	Na ₂ CO ₃
Catalyst Loading, g/g waste	1.2		0.33		0.33
Temp, °C	400	400	400	400	400
Final Press, PSIG	5510	4780	4810	4680	4700
Waste Feed	p-cresol	hexone	hexone	p-cresol	p-cresol
Concentrations, wt%	10.0	10.0	10.0	10.0	10.0
Waste Conversion, wt%	99.9	6.0	7.9	trace	2.1
Carbon Conversion to Gas, wt%	95.1	1.2	1.2	trace	0.4
Gas Yield, mL/g waste	1547	2.2	13.6	--	17.4
Gas Composition, vol%					
H ₂	2.7	20.9	39.4		81.8
CO ₂	35.4	11.0	1.1		1.1
CH ₄	61.9	40.7	42.5		4.4
C ₂	0.1	--	--		3.2
CO	--	--			--
Backflush	--	12.1	17.0		--
Other Products, yield, wt%					
Acetone	--	1.2	2.6		
Other liquids	--	3.5	4.1		1.7
Toluene				Trace	
Wt% Carbon on Catalyst	3.5				6.5
Mass Balance, wt%	96	100	100	100	98.6
Carbon Balance, wt%	95	88	90	106	108

CATALYTIC DESTRUCTION OF HAZARDOUS WASTE

Run #	14	15	16	17	18
Date	5/5/87	5/6/87	5/16/87	5/20/87	5/21/87
Catalyst	Ni 1404	Ni 1404	KAT 479	LZY82	G-90C
Catalyst Loading, g/g waste	1.2	1.2	1.2	1.2	1.2
Temp, °C	400	400	400	400	400
Final Press, PSIG	4500	4600	4400	4280	4350
Waste Feed	hexone	cresol	hexone	hexone	hexone
Concentrations, wt%	2.0	2.0	10.0	10.0	10.0
Waste Conversion, wt%	99.99	99.99	23.1	13.4	14.6
Carbon Conversion to Gas, wt%	96.8	100.0	7.2	2.5	4.8
Gas Yield, mL/g waste	1730	1930	104	30	69
Gas Composition, vol%					
H ₂	27.8	19.0	12.7	12.9	30.1
CO ₂	27.2	28.3	17.5	4.8	21.7
CH ₄	40.7	52.0	42.8	44.8	32.5
C ₂	0.3	0.2	0.7	0.3	0.1
CO	--	--	19.3	27.3	3.0
Backflush	4.0	0.5	7.1	9.8	12.5
Other Products, yield, wt%					
Acetone			15.9	10.3	9.8
Other Liquids				0.6	
Wt% Carbon on Catalyst	2.1	1.3	0.3	1.8	1.1
Mass Balance, wt%	98.9	97.9	97.0	98.5	99
Carbon Balance, wt%	97.2	100.0	128.1	96	81(b)

CATALYTIC DESTRUCTION OF HAZARDOUS WASTE

Run #	19	20	21	22	23	24
Date	5/26/87	5/27/87	5/28/87	5/29/87	6/1/87	6/2/87
Catalyst	Ni 1404	Ni 1404	Ni 1404	Ni 1404	Ni 3288	Ni 1404
Catalyst Loading, g/g waste	0.4	3.6	1.2	0.4	1.2	1.2
Temp, °C	400	400	350	400	400	350
Final Press, PSIG	5070	5400	3610	5290	5280	3890
Waste Feed	hexone	hexone	hexone	cresol	hexone	cresol
Concentrations, wt%	10.0	10.0	10.0	10.0	10.0	10.0
Waste Conversion, wt%	88.9	99.6	99.5	99.9	99.5	99.4
Carbon Conversion to Gas, wt%	77.0	99.4	83.5	99.4	99.6	95.0
Gas Yield, mL/g waste	1017	1367	950	1615	1257	1492
Gas Composition, vol%						
H ₂	8.9	3.8	3.3	5.6	5.0	4.2
CO ₂	24.2	32.2	30.2	35.6	26.9	46.3
CH ₄	56.5	58.7	49.9	56.6	57.2	46.6
C ₂	0.9	0.3	0.8	0.5	0.8	0.5
CO	--	--	--			--
Backflush	9.5	5.0	7.9	1.2	10.1	2.4
Other Products, yield, wt%	backflush isobutane hexone			toluene 0.2% yield		toluene benzene 4% yield
Wt% Carbon on Catalyst	2.4	2.3	5.8	3.9	0.4	3.3
Mass Balance, wt%	97	97	99	102	99	102
Carbon Balance, wt%	88	100	92	100	100	100

CATALYTIC DESTRUCTION OF HAZARDOUS WASTE

Run #	25	26	27	28	29	30
Date	6/3/87	6/4/87	6/8/87	6/12/87	6/15/87	6/16/87
Catalyst	G-47	Ni 1404	Ni 1404	Ni 1404	Ni 1404+ Na ₂ CO ₃	Ni 1404
Catalyst Loading g/g waste	1.2	1.2	1.2	1.2	1.2/0.32	3.6
Temp, °C	400	390	400	400	400	400
Final Press, PSIG	4330	5460	5410	4610	4640	4720
Waste Feed	hexone	naphthalene	hexane	chloro- benzene	chloro- benzene	chloro- benzene
Concentrations, wt%	10.0	10.0	10.0	2.0	2.0	2.0
Waste Conversion, wt%	6.4	99+(c)	99.7	97.8	98.9	98.7
Carbon Conversion to Gas, wt%	3.6	97.0	103.0	2.4	7.5	5.2
Gas Yield, mL/g waste	773	1893	1829	48	247	36
Gas Composition, vol%						
H ₂	29.1	2.2	3.7	43.2	11.2	11.0
CO ₂	24.4	38.3	23.2	51.4	74.6	87.0
CH ₄	18.7	59.5	72.9	5.4	3.9	2.0
C ₂	0.4	--	0.2	--	--	--
CO	2.2	--	--	--	--	--
Backflush	25.3	0.0	--	5.6	10.2	0.0
Other Products, yield, wt%	acetone 2.8%			benzene	benzene	benzene
Wt% Carbon on Catalyst	0.0	3.4	2.6	1.9	2.8	2.4
Mass Balance, wt%	99	99	101	96	99	99
Carbon Balance, wt%	93	97+(c)	103	(d)	18	17

CATALYTIC DESTRUCTION OF HAZARDOUS WASTE

Run #	31(j)	32	33	34	35	36
Date	6/17/87	6/19/87	6/25/87	6/29/87	7/16/87	7/21/87
Catalyst	Ni 1404	G-65B R/S	Ni 1404	C-73	G-65	C-73 R/S
Catalyst Loading, g/g waste	1.2	1.2	3.6	1.2	1.2	1.2
Temp, °C	400	400	400	400	400	400
Final Press, PSIG	5230	5250	4900	4360	4500	4680
Waste Feed	benzene	hexone	chloro- benzene	hexone	hexone	hexone
Concentrations, wt%	10.0	10.0	2.0	10.0	10.0	10.0
Waste Conversion, wt%	90.0	99.4	99.9+(f)	6.9	12.2	5.5
Carbon Conversion to Gas, wt%	84.8	108.0	5.5	1.8	6.0	--
Gas Yield, mL/g waste	1610	1409	71	37	89	454(g)
Gas Composition, vol%						
H ₂	3.9	5.6	80.7(e)	67.7	25.5	99.5(g)
CO ₂	7.2	30.0	18.2	6.4	32.2	--
CH ₄	7.4	55.2	1.1	19.6	27.3	0.5
C ₂	0.4	0.5	--	0.2	0.1	--
CO	0.0	0.8	--	--	--	--
Backflush	1.0	8.7	--	6.1	24.0	--
Other Products, yield, wt%	wt% trace toluene	backflush C ₄	benzene 3.9%	acetone backflush (C ₃ -C ₄)	acetone C ₃ -C ₄	
Wt% Carbon on Catalyst	2.2	5.4	2.5	0.7	4.5	0.0
Mass Balance, wt%	102	101	99	97	97	99
Carbon Balance, wt%	95	108	9	83	89	87

CATALYTIC DESTRUCTION OF HAZARDOUS WASTE

Run #	37	38	39	43	44(j)
Date	7/22/87	7/24/87	7/27/87	8/8/87	8/10/87
Catalyst	Ni 1404	Ni 3263	Ni 1404 C-73 R/S	Ni 1404 NaOH	Ni 1404
Catalyst Loading, g/g waste	3.6	1.2	3.6	1.2/0.38	1.2
Temp, °C	400	400	400	400	400
Final Press, PSIG	4944	4330	4820	4200	4660
Waste Feed	TCE	hexone	chloro- benzene	chloro- benzene	hexone cresol
Concentrations, wt%	2.0	10.0	2.0	10.0	5.0/5.0
Waste Conversion, wt%	99.9(h)	8.1	99.9(f)	99.1	85.0 86.4
Carbon Conversion to Gas, wt%	62.0	2.7	4.0	5.5	36.1
Gas Yield, mL/g waste	340	49	267(g)	77	494
Gas Composition, vol%					
H ₂	42.6	25.5	83.1(g)	8.3	16.9
CO ₂	46.5	31.7	14.1	89.1	33.0
CH ₄	4.0	36.1	1.9	2.7	36.1
C ₂	3.4	--	--	--	0.3
CO	--	3.0	--	--	--
Backflush	3.5	3.7	0.9	--	13.7
Other Products, yield, wt%				Benzene 0.6%	Benzene Toluene
Wt% Carbon on Catalyst	3.7	2.7	2.0	5.5	3.4
Mass Balance, wt%	94	97	96	96.7	98
Carbon Balance, wt%	92	77	7.2	12.4	55.8

CATALYTIC DESTRUCTION OF HAZARDOUS WASTE

Run #	46(j)	47	48(j)	49	50	51
Date	8/4/87	8/15/87	8/24/87	8/29/87	9/1/87	9/8/87
Catalyst	Ni 1404	Ni 1404	Ni 1404	Ni 1404	Ni 1404	G-62RS
Catalyst Loading, g/g waste	1.2	3.2	1.2	1.2	1.2	1.2
Temp, °C	400	350	400	400	400	400
Final Press, PSIG	4560	2900	4610	5200	5348	4450
Waste Feed	mixed waste(k)	TCE	hexone	hexone	hexane hexone benzene naphthalene	benzene
Concentrations, wt%	10.0	5.0	10.0	10.0	2.5% each	10.0
Waste Conversion, wt%	56.8 83.5 35.4 13.8	99.9+(h)	74.8	99.8	99.7	14.9
Carbon Conversion to Gas, wt%	13.1	37.8	32.9	89.0	78.1	62
Gas Yield, mL/g waste	254	208	441	1090	1324	237(q)
Gas Composition, vol%						
H ₂	26.5	44.9	13.1	5.6	4.9	69.6(q)
CO ₂	37.1	39.9	33.9	27.2	29.6	15.7
CH ₄	29.1	3.4	41.3	54.3	61.3	9.2
C ₂	0.2	1.5	0.7	0.7	0.3	0.3
CO	--	3.4	--	--	--	0.9
Backflush	7.1	4.6	11.09	12.3	3.9	4.3
Other Products, yield, wt%	toluene and other hydrocarbon		C ₃ ,C ₄ hydro- carbons	C ₃ ,C ₄ hydro- carbons	other liquids 0.4%	other liquids 8.6%
Wt% Carbon on Catalyst	6.9	4.1	2.7	3.7	5.5	7.2
Mass Balance, wt%	96.5	100	97	99	98	99
Carbon Balance, wt%	71.6	70	58.8	89.3	87	83

CATALYTIC DESTRUCTION OF HAZARDOUS WASTE

Run #	52	53	54	
Date	9/12/87	9/14/87	9/15/87	
Catalyst	Ni 1404	Ni 1404	Ni 1404	
Catalyst Loading, g/g Waste	1.2	1.2	1.2	
Temp, °C	400	400	300	
Final Press, PSIG	5340	5410	2130	
Waste Feed	p-cresol	benzene	hexone	
Concentrations, wt%	10.0	10.0	10.0	
Waste Conversion, wt%				
Carbon Conversion to Gas, wt%	99.5	102	49.8	
Gas Yield, ml/g waste	1739	1929	622	
Gas Composition, vol%				
H ₂	10.4	2.7	5.2	
CO ₂	31.4	35.5	32.3	
CH ₄	57.7	60.6	54.2	
C ₂	0.2	0.3	0.6	
CO	--	--	--	
Backflush	0.4	0.9	7.8	
Other Products, yield, wt%				
Other Liquids	0.8	0.4		
Wt% Carbon on Catalyst	10.9	3.6	3.1	
Mass Balance, wt%	99	104	94	
Carbon Balance, wt%	116	103	56	

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