
Low-Temperature Catalytic Gasification of Wet Industrial Wastes

FY 1993 – 1994 Interim Report

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Pacific Northwest Laboratory
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Richland, Washington 99352



Summary

Process development research is continuing at Pacific Northwest Laboratory on a low-temperature, catalytic gasification system that has been demonstrated to convert organics in water (dilute or concentrated) to useful and environmentally safe gases. The system, licensed under the trade name Thermochemical Environmental Energy System (TEES®), treats a wide variety of feedstocks ranging from hazardous organics in water to waste sludges from food processing. The current research program is focused on the use of continuous-feed, tubular reactors systems for testing catalysts and feedstocks in the process. A range of catalysts have been tested, including nickel and other base metals, as well as ruthenium and other precious metals.

Results of extensive testing show that feedstocks, ranging from 2% para-cresol in water to potato waste and spent grain, can be processed to >99% reduction of chemical oxygen demand (COD). The estimated residence time is about 10 min at 350°C and 21 MPa, not including about 3 min required in the preheating zone of the reactor. The liquid hourly space velocity varies from 1.0 to 4.8 L feedstock/L catalyst/hr, depending on the feedstock. The product fuel gas contains from 40% up to 75% methane, depending on the feedstock. The balance of the gas is mostly carbon dioxide with <5% hydrogen and usually <1% ethane and higher hydrocarbons. The byproduct water stream carries residual organics from 10 to 1000 mg/L COD, depending on the feedstock.

The TEES process has now been demonstrated in continuous-feed, fixed-bed catalytic reactor systems on four scales of operation ranging from 0.03 L/hr to 33 L/hr. The systems have been operated with consistency at conditions of 350°C and 21 MPa. The demonstrated effective heat recovery in a tube-in-tube heat exchanger should be beneficial for economical operation of TEES. Aqueous effluents with low residual COD (<100 ppm) and a product gas of medium-Btu quality have been produced. Catalysts have been demonstrated for over 5 months of operation with reasonable stability. However, catalyst lifetimes and the effect of feedstock contaminants on the catalyst continues to be a major part of our investigations. A wide range of feedstocks have been processed effectively, including various organic model compounds, food processing wastes, and organic chemical manufacturing wastewaters.

The level of development of TEES has progressed to the initial phases of industrial process demonstration. Testing of industrial waste streams is under way at both the bench scale and engineering scale of development. Plans for FY 1995 include the operation of an Industrial Onsite Demonstration Unit at industrial sites of cooperating companies. Long-term testing of actual industrial feedstocks are planned for FY 1995. Testing includes new catalyst formulations identified in this research, which have been produced in larger-scale operations to verify fabrication techniques.

®TEES is a registered servicemark of Onsite*Offsite, Inc., Duarte, California, the process licensee.

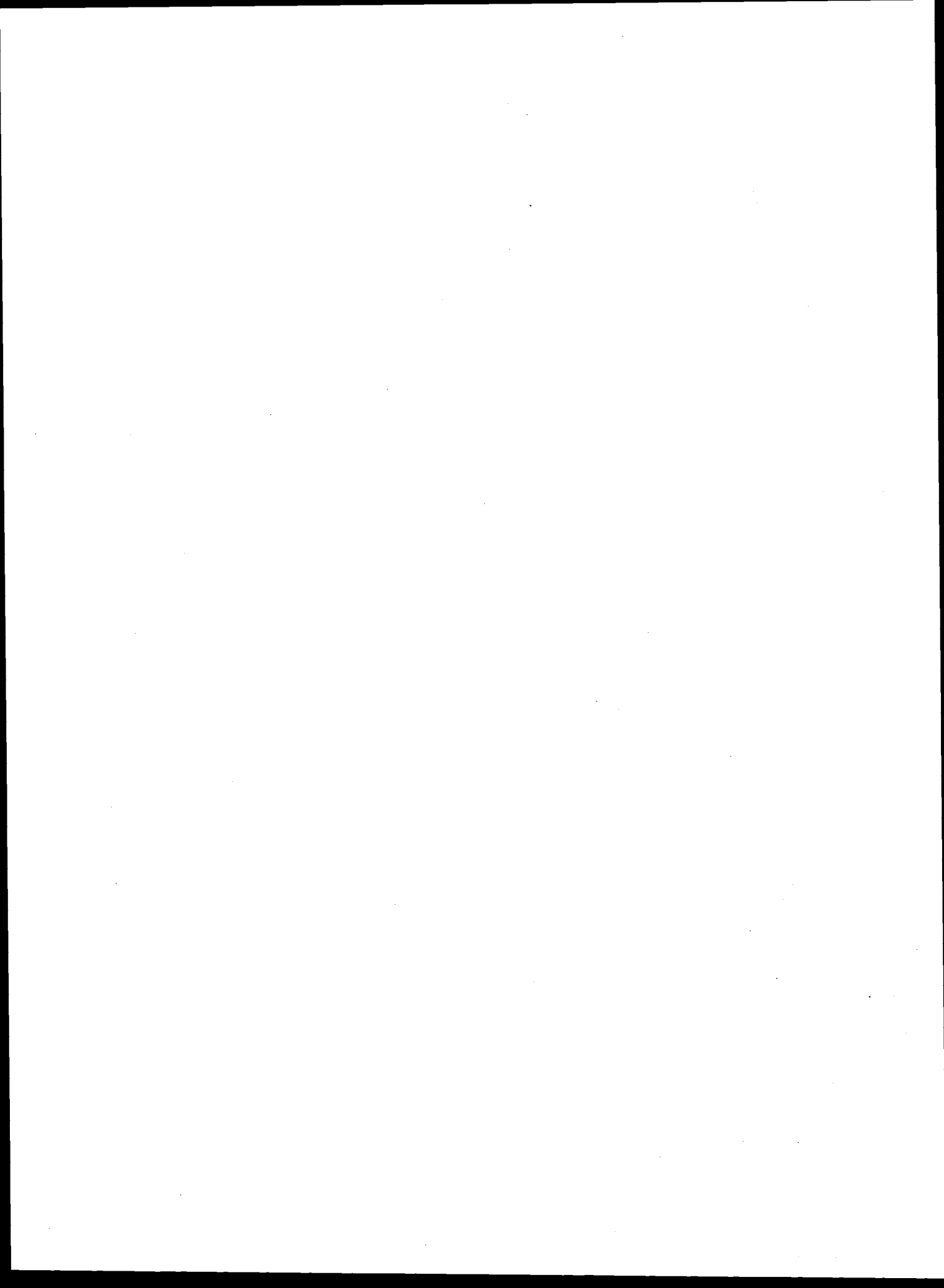
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We acknowledge the continuing support of Onsite*Ofsite, Inc., the TEES process licensee, and its company president, N. G. Banns.

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Contents

Summary	iii
Acknowledgments	v
Introduction and Background	1
Conclusions and Recommendations	3
Batch Reactor Studies	5
Summary	5
Model Compound Tests	5
Preliminary Feedstock Tests	7
Continuous-Flow Reactor Waste Treatment Studies	11
Summary	11
Bench-Scale Reactor Tests	12
Microtubular Reactor Tests	16
Catalyst Activities and Lifetimes	19
Summary	19
Nickel Catalyst Systems	19
Ruthenium Catalyst Systems	21
Extended Batch Tests in Water	23
Zirconia-Catalyzed Aqueous Organic Destruction	23
Continuous-Feed Reactor Tests	24
Long-Term Microreactor Tests	27
Technology Transfer	29
Industrial Interaction	29

Industrial Onsite Demonstrations	29
Future Work	33
Related Publications	35
References	37

Figures

1 Schematic of a Microreactor System	17
2 Industrial Onsite Demonstration Unit Available for Demonstrating TEES Process	31

Tables

1 Model Compound Treatment Test Results	6
2 Preliminary Feedstock Test Results	8
3 Bench-Scale Industrial Waste Test Results	13
4 Innovative Nickel Catalysts Tested in TEES	20
5 Results of Tests with Innovative Nickel Catalysts	21
6 Ruthenium Catalysts Tested in TEES	22
7 Results of Tests with Ruthenium Catalysts	22
8 Effect of Reduction Temperature on Ruthenium Catalysts	24
9 Hot Pressurized Water Treatment of Catalytic Materials	25
10 Comparison of TEES and ZrO ₂ -Catalyzed Gasification	25
11 Bench-Scale New Catalyst Test Results	26
12 Long-Term Experimental Results	28
13 Information Requests for TEES	30

Introduction and Background

The catalytic gasification system discussed in this report operates in a pressurized water environment to convert organics in water to gases that are safe for the environment and often useful as auxiliary fuels. The system, developed at Pacific Northwest Laboratory (PNL),^(a) has undergone continuous development and refining for over 12 years to address commercial needs. The initial experiments, which were performed for the Gas Research Institute, were aimed at developing kinetics information for steam gasification of biomass in the presence of catalysts.¹ In that work, the combined use of alkali and metal catalysts was first reported² for gasification of biomass and its components at low temperatures (350°C to 450°C).

From the fundamental research evolved the concept of a pressurized, catalytic gasification system for converting wet biomass feedstocks to fuel gas.³ Extensive batch reactor testing⁴ and limited continuous reactor system (CRS) testing⁵ were sponsored by the U.S. Department of Energy. A wide range of biomass feedstocks were tested and the importance of using a nickel metal catalyst was identified.

The applicability of this process for treating industrial processing wastes was first studied by Baker et al. using hazardous wastewater streams, and results were reported for both batch reactor tests^{6,7} and continuous reactor tests.⁸ The concept application was further expanded to encompass cleanup of food processing wastes.⁹ Continuing work at PNL has focused on refining the catalyst¹⁰ and scaling the system to long-term industrial needs and includes both bench-scale and engineering development systems.^{11,12}

The process is licensed as the Thermochemical Environmental Energy System (TEES®) to Onsite*Ofsite, Inc., of Duarte, California, a turnkey design engineering and construction management firm. In 1989 TEES was recognized with an R&D 100 Award from *Research and Development Magazine* as one of the top 100 new technical developments to reach the marketplace.

This report is a follow-on to the Interim Reports from 1989-90¹³ and 1991-1992,¹⁴ which reviewed the results of the studies conducted with batch and continuous-feed reactor systems. The discussion here provides details of experiments on the wide range of potential feedstock materials conducted in a batch reactor; tests performed in continuous-flow reactors at three scales; and development of new catalyst materials. The activities conducted for further transferring the technology to industry are also discussed.

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Conclusions and Recommendations

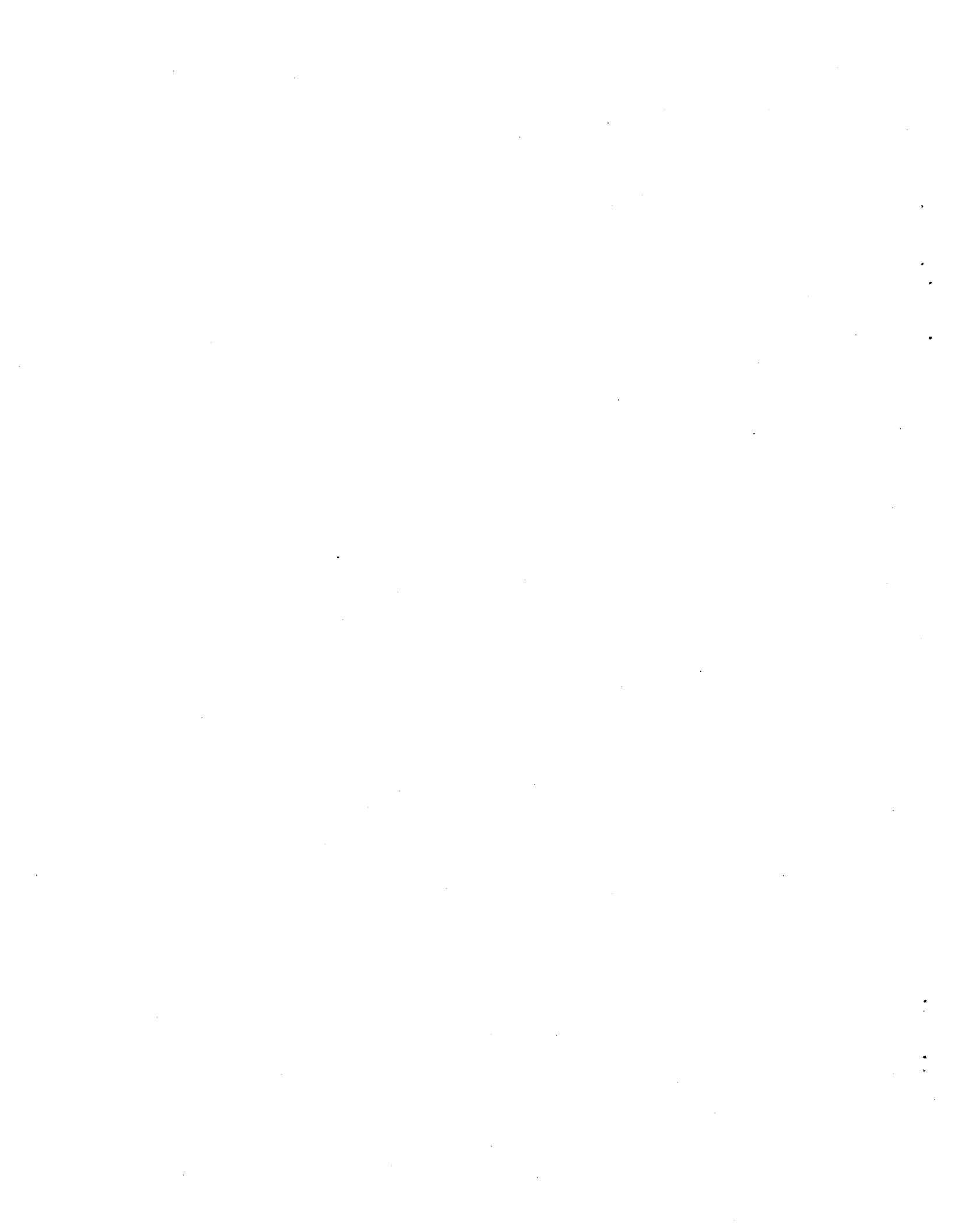
As a result of the work presented here, we can make the following conclusions and recommendations.

Conclusions

- A wide range of organic materials in water can be converted to near extinction in TEES. High methane yields are produced from reaction of the organics with water, and the product effluent is substantially clean.
- Of the wide variety of catalysts evaluated, several useful compositions have been identified. In particular, good stability over 5 months of operation was verified for one formulation. Trace contaminants in feedstocks can have deleterious effects on the catalyst.
- The tubular reactor design has been tested at three scales of operation. Scaleup of the fixed-bed tubular reactor to 5 gallons per hour, including heat recovery by exchange between the feed and the reactor effluent, has been demonstrated successfully.

Recommendations

- Continue bench-scale testing of TEES to include other feedstocks of industrial interest and verify catalyst compatibility. These tests are a necessary precursor to demonstration tests. Because TEES has such wide application to different feedstocks, effects of specific components are still unknown, even at this point in development after so much testing.
- Perform long-term tests to evaluate catalyst stability with industrial waste streams. Catalyst cost is a key economic factor for TEES. Catalyst lifetime must be determined in order to evaluate process economics with certainty.
- Operate the Industrial Onsite Demonstration Unit to provide in-plant experience with TEES for potential users. TEES is a unique processing system unlike other wet waste treatment systems. At this point in the process development, industrial experience is a key factor needed to accomplish commercial implementation of the technology.



Batch Reactor Studies

Batch reactor studies on a wide range of industrial wastes and model organic functional types are discussed in this section. These batch reactor tests were an important beginning step in developing industrial systems based on this technology. They provided a quick and cost-effective method to determine applicability of TEES to the specific feedstock. While these tests provided only a preliminary view of the kinetics, catalyst compatibilities, and products, they gave an initial screening of the potential use of a feedstock.

Summary

The batch reactor was a standard Autoclave Engineers bolted-closure vessel modified in our laboratory to allow samples to be withdrawn at reaction conditions. With this capability, a single batch cycle could provide several data points over time to allow a preliminary assessment of kinetics. The reactor and procedure are detailed in an earlier report.¹¹ For the experiments described here, a nominal 10 wt% organic in water feed was used with a standard nickel catalyst (Engelhard Ni-0750, powdered). Standard test temperature was 350°C for 1 to 2 hours. Multiple gas samples were recovered during each test to increase the amount of information gained from each test.

A large number of tests were performed to evaluate the feedstock effects; in total the tests included 54 experiments, 31 performed with actual industrial waste samples. A Treatability Test Tracking program had to be set up in the laboratory for the tests with actual hazardous waste samples. All hazardous waste samples were logged in upon receipt and tracked through the testing cycle until their final disposal. Reporting of tests was made to Laboratory Safety at PNL and was forwarded to the Washington State Department of Ecology.

Industrial input to this research program was an important aspect. For these batch tests, waste samples were received from 16 different producers both directly and through our process licensee.

Model Compound Tests

A number of different model compounds were tested to extend our understanding of the effect of various functional types in the reaction process. The results of these tests are given in Table 1. Feedstocks are added at 10% in water unless otherwise noted. These test results show a variety of important feedstock effects, which are discussed below.

Aniline and pyridine were tested to evaluate nitrogen-containing functional groups as potential feedstocks for TEES. The high chemical oxygen demand (COD) conversions suggest that these groups would be excellent feedstocks for TEES. The fate of the nitrogen in these tests is unclear. Ammonia analysis by a semi-quantitative test strip method suggested that little ammonia was formed, in contrast to expectations based on earlier nitrogen-containing feedstocks.¹¹ Nitrate analysis by the colorimetric method found only low levels of nitrate. Less than 1% nitrogen was found in the product gas. Overall, the nitrogen balance for these tests was poor, 6% to 8%.

Table 1. Model Compound Treatment Test Results (all tests at 350°C, autogenic pressure, nominal 2-hr test)

Feedstock	Catalyst ^(a) / Cocatalyst	Product Gas Composition, vol%					Destruction of COD, %	Product COD, ppm	Other, ppm
		CH ₄	CO ₂	H ₂	C ₂	BF			
Aniline (14%)	Ni only	70.7	22.7	3.3	0.6	1.7	99.7	1450	10 NH ₄ ⁺ + 650 NO ₃ ⁻
Pyridine	Ni only	65.2	30.2	1.3	1.1	1.5	99.2	2500	10 NH ₄ ⁺ + 750 NO ₃ ⁻
Benzene Sulfonic Acid	Ni only	0.1	7.3	92.8	0.0	0.0	81.2	30,500	
p-Cresol	(NH ₄) ₂ SO ₄	7.1	0.5	92.5	0.0	0.0	NA	saturated	6.2% gas
p-Cresol	1/10 (NH ₄) ₂ SO ₄	38.1	44.4	16.1	0.4	0.5	NA	saturated	18% gas
p-Cresol	NaOH	60.8	27.8	10.5	0.3	0.6	NA	saturated	68% gas
p-Cresol	1/10 NaOH	56.3	39.9	3.2	0.3	0.4	99.7	1180	66% gas
p-Cresol	Na ₂ CO ₃	53.7	33.8	11.7	0.3	0.5	NA	saturated	52% gas
p-Cresol	1/10 Na ₂ CO ₃	58.5	35.9	4.6	0.3	0.6	99.97	105	72% gas
p-Cresol	NaHCO ₃	40.0	40.1	19.0	0.3	0.4	NA	saturated	43% gas
p-Cresol	1/10 NaHCO ₃	61.2	36.9	1.0	0.4	0.6	97.2	10,625	74% gas
p-Cresol	Ni only	57.3	37.2	4.7	0.3	0.5	99.9	210	91% gas
Phenol	Ni only	59.1	39.3	1.0	0.2	0.6	99.9	250	90% gas
Phenol	no catalyst	0.0	40.0	60.0	0.0	0.0	NA	saturated	0.09% gas
Phenol	ATP/Ca	58.7	39.2	1.2	0.4	0.6	99.9	175	

(a) All tests included Ni-0750 catalyst except the phenol test specified as having no catalyst.
BF = backflush from chromatography columns, assumed to be higher hydrocarbons.

The sulfate-containing tests were performed to evaluate the effect of sulfur on the nickel catalyst. While reduced sulfur is well-known as a catalyst poison for nickel metal, the sulfate is expected to be more benign. The benzene sulfonic acid was destroyed to a great degree based on the large decrease in COD; however, the organic sulfonate group, and its strong acid characteristic (initial pH of 0.3), had an extraordinary effect on the catalyst. The nickel metal was reacted to a large extent to complex, unidentifiable hydroxide/oxide minerals. X-ray diffraction (XRD) analysis of the spent catalyst material suggested the possibility of carbonate or citrate structures as well. In the case of the ammonium sulfate tests, there was a strong inhibition of the p-cresol gasification. With the high loading of ammonium sulfate (5 wt% in the feedstock solution) the gasification stopped almost entirely. XRD analysis of the used catalyst after the test showed a significant portion of the nickel metal (approximately 30%) was changed to the oxide form. Even with a lesser amount of added ammonium sulfate (0.5 wt%), the inhibition of the p-cresol gasification was still evident.

The effect of alkali in TEES has been studied on a number of occasions relative to the alkali metals found in some feedstocks. The tests reported here are meant to clearly demonstrate the inhibition of alkali on the TEES process in the case of monomeric chemical feedstocks. The sodium was added in equimolar concentration for the three alkalis tested, hydroxide, carbonate, and bicarbonate. The high loading (5 wt % sodium) had a strongly negative effect in all three cases. The gasification was inhibited to the extent that sufficient p-cresol remained to saturate the water and form a separate phase, indicating a less than 80% conversion. The hydrogen concentration in the product gas was elevated compared with the alkali-free test, suggesting catalysis of the water-gas shift reaction, a subject of our earlier research.¹⁵ At 1/10th molar loading (0.5 wt % sodium), the effect was nearly eliminated. The gas composition was nearly the same as the alkali-free test, and the COD conversion was high. Recovery of carbon as gases, even after correction of alkali carbonate formation, was still somewhat lower than expected. The effect of pH was not consistent throughout the tests. The differences among the three alkalis were not great, but the carbonate, which produces the intermediate pH, appeared to have the least negative effect.

For comparison, a second model compound, phenol, was evaluated. Phenol is less toxic, and wastewater contaminated with it is less severely regulated than p-cresol. The data in Table 1 show that phenol reacts in a manner similar to p-cresol. It has been used in this project since July 1993 as the compound for comparative tests of different catalysts. As the data indicate, phenol is quite stable in the aqueous media in the absence of a gasification catalyst (only 0.09% of carbon recovered as gas). However, it is nearly completely gasified in the presence of an active nickel catalyst (90% of carbon recovered as gas and 99.9% reduction of COD).

One model compound test was performed using phenol in the presence of adenosine triphosphate and calcium gluconate (ATP/Ca in Table 1). These two additives were introduced to mimic biological sources of calcium and phosphorus. Calcium hydroxyphosphate (hydroxylapatite) has been identified as a catalyst deposit in tests with biomass feedstocks like spent grain and cheese whey.¹⁴ Hydroxylapatite was determined to be a stable molecule for calcium and phosphate to form at TEES processing conditions.¹⁶ Following the ATP/Ca test, hydroxylapatite was also identified in the residual catalyst material. This result shows that hydroxylapatite can form at TEES processing conditions from the biological forms of calcium (organic acid salts) and phosphorus (adenosine phosphate energy transfer agents) commonly found in food processing waste feedstocks. In a single cycle, the addition of the calcium (1255 ppm) and phosphorus (1090 ppm) did not affect the catalyst activity, as shown by the data in Table 1.

Preliminary Feedstock Tests

A number of different industrial waste feedstocks were evaluated in the batch reactor system. The results of these tests are shown in Table 2.

The first two wastes were provided through the Pacific Northwest Pollution Prevention Research Center. These waste stream samples were recovered from a fish processing plant in Astoria, Oregon, and each processed at 10% dry solids in water. High COD destruction was achieved in these two tests, although the gas product composition is indicative of less favorable catalyst activity. The high ammonia contents in the product water effluent may require further treatment. High ash contents were measured in these two feedstocks, indicating a potential for inorganic deposits in the catalyst bed.

Table 2. Preliminary Feedstock Test Results (all tests at 350°C and autogenic pressure)

Feedstock	Time at Temperature	Product Gas Composition, vol%					Destruction of COD, %	Product COD, ppm	Other, ppm
		CH ₄	CO ₂	H ₂	C ₂	BF			
Shrimp waste	100 min	31.8	43.1	21.3	1.3	2.5	98.2	1490	7983 NH ₄ ⁺
Bottom fish	105 min	23.3	46.7	26.3	1.4	1.7	85.4	23,500	6711 NH ₄ ⁺
1% unleaded	118 min	17.6	33.2	49.2	0.1	0.0	99.9	30	21% gas
1% leaded	122 min	20.7	43.0	36.1	0.0	0.0	99.6	135	29% gas
10% unleaded	120 min	64.0	30.7	4.7	0.1	0.4	99.95	170	33% gas
10% leaded	120 min	53.1	32.5	11.6	0.1	2.7	99.8	620	29% gas
Spent grain									
filtered	120 min	34.2	51.3	12.9	1.3	0.1	99.6	120	100% gas
ion stripped	120 min	6.6	70.0	21.4	0.8	1.1	41.7	25,000	40% gas
acid washed	131 min	40.9	46.4	11.2	0.8	0.6	99.2	480	58% gas
ion exchanged	120 min	43.2	43.2	11.3	0.9	1.3	97.8	2750	48% gas
Potato crumbs									
MeCl ₂ rinsed	95 min	42.0	43.9	13.0	0.7	0.4	99.8	260	37% gas
10% solids	95 min	49.2	41.8	8.4	0.4	0.3	99.9	117	23% gas
33% solids	130 min	53.4	42.1	3.5	0.6	0.3	99.6	1050	38% gas
51% solids	120 min	51.6	43.7	3.6	0.6	0.4	99.7	1200	36% gas
Polyol wastewater									
as received	75 min	2.4	36.6	60.5	0.3	0.0	94.8	520	100% gas
ion stripped	45 min	6.5	52.8	40.1	0.4	0.0	98.8	87	96% gas
Gasification wastewater	125 min	5.6	42.4	52.5	0.0	0.0	93.6	290	29% gas

All tests included Ni-0750 catalyst.

BF = backflush from chromatography columns, assumed to be higher hydrocarbons.

Four tests were performed with gasolines in water as a means to evaluate the potential for petroleum refinery wastewater or tank cleanout wastewater treatment with TEES. High COD destructions were achieved in all tests, but low carbon balances are reflected in the low level of gasification reported. Some loss of the gasoline was demonstrated in a cold batch test in which 1.21 g were lost from a charge of 8.60 g gasoline in 198.04 g water by simply filling the reactor, purging it with the nitrogen cover gas, and opening it again. However, it is clear that gasoline components can readily be processed in TEES. These batch tests show reduction to the low tens of ppm COD with a starting

material containing about 30,000 ppm COD. There is no apparent effect from the lead in the gasoline; however, longer tests would likely be required to see an effect on catalyst degradation.

Four types of a brewer's spent grain feedstock were tested. The feedstock was malted barley from Anheuser-Busch Companies in St. Louis, Missouri, and was either filtered, ion stripped, acid washed, or ion exchanged. The tests were made to evaluate the effect of ion exchange to remove inorganic ions from the spent grain. The first "filtered" sample demonstrates the ready reaction of the dissolved spent grain materials in the TEES process. The second test demonstrates that ion exchange of all ions from the spent grain (following preliminary acid digestion) actually leaves it less reactive than the original spent grain. This effect is not surprising considering the catalytic effect of the alkali metals in spent grain. The third test shows that using only the acid digestion process has no negative effect on the process result. The fourth test shows that an ion exchange of sodium for the calcium and magnesium (following mild acid digestion) also yields a highly reactive feedstock. This result is particularly important in light of the catalyst poisoning problem identified earlier that resulted from calcium salt deposition in the bed in continuous-flow reactor tests.¹⁴

The potato crumb tests were performed with a feedstock from the Lamb-Weston potato processing plant in Richland, Washington. The crumbs were oil-soaked potato pieces recovered from the bottom of the fryer, which are useless as animal feed and are currently land-filled. As high-molecular-weight hydrocarbons are known to be less reactive in TEES, the first test was performed with the "potato-only" material after the oil was washed off with methylene chloride. This test can be compared with the whole crumbs test at 10% solids as that parameter was held constant. Only very minor differences (within the range of experimental error) occurred. The two higher concentration feedstock tests went equally well. All the tests suggest that potato crumbs, as produced, would be a good TEES feedstock.

The two polyol wastewater tests were performed to assess the utility of ion exchange as a pretreatment step to remove potassium from the stream. The polyol water was passed over the acid form of a cation exchange resin so that potassium in the stream was replaced with protons. Both the "as-received" waste and the pretreated stream were effectively treated by TEES. It is apparent that in the as-received waste the potassium acts to catalyze the water-gas shift reaction to produce more hydrogen and inhibit methane formation. Also, the preliminary kinetics information produced in these tests suggests that the potassium-stripped stream should be processed more quickly in TEES.

The last listing in Table 2 is for a test with a wood gasification wastewater. The feedstock was produced in an experimental reactor equipped with a venturi scrubber for removal of contaminants from the gas product. The wastewater is representative of one type of gasifier and contains a low level of organic and inorganic contaminants. In the TEES test, the COD destruction was moderately high, but the gas composition suggests poor catalyst activity (low methane yield).

Continuous-Flow Reactor Waste Treatment Studies

The continuous-flow reactor studies were designed to provide information for further TEES process scale up for industrial use. By operating TEES at three different scales with selected catalysts, we have determine specific conditions for commercial optimization.

Summary

Gasification tests were carried out in three scales of fixed-bed catalytic tubular reactor. The bench-scale unit was described in detail in an earlier report.¹³ The unit consisted of a 6 ft long x 1 in. I.D. tube that was fed from a cylindrical feed tank by a reciprocating plunger pump. The reactor was heated by an electrical resistance furnace and essentially served as both the preheater and the reactor. Pressure was controlled in the reactor by a dome-loaded, back-pressure regulator. The pressure regulator was followed by a condenser/separator system in which liquid samples were recovered. Uncondensed product gas was passed through flow meters and vented.

A microtubular version of this reactor system was used initially for catalyst lifetime studies. All the components in the bench-scale unit were the same for the microtubular reactor system except for the pump and the reactor. A smaller reciprocating plunger pump was used to feed a reactor consisting of 12 in. of 1/2-in. 316SS tubing. In addition to the reactor, there was a preheater section consisting of 7 ft of 1/8-in. tubing. Both the reactor and the preheater were contained in the electrical resistance reactor furnace.

During FY 1994, a dual microreactor system was assembled to allow long-term catalyst testing to continue while bench-scale test operations were also under way. This system included components for two independent reaction systems. The systems were similar to the original microreactor system except that the reactor and preheater were contained in a small tubular furnace. The systems included individual feedtanks, pumps, condensate recovery systems, and gas meters. Continual gas analysis was provided by the Foxboro process gas chromatograph used in the bench-scale reactor. All process data were recovered and stored by a Sentinel data acquisition system.

A mobile Industrial Onsite Demonstration Unit based on the tubular reactors being used at PNL was designed and built within a fifth-wheel mounted trailer. The system is designed to operate at a scale of 60 gallons per day of wet feed, and contains four 3 1/2 ft x 1 1/2 in. I.D. fixed-bed tubular reactors and supporting equipment to achieve conversion of waste to clean water and fuel gas. Design working conditions for the reactors are 350°C at 22.1 MPa.

The tests in these reactor systems totaled an impressive amount of operating time on stream. The bench-scale reactor was operated in 22 experiments lasting from 5 to 13 hours for a total operating time on stream of 155 hours. Eight microreactor tests were performed lasting from 60 to >1300 hours for a total operating time on stream of over 4500 hours. The Industrial Onsite Demonstration Unit was operated in 2 tests lasting for a total on-stream operating time of 132 hours.

Bench-Scale Reactor Tests

Bench-scale tests are the next logical step in the process development following a batch reactor test. Tests in the bench-scale reactor have been performed primarily to verify operability in continuous TEES systems. These tests also provide a preliminary verification of catalyst stability in processing a specific feedstock. The test results are given in Table 3.

The first group of tests was performed using wastewater streams. The POSM water is waste from a propylene oxide/styrene monomer process. The polyol waters are from several polypropylene oxide plants. The POSM water is a solution (~10 wt%) of sodium salts of phenol and benzoic acid with propylene glycol in water. As shown in earlier studies,¹¹ the sodium salts of these components react less readily than organics only.

In the first, test the full concentration POSM waste stream was tested. After 3 hours on stream the reactor plugged. After shutdown and cleanout of the system the catalyst bed was found encased at one point toward the lower end of the bed with crystalline sodium carbonate and sodium carbonate hydrate. Apparently, the carbon dioxide gas product reacts with the dissolved alkali and at sufficient concentration precipitates from the reaction solution onto the catalyst pellets. The solubility limit of Na_2CO_3 is given as 1.96 wt% at 348°C in pressurized liquid water (~8500 ppm Na).¹⁷ The concentration of Na measured in the feed, 24,972 ppm, is well above this limit, and Na_2CO_3 would be expected to precipitate. Later tests (see Table 3) showed that diluted POSM water could be processed without plugging of the catalyst bed, but high conversion of COD could only be achieved at relatively low processing rates. Lower temperature tests were also carried out in order to avoid precipitation of Na_2CO_3 (the solubility limit of Na_2CO_3 increases to 8.0 wt% at 300°C). Other interesting effects were noticed in these tests:

- Increased methane and decreased hydrogen concentrations in the product gas at lower temperature—predictable from thermodynamics.
- The high pH waste stream, 12.5, was nearly neutralized (6.7 to 7.0 and 7.4 to 8.0 when processing at 350°C and 300°C, respectively) in the TEES process by the production of carbon dioxide and its formation of sodium salts and carbonic acid.
- Some of the unreacted organic could be recovered as a separate liquid product phase containing benzene, toluene, phenol, and cresol.
- Na_2CO_3 deposition on the catalyst caused a dramatic reduction of surface area and pore volume, 12 m²/g and 0.07 cc/g vs. 272 m²/g and 0.29 cc/g in the fresh catalyst.

The polyol wastewater tests included early tests with the raw wastewater and a later test with potassium-stripped wastewater. In the early tests, the polyol was destroyed by the TEES process but at rates much lower than expected. While potassium was a significant component in the feedstock (3400 ppm), its precipitation and plugging of the catalyst bed was not an important consideration. K_2CO_3 has a higher solubility relative to Na_2CO_3 (although K_2CO_3 solubility data were not found for as high a temperature as 350°C). By difference in concentration of potassium in the feed than in the effluent, potassium was found to have deposited into the catalyst bed during the first 4 hours of

Table 3. Bench-Scale Industrial Waste Test Results

Feedstock	Catalyst	Product Gas Composition, vol%					Destruction of COD, %	LHSV 1 / 1/ hr	Gasification ^(a) of carbon, %
		CH ₄	CO ₂	H ₂	C ₂	BF			
POSM wastewater									
220,000 ppm	BASF	59.6	34.6	5.0	0.3	0.5	84.9	1.44	77
126,000 ppm	part reduced	65.0	28.7	5.0	0.5	0.8	48.0	1.09	46
13,600 ppm	BASF	59.5	36.5	2.6	0.4	0.7	85	0.92	85
177,500 ppm	BASF@302°C	75	23	0.8	0.6	0.7	42	0.85	36
63,500 ppm	BASF@312°C	75	22	1.1	0.5	0.8	48	1.09	48
26,000 ppm	BASF@304°C	82	15	1.6	0.6	0.7	50	1.00	46
Polyol wastewater									
as received	BASF	53	1.7	32	7.8	5.6	68	3.11	96
as received	BASF	48	0.5	35	7.0	5.0	73	1.84	100
as received	BASF	32	15	37	2.4	2.3	85	1.15	103
as received	BASF	38	7.5	42	3.4	3.5	89	0.81	99
ion stripped	BASF ^(b)	36	36	26	0.9	0.2	99.0	4.14	20
ion stripped	BASF ^(b)	57	32	10	0.8	0.2	97.0	4.29	38
Acrylonitrile wastes									
K013	BASF	54.1	37.5	4.7	2.2	1.0	93.9	2.18	77
K011,013,014	Ni-0750	86.5	8.4	4.2	0.9	0.0	83.1	1.74	72
nitrophenol	BASF	30.1	0.2	12.0	0.2	0.2	55.1	2.66	121
Spent grain									
ion exchanged	BASF ^(b)	55	40	2.0	0.0	1.5	99.5	2.09	80
ion exchanged	BASF ^(b)	58	33	2.4	0.0	1.5	98.3	3.46	64
Vinasse	BASF ^(b)	56	40	2.2	0.8	0.5	88.6	3.27	97
Potato crumbs									
350°C	BASF ^(b)	52.3	41.1	5.6	0.5	0.4	77.0	2.24	55
350°C	BASF ^(b)	51.9	42.7	4.3	0.6	0.5	84.8	1.99	60
420°C	BASF ^(b)	54.2	35.9	9.3	0.3	0.1	97.4	2.35	94

(a) Gas yields include a correction for carbon dioxide dissolved in the aqueous effluent as alkali and ammonium bicarbonates when alkali is found in the feed or ammonia is found in the product aqueous.

(b) Modified BASF catalyst (mod2).

operation. At that point, an equilibrium was achieved, and nearly equal amounts of the potassium were found in the feed and the effluent. Washing the bed with water removed some of the potassium, but it was reloaded to the catalyst upon restart of the feed. The high gasification levels reported are probably due to an over-correction for bound carbon dioxide in the water when not all the potassium came through the reactor. The activity of the used catalyst from these polyol tests was significantly reduced as shown by the activity tests in a batch reactor with p-cresol as the feed. The used catalyst produced only 11% gasification compared with 41% gasification from the same type of catalyst used in the bench-scale reactor to process p-cresol solution.

A second polyol wastewater was treated by TEES following ion exchange pretreatment. As described in the Batch Reactor Test section above, the ion exchange involved passing the waste through a column filled with the proton form of a resin, which exchanged protons for the potassium. In this process, the pH was reduced from 12.75 to 4.5 while a minor dilution occurred from 10,375 ppm COD to 9940 ppm COD. With this potassium-stripped wastewater, sufficient COD destruction could be accomplished at about eight times the rate achieved in the earlier tests, and these later tests used a waste at about twice the concentration of the earlier tests. Another important difference is the use of the modified BASF catalyst, which has shown a better long-term stability (see the Catalyst Development section below) and may also be somewhat more active. The higher conversion results include a better breakdown of hydrocarbon gases to methane. In the absence of alkali, the water-gas shift reaction is less obvious, as shown by less hydrogen production. The inordinately low levels of recovery of gas products are not yet understood.

A series of bench-scale tests were also performed with wastewater streams from acrylonitrile manufacturing. A mixed-nitrophenol simulated wastewater stream was also tested. The K013 (stripper column bottoms) is a mixture of approximately 2% organics (nitriles) in water. The pH of this sample was measured at 10.1, significantly higher than the slightly acid, 6.0, pH typical of this stream. The feedstock showed high activity for COD reduction (from 16,900 ppm to 1030 ppm), with significant ammonia production (2200 ppm) in the aqueous effluent stream. Toward the end of the test, some loss of catalyst activity was evident based on higher COD measurements and higher hydrogen and ethane concentrations in the product gas.

Further evidence in catalyst activity loss was found in reusing the catalyst bed. The K014 waste stream (ACE column bottoms, which is 5 wt% NaCN in water with high boiling organics) was processed through this catalyst bed on the following day. Reduction in COD was very low, <30%, compared with 94% in the batch reactor. Follow-on processing of phenol gave equally poor results. Additional tests included batch reactor tests of the used catalyst samples from after the K013 test and again after the K014 test. In both batch tests, the catalyst was essentially inactive, i.e., no methane production from p-cresol. Even after a reduction pretreatment of the catalyst from the K014 test, there was no catalyst activity evident in a batch test with p-cresol.

The test with the mixed waste stream containing three of the U.S. Environmental Protection Agency (EPA)-listed acrylonitrile waste streams (K011,013,014) showed initial activity which decreased during the course of the run. Over the course of the 8 hour run, the processing rate was decreased to 0.53 liquid hourly space velocity (LHSV), and COD reduction dropped to only 38%. Methane concentration in the product gas remained high (71%), while hydrogen and ethane increased to 16% and 11%, respectively. The reason for the loss of catalyst activity was not identified, but analysis indicated that neither the loss of catalyst surface area nor metal dispersion was the cause, as these parameters remained within acceptable bounds.

The test of the nitrophenol solution was performed as a simulant of a hazardous wastewater stream. The solution contained 0.65% picric acid, 0.05% dinitrophenol, 0.2% nitrobenzene, and 3.42% ammonium hydroxide and had a pH of 8.5. This feedstock did not react readily in TEES. In addition to the gas product components listed in Table 3, the product gas also contained 2% carbon monoxide and 55% nitrogen. The nitrogen is expected from the reaction of the ammonia with nitrate produced by TEES destruction of the nitroorganics. During the test, the catalyst underwent a more rapid metal agglomeration than is normally seen. The nickel metal crystallite size determined by XRD was calculated at 450Å after just 10 hours on line. The higher partial pressure of CO in the reactor is a possible explanation of the metal migration through the formation of unstable nickel carbonyls.

Three tests were performed with food processing wastes. A spent grain sample and a rum vinasse sample were ion exchanged prior to TEES processing. The potato crumbs described earlier were processed directly. The ion exchange was used to remove primarily calcium (but all multi-valent ions) from the feedstocks by sodium substitution so that calcium phosphate deposits should not form in the catalyst bed. The spent grain was first hydrolyzed with a mild nitric acid treatment to make the calcium available for the ion exchange. The hydrolyzed spent grain was then filtered prior to the ion exchange treatment, while the vinasse was ion exchanged directly. Analysis showed that the calcium level in the spent grain was reduced below 60 ppm by the treatment. The potato crumbs contained < 60 ppm calcium as received, while the spent grain contained 130 ppm and the vinasse 1600 ppm calcium.

The three feedstocks were readily processed in TEES at 350°C. Much higher conversion was achieved with the spent grain (4 wt% dry solids) than has been reported earlier.^{13,14} Pumping the feed was difficult after remixing the filtered solids back into the ion-exchanged material. Plugging occurred at the inlet to the bed where stainless steel shot was used as spacers, and the feed had not yet contacted the catalyst bed. There was a slight trend indicating loss of catalyst activity over the 7-hour run. In the vinasse test (5 wt% dry solids) there also appeared to be a trend toward lesser catalyst activity. Sugar cane contains a sulfur component which finds its way into the vinasse during the rum production process. Sulfur reaction with the catalyst was suspected as the cause of the loss of activity. However, elemental analysis of a sample of the spent catalyst after the vinasse test showed no evidence of sulfur. The potato crumbs (14 wt% dry solids) were processed at two temperatures during a 12-hour run. COD reduction was good at the conventional 350°C operating temperature, but the aqueous product contained a white emulsion which was later determined to be long chain hydrocarbons. These long chain hydrocarbons (up to C₁₇ and primarily C₁₅ and C₁₇), which are less readily processed in TEES, were produced from the frying oil. At higher temperature, these components were more completely broken down to gas. There was no evidence of catalyst bed plugging in any of these three tests.

Two bench-scale tests were also performed with a groundwater sample from the McClellan Air Force Base near Sacramento, California, which contained chlorinated hydrocarbon solvent contaminants. A gas chromatograph with an electron capture detector was used to monitor the chlorinated substances. Analyses from McClellan showed numerous components in the water at levels of 5 to 400 ppb. Our analysis showed at least 11 components at 100 ppb or less. The minimum detectable amount would be 1 ppb, and all samples acquired after TEES processing of this groundwater showed no detectable amount of chlorinated solvents. COD reductions were 85% to 92% at space velocities from 1.95 to 1.5 l/l/hr starting from a feed with 1120 ppm COD. These results are particularly noteworthy because similar results were obtained both in a test with the nickel catalyst and in a test

without the nickel catalyst in the reactor. The components treated in this test were multi-carbon compounds as compared to our earlier report for non-catalytic treatment of single-carbon chlorinated solvents.

Microtubular Reactor Tests

The dual microtubular reactor system was assembled based on the good results obtained in the bench-scale reactor system modified with a microtubular reactor train (described earlier). The microreactor system is used for long-term unattended testing. The system is more economical to operate than the bench-scale system because of the lower labor costs and less waste handling and disposal costs. The reactor system is shown schematically in Figure 1.

The microreactor is being used primarily for long-term testing of catalysts to verify useful lifetime. These tests and results will be presented in the next section. However, one attempt was made to do a long-term test with an industrial waste stream. The K013 waste from DuPont (stripper column bottoms from acrylonitrile manufacture) was tested to evaluate long-term effects of the feedstock on the catalyst.

This test was short-lived because of loss of catalyst activity. After 16 hours, only moderate activity was measurable (72% COD destruction @ 1.72 LHSV). By 40 hours on stream, no measurable gas product was being produced and the COD reduction had dropped to only 32.2% @ 1.27 LHSV. Detailed analysis of the K013 feedstock showed relatively large iron (550 ppm) and sulfur (100 ppm) concentrations. Comparative analysis of the catalyst before and after the test showed significant buildup of these two elements during the test (0.17 wt% each). The mass of these two elements is in a near stoichiometric proportion to suggest iron sulfate deposition onto the catalyst. Alternatively, the sulfur could account for reacting about 11% of the catalytic metal to the inactive sulfide form. Neither mechanism could be confirmed. Transmission electron microscopy analysis showed some (an amount believed to be an insignificant) agglomeration of the apparent catalytic metal particles, and energy dispersive x-ray spectrometry detected iron-containing particles that appeared to be iron oxide. Neither method detected any difference in the support material, nor did powder XRD analysis.

This test underlines the need for feedstock-specific testing in longer-term tests. The trace contaminants appear to be the cause of the catalyst activity loss. This problem was not obvious from the short-term continuous reactor tests.

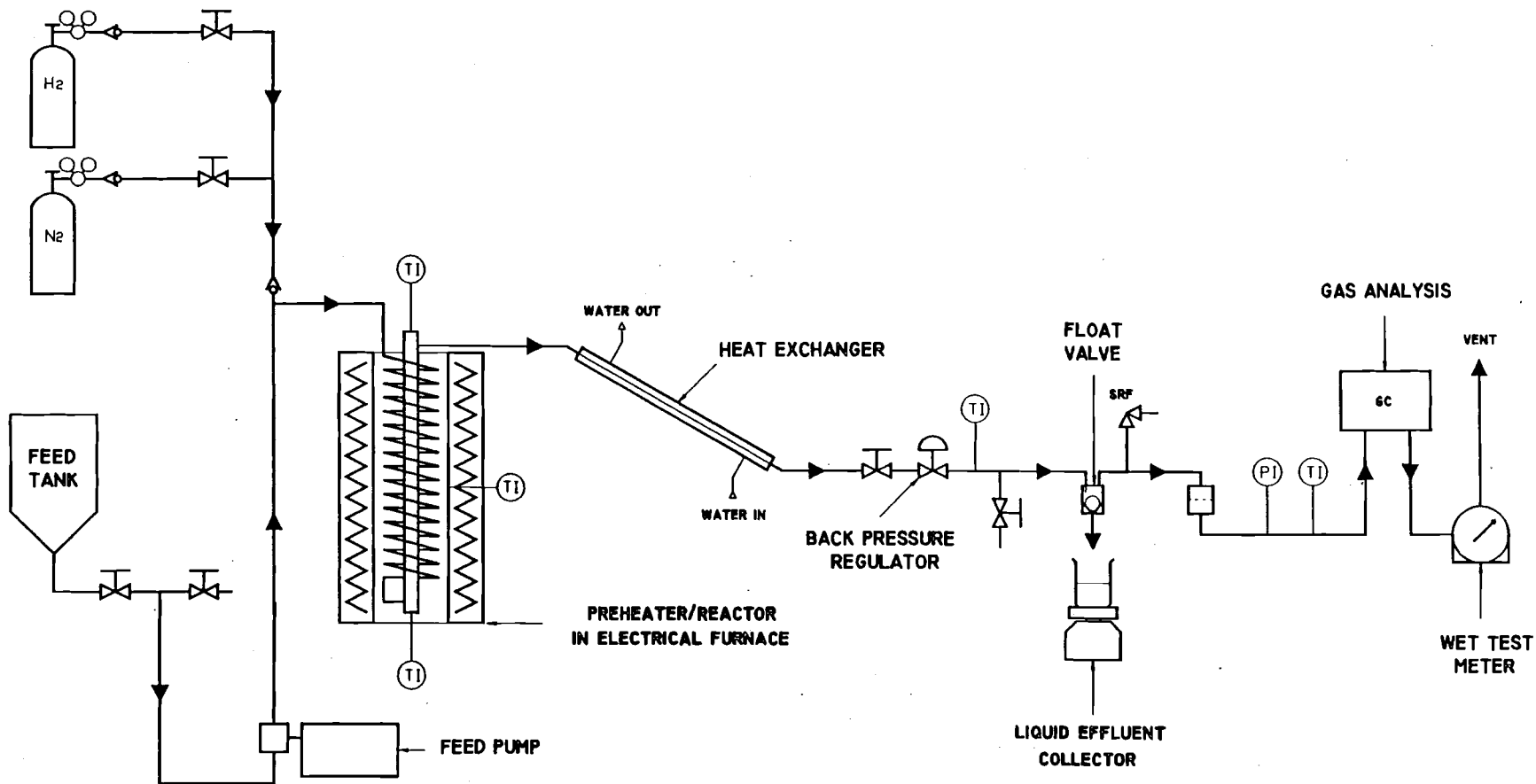


Figure 1. Schematic of a Microreactor System

Catalyst Activities and Lifetimes

This section describes the experiments conducted on several catalysts and support materials and summarizes the results of the tests.

Summary

The experiments were performed initially in a 1-liter stirred batch reactor. The batch reactor was the same system used for the batch reactor feedstock tests described above.

Three types of experiments were performed in the batch reactor. The first type of experiment was reduction of the metal catalyst in hydrogen. All catalysts were tested in a reduced metallic state. Reduction was required for many of the catalysts; the powdered catalyst was reduced in the batch reactor by preheating in excess hydrogen gas. The second type of experiment was the standard test of catalyst activity, a 1- to 2-hour test of the powdered catalyst in a slurry with 10 wt% p-cresol or phenol in water. Autogenic pressure in the sealed reactor and gas composition were measured as functions of time. A third type of batch test was a long-term stability test performed in water only. After exposure to the high-pressure water system (350°C and 21 MPa) for 1 to 6 days, exposed catalyst properties were measured and compared with the fresh catalyst.

A total of 35 catalyst tests requiring 28 additional reduction cycles and 5 long-term catalyst tests were conducted. After verification of catalyst activity in the batch reactor, long-term activity tests were performed in continuous-flow reactors. Catalyst lifetime in excess of 5 months has now been demonstrated in tests in the microreactor system.

Nickel Catalyst Systems

Nickel was identified as an active catalyst for this process at the earliest stages of this development effort. Stability of a well-dispersed metal component has been a key factor in long-term catalyst activity. During the period covered by this report, numerous nickel systems were tested as catalysts in the batch reactor. The catalysts are described in Table 4, and test results can be found in Table 5.

The INCO 210 product is a nickel metal powder. It is reported to have a small particle size with feather-like structure, giving it a high surface area, which makes it useful as a catalyst for some applications. This metal powder was reduced in hydrogen at 400°C before the test.

The Ni/Zr alloy was prepared as a catalyst by the method of Wright et al.¹⁸ in which the powdered alloy is oxidized fully, and the nickel is preferentially reduced to metal. In this manner, small nickel crystallites are expected to form on the surface of the zirconium oxide. Through XRD, we determined that the nickel portion of the alloy did not fully oxidize, but only zirconium oxide could be found. The nickel oxide that did form had a small crystallite size, 19 nm. After the reduction step, the zirconium remained oxidized, but the nickel was reduced to metal; however, the average crystallite size was greatly increased to over 50 nm.

Table 4. Innovative Nickel Catalysts Tested in TEES

Catalyst	Form	Comments
INCO type 210	powder	low #VM1410, nickel only
NiZr alloy	150 μ m powder	70/30:Ni/Zr, Goodfellow Corp.
Nickel/HTO ^(a)		
A	powder	PNL:Ni ₂ Ti ₉ O ₂₀
B	powder	calcined HTO
C	powder	thermal/aqueous treated HTO
Nickel RTDS ^(b)		
A	powder	NiO/Ni(OH) ₂ , 17 nm
B	powder	NiO/Ni(OH) ₂ , 15 nm Ni metal, 29 nm
RTDS special	powder	NiO, 24 nm

(a) Hydrous titanate.

(b) Rapid Thermal Decomposition of precursors in Solution.

The nickel/HTO catalysts were made by ion exchanging nickel from nitrate solution onto layered hydrous titanate (HTO). Nickel loadings up to 13% onto the HTO (250 m²/g BET surface area) could be achieved by this method. The HTO was used as produced in the first catalyst, calcined at 350°C for 4 hours before making the second catalyst, and treated in water at 350°C for 16 hours before making the third. After ion exchange with five-fold excess solutions, the catalysts were then calcined in a muffle furnace at 400°C. XRD analysis of the catalysts confirmed that the HTO remained layered after the oxidation step. The water treatment step may have destroyed much of the layered structure. The amount of nickel actually exchanged into the HTO was not directly measured. The catalysts were treated under hydrogen pressure at 300°C before use.

The RTDS process is a new materials production process developed at PNL.¹⁹ It produces small (nanoscale) particle size materials through thermal decomposition of metal salts (at 250°C to 350°C) in water solution. The nickel oxides and hydroxides produced by this method were then reduced to metal under hydrogen pressure at 400°C. Significant crystallite growth resulted from the reduction process. XRD analysis shows a doubling of average crystallite diameter. The last RTDS catalyst listed in Table 4 has a proprietary composition.

Of all the innovative nickel catalysts tested in the batch reactor, only the special RTDS catalyst showed any significant activity. The uncatalyzed test result is also given in Table 5 for comparison.

Table 5. Results of Tests with Innovative Nickel Catalysts (batch test results at 350°C and autogenic pressure)

Catalyst	% Carbon Conversion	Product Gas, Vol%			Time, min	Feed
		CH ₄	CO ₂	H ₂		
INCO (450°C reduced)	1.84	8.8	17.1	74.0	100	p-cresol
INCO (400°C reduced)	0.18	0.0	9.7	90.3	93	p-cresol
Ni/Zr (single treatment)	1.22	1.9	31.4	65.5	105	p-cresol
Ni/Zr (double treatment)	0.01	0.2	0.1	99.7	100	p-cresol
Nickel/HTO						
A	0.04	0.0	1.0	99.0	120	p-cresol
B	1.81	1.1	23.3	75.4	120	p-cresol
C	0.17	0.0	74.2	25.8	90	p-cresol
Nickel/RTDS						
A	0.01	1.5	0.0	98.4	100	p-cresol
B	0.00	0.0	0.0	100	85	phenol
RTDS special form	7.42	13.9	38.2	43.8	120	phenol
None	0.09	0.0	40.0	59.9	118	phenol

The INCO nickel powder had slightly more activity after higher-temperature hydrogen pretreatment than after lower-temperature reduction. The Ni/Zr alloy had only a low level of activity, although the referenced catalyst preparation technique appeared to work as described. A second round of oxidation and reduction did not improve the activity of this material. None of the nickel-HTO catalysts had any significant activity. Following the tests, the pillared titanate structure had been destroyed based on XRD analysis and BET surface areas reduced to only 25 m²/g. The nickel RTDS catalysts showed no significant activity and great increases of crystallite size (from 29 nm to 48 nm) such that active metal surface area would be greatly reduced. The special RTDS catalyst was particularly interesting because the crystallite growth problem was nonexistent with this formulation. The nickel metal crystallite size after the test was the same as the nickel oxide crystallite size before the test.

Ruthenium Catalyst Systems

Ruthenium was identified in 1992 as a catalyst for TEES, and a patent application has been filed. Several formulations were tested in a batch reactor using phenol as a model feedstock. Much of the specific information about the useful formulations is being held proprietary until the patent issues. The catalysts are described in Table 6, and the results of the batch tests are given in Table 7.

Table 6. Ruthenium Catalysts Tested in TEES

Catalyst	Form	Comments
Ru/MnO ₂	tablets	5% Ru on MnO ₂
Ru/ZrSiO ₄	powder	5% Ru on ZrSiO ₄
Ru/carbon	granules	Aldrich, 5% Ru on carbon
Ru/HTO	powder	PNL:Ru _{1.25} Ti ₅ O ₂₀
Engelhard	tablets	proprietary
BASF Mod1	tablets	proprietary
BASF Mod2	tablets	proprietary
Degussa	powder	proprietary
Degussa	tablets	proprietary

Table 7. Results of Tests with Ruthenium Catalysts (batch test results at 350°C and autogenic pressure)

Catalyst	% Carbon Conversion	Product Gas, Vol%			% COD, Conv.	Time, min
		CH ₄	CO ₂	H ₂		
Degussa powder	83.9	38.8	40.3	13.0	99.96	117
Degussa tablet	83.9	52.2	43.7	2.2	99.96	115
BASF mod1	89.8	59.7	36.5	3.0	99.6	115
BASF mod2	ND	57.5	37.8	3.8	99.6	125
Engelhard	46.9	44.3	37.1	9.0	99.4	122
Ru/carbon	45.9	45.9	42.5	3.0	99.8	80
Ru/MnO ₂	1.45	6.6	8.1	83.2	~32	125
Ru/ZrSiO ₄	1.10	5.3	11.9	82.8	org ^(a)	112
Ru/HTO/p-cresol	0.54	1.1	6.9	92.1	org	140

ND = no data

(a) org = saturated water with immiscible organic product layer.

These results show that there are several proprietary ruthenium catalysts being tested at PNL that have activities as good or better than a commercial ruthenium-on-carbon catalyst. These catalysts can be used to obtain a nearly complete conversion of phenol in water to a medium-Btu fuel gas. The last three experimental catalysts were not as useful, with extremely low activities. Specific activity of these catalysts is a function of both the surface area of the support (and the resulting distribution of the metal after impregnation) and the metal-support interaction (which can effect changes in the metallic catalytic properties). XRD analysis of the spent catalysts showed that the MnO_2 had reacted to monoxide, hydroxide, and carbonate; the zirconium silicate remained unchanged.

Another issue of importance to the activity of these metallic catalysts is the reduction of the catalytic element to the metallic form. We have found there is an important range of processing conditions that must be used to produce a useful catalyst form. The data in Table 8 show the effect of the reduction severity on the catalytic activity. Beginning at the top of the table, the severity of reduction increases downward as a step function of time and temperature. Moderate activity is seen with the 2% catalyst in all the tests performed at 200°C to 300°C. However, treatment at 350°C resulted in an inactive catalyst with little conversion evident even though a larger amount of catalyst was used. This effect is seen for both the 2% and the 1% catalysts. The loss of activity at 350°C is so great that even the unreduced catalyst shows more activity. This high-temperature deactivation is an example of strong metal-support interaction, which has been studied extensively.²⁰ The catalytic reduction of the support by the metal is believed to play a role in reduced activity.

Extended Batch Tests in Water

Extended time batch reactor tests of samples are conducted to evaluate material stability in the TEES operating environment. These tests evaluate the effect of the high-pressure, hot water system only and not the effects of the organic material or the gas products. The results of extended batch tests are given in Table 9. All the materials appeared to be relatively stable with the exception of the alumina borate. This material appeared to react/dissolve and recrystallize as hydroxides, which makes it very unstable at TEES processing conditions.

Zirconia-Catalyzed Aqueous Organic Destruction

Another technology for gasification of organics in wastewater streams²¹ was reviewed for comparison with the PNL technology. This process uses a different catalyst system, zirconia and potassium carbonate, and produces a different product gas, primarily hydrogen and carbon dioxide. We had not tested zirconia alone as a catalyst, and our earlier results showed that alkali typically interfered with the gasification of organics and catalyzed the water-gas shift reaction instead of methanation. Batch reactor tests were performed for comparison of this technology with TEES.

Phenol (10% in water) was used as the feedstock for the comparative tests listed in Table 10. The TEES catalyst system, metallic nickel, is much more effective at gasification of organics in water and in the production of a useful fuel gas product. The zirconia test result suggests only a minor increase in activity over the uncatalyzed test for organic destruction at 350°C. The COD reduction in the system can be explained by absorbance of the phenol onto the zirconia powder. The difference with

Table 8: Effect of Reduction Temperature on Ruthenium Catalysts (batch test results at 350°C, autogenic pressure)

Reduction (in hydrogen)	% Carbon Conversion	Product Gas, Vol%			% COD, Conv.	Time, min
		CH ₄	CO ₂	H ₂		
2% catalyst, 15 g						
3hr@201°C	32.1	42.0	40.9	13.3	95.3	120
16hr@202°C	34.4	48.1	38.3	11.1	99.4	120
3hr@246°C	27.8	35.4	44.6	15.1	96.7	120
14hr@245°C	35.7	42.6	35.1	19.3	98.4	121
3hr@293°C	32.7	38.3	41.6	15.5	97.2	120
16hr@293°C	33.7	42.7	36.6	16.6	98.2	120
3½hr@300°C	23.4	32.0	47.1	15.2	96.2	120
~16hr@350°C, 35 g	0.07	0.5	4.8	93.9	org ^(a)	95
13hr@200°C, 35 g (p-cresol feedstock)	54.45	59.8	35.2	3.7	99.76	120
Unreduced, 15 g (p-cresol feedstock)	1.71	3.2	29.2	66.5	org	118
1% catalyst, 15 g						
~16hr@300°C	2.0	3.0	65.8	29.0	36.9	120
1% catalyst, 35 g						
~16hr@350°C	0.04	0.5	4.7	94.2	org	85

(a) org = saturated water with immiscible organic product layer.

the addition of alkali is primarily resulting from water-gas shift activity, which was demonstrated long ago. The uncertain COD conversion number results from the formation of a small amount of a separate organic phase, which accounts for some of the 13.4% loss.

Continuous-Feed Reactor Tests

As followup to the batch reactor tests with new catalyst formulations, continuous-feed reactor system tests were performed to better specify catalytic kinetics and to determine long-term catalyst lifetimes. A series of tests were performed in the bench-scale reactor to evaluate one of the proprietary catalyst formulations presented above. The tests used phenol (5% in water) as the feedstock in the first 2 days of tests (with a short period of p-cresol), followed by 2 days of tests with acetic acid (white vinegar), and completed with 1 more day of phenol feedstock.

Table 9. Hot Pressurized Water Treatment of Catalytic Materials

Material	Time	Product Description
Degussa 7701	63 hr	titania, rutile with anatase
Degussa 7702	63 hr	slight growth of anatase crystallite size and shift to rutile crystallite form
Degussa, powder	63 hr	slightly greater growth of anatase crystallite size and shift to rutile crystallite form
DFH-12-23/E	133 hr	softened titania extrudate
Engelhard	84 hr	cubic ZrO ₂ shifted to monoclinic
Degussa, tablet	84 hr	slight shift from anatase to rutile crystallite form
9Al ₂ O ₃ -2B ₂ O ₃	67 hr	~70% Al hydroxides and silicates with some evidence of B(OH) ₃

Table 10. Comparison of TEES and ZrO₂-Catalyzed Gasification

Catalyst	% Carbon Conversion	Product Gas, Vol%			% COD Conv.	Time, min
		CH ₄	CO ₂	H ₂		
ZrO ₂	0.33	1.4	41.2	57.7	44.9	124
ZrO ₂ with K ₂ CO ₃	1.48	0.2	25.1	74.6	<13.4	120
Uncatalyzed	0.09	0.0	40.0	59.9	ND	118
Nickel on Al ₂ O ₃	90.0	59.1	39.3	1.0	99.9	100

Analysis of the data in Table 11 indicates strong gasification through the first 2 days of tests. Very high space velocities with nearly complete elimination of COD from phenol were achieved. A batch test of the used catalyst after 2 days of operation showed that it was still highly active, producing a 99.8% COD reduction in the batch test with 70% gasification to recovered gas products. During the 2 days, nickel crystallite size had increased significantly from the original 4.5 nm to 23 nm based on XRD. This increase is an improvement over that measured for the unmodified BASF, catalyst, which had increases to the 25 to 35 nm range after this period (15 to 20 hours) of operation.

During the second 2 days of operation, using acetic acid as the feedstock, the activity of the catalyst fell significantly. On the last day of the test, the conversion rate of phenol was greatly reduced. Analyses were performed on the catalyst after each of the 2 days of operation. The nickel crystallite was found to be smaller than the sample recovered after the first 2 days of testing. Seven samples fell in the 10 to 17 nm range, suggesting that the 23 nm number is not representative of the bed. No deposits of inorganic precipitates were visible in the catalyst bed. Physical changes were

Table 11. Bench-Scale New Catalyst Test Results [modified BASF catalyst (mod1), 350°C, 204 atm]

Feedstock	Product Gas Composition, vol%					% COD Reduced	LHSV, 1/1/hr	Gasification of carbon
	CH ₄	CO ₂	H ₂	C ₂	BF			
5% phenol	53.5	41.4	3.8	0.5	0.6	99.89	2.55	84
	56.0	41.5	1.7	0.5	0.6	99.94	2.67	70
	54.4	42.7	1.9	0.6	0.6	99.83	3.74	75
	52.5	41.5	4.5	0.6	0.7	99.73	4.06	88
2% p-cresol	55.4	41.9	1.8	0.4	0.4	99.89	4.25	96
5% acetic acid	52.7	40.7	2.8	0.1	3.1	99.89	3.11	101
	44.4	46.6	8.0	0.1	0.1	99.91	6.30	105
	44.9	45.3	8.7	0.1	0.1	88.88	6.67	104
	47.3	45.5	6.3	0.1	0.1	97.12	3.28	88
	46.1	47.2	6.0	0.1	0.1	91.15	3.21	90
	46.5	47.3	5.6	0.1	0.1	84.0	3.30	91
5% phenol	49.9	41.6	2.6	0.9	5.0	73.3	2.25	53
	48.5	41.3	2.9	1.0	6.3	83.5	1.76	58
2% phenol	45.8	45.5	2.2	1.0	5.2	83.0	1.78	71

BF = backflush from chromatography columns, an approximation of propane/butane; no olefins or CO are found in the product gas.

noted in the catalyst material, including a softening and a color change from black to gray in portions of the bed. Elemental analysis showed no loss of catalyst metal. Atomic emission spectrometry analysis showed no catalyst metal in the effluent with a minimum detectable limit of 0.08 ppm. However, one component of the support was being eluted from the reactor during the test. The BET surface area measurements showed a loss of surface area from 171 m²/g after the phenol portion of the run, to 142 m²/g after 1 day of acetic acid testing, to 124 m²/g at the end of the test.

During the acetic acid tests, the feedstock and products were both more acidic than with the phenol. The phenol feed was a pH of 5 and the vinegar was pH 2.5. The products from the phenol in the first 2 days were at pH 6 but were less than 5 in the last day under conditions of lower conversion.

The acetic acid products began at 6 pH but steadily dropped to <5 even at high conversion and then down to <3 at lesser conversion conditions at the end of the fourth day. These low pH conditions could have degraded the catalyst support.

A useful piece of information is found in comparing the last two data sets for operation with phenol. The same percentage conversion was achieved at the same space velocity for two different concentrations of phenol. These data support our earlier conclusion of a first-order rate of reaction for TEES.⁸

Long-Term Microreactor Tests

The microreactor system was assembled to allow long-term testing to verify catalyst lifetimes. The unit was originally assembled with the bench-scale reactor system, but during 1994 a separate dual-train microreactor system was assembled. These microreactor systems were used for extensive long-term tests of several of the promising catalyst formulations for TEES. Some results for these tests are given in Table 12. Through modern, computer-driven data acquisition and control systems, the dual microreactor system can operate unattended. Operator input is needed only to refill feedtanks, drain product effluent receivers, take liquid samples, and collect the data. The data acquisition system monitors 15 channels of data, including temperatures, furnace outputs, pressures, feed and product levels, and gas product composition. These data are recorded every 5 minutes, resulting in an EXCEL file of about 1.3 Mbytes each week.

As seen from the data in Table 12, good processing results have been achieved over long operating periods. The Degussa catalyst operated for about 2 months before showing significant loss of activity. The test with this catalyst was terminated shortly after the last data window in Table 12. The Engelhard catalyst is still on stream. The BASF mod1 catalyst gave very good results for nearly a month of operating time. The test was terminated when the mod2 catalyst became available. The mod2 test is also still progressing. After 5 months of operating time the catalyst is still functioning well, although the signs of lower activity (higher hydrogen and hydrocarbon concentration in the product gas, reduced processing rate) are evident. However, COD conversion remains at >99%. Atomic emission spectrometry analysis was also done on product samples from these tests. As noted above, there is no evidence of the catalyst metal in these effluents (<0.08 ppm).

Table 12. Long-Term Experimental Results

	Degussa				Engelhard		BASF mod1		BASF mod2		
	238	621	1148	1565	90	387	293	580	498	1165	2182
Time on Stream, hr:	238	621	1148	1565	90	387	293	580	498	1165	2182
Results											
Gasification of Carbon, %	99.99	99.3	102	46.5	100	102	99.4	96.6	101	95	97
Reduction of COD, %	99.99	99.7	99.99	98.6	99.7	99.4	99.9	99.8	99.99	99.9	99.7
LHSV, L/L/hr	2.09	1.69	1.75	1.73	1.66	2.11	1.76	1.95	1.71	1.71	1.57
Gas Yield, L/g	1.42	1.42	1.45	0.55	1.44	1.44	1.33	1.28	1.41	1.31	1.28
Effluent COD, ppm	15	360	13	2000	330	822	122	205	20	110	431
Gas Composition, volume %											
Methane	58.1	58.4	58.2	45.0	58.5	55.4	52.6	52.8	54.4	53.2	52.0
Carbon Dioxide	40.8	41.0	41.2	43.0	40.3	39.3	42.5	41.6	42.3	42.4	40.0
Hydrogen	0.3	0.5	0.3	0.5	1.0	0.9	0.7	0.9	1.3	1.3	2.5
Ethane	0.5	0.1	0.1	4.8	0.2	2.4	1.8	2.0	0.9	1.5	2.5
Backflush	0.2	<0.1	0.2	6.7	0.0	2.0	2.4	2.7	1.0	1.6	3.3
Btu/SCF	605	597	599	738	599	667	637	651	601	617	675

Catalyst bed conditions: 350°C and 21 MPa.

Technology Transfer

Transferring the TEES technology for commercial usage is the primary goal of this project. As part of this objective, we have made arrangements with several groups to broaden the public awareness to TEES. Also, we have designed our research program around interactions with industry to demonstrate the TEES technology in meaningful ways.

Industrial Interaction

The TEES technology was selected as one of six technologies from the Hanford Site for support in the Tri-Cities Commercialization Partnership. This effort with funding from the National Center for Technology Transfer is aimed at the development of new jobs in the Tri-Cities, Washington, area by commercializing technologies developed at DOE's Hanford Site. Consequently Tri-City interests have shown support. The Tri-Cities Industrial Development Council (TRIDEC) has arranged meetings with local food processors, Washington State Department of Ecology staff, and local city staff with responsibility for waste treatment systems. These contacts have led to some of the vegetable processing waste tests described in this report. Another contact is the Pacific Northwest Pollution Prevention Research Center in Seattle. Their contacts in the fish processing industry led to the fish waste tests. The Department of Ecology lists of hazardous waste generators and the U.S. Environmental Protection Agency lists of deep well injection hazardous waste disposal permits have also been reviewed.

PNL has produced technical publications and presentations, with direct marketing handled by the process licensee, Onsite*Ofsite, (O*O), through paid advertisements. As a result of the technology transfer efforts, PNL has received and responded to 67 requests regarding potential TEES applications in the last 2 years. Table 13 illustrates the geographical distribution and the applications being considered.

Industrial Onsite Demonstrations

Another technology transfer accomplishment is the fabrication of the Industrial Onsite Demonstration Unit. Figure 2 shows a drawing of this mobile unit, a 60-gallon-per-day operating system, which is self-contained and includes a small operations office/analytical laboratory.

PNL and O*O have entered into a CRADA (Cooperative Research and Development Agreement) to show this Industrial Onsite Demonstration Unit to the potential users. The Unit is to be operated in industrial settings with the help of the industrial participants.

The benefit to DOE from this CRADA is the transfer of a DOE-enhanced technology to the private sector. Utilization of this technology will provide an energy savings for industry by the conversion of waste organics into fuel gas. In addition, the technology will result in a cleaner environment through the utilization of waste for energy production.

Table 13. Information Requests for TEES

DOMESTIC			
State	Type of Company	State	Type of Company
New Jersey	chemical manufacturing	Washington	pulp & paper waste
California	petrochemical wastewater	Wisconsin	pulp & paper waste
Tennessee	chemical manufacturing	Utah	engineering consultant
California	environmental engineer	New York	chemical manufacturing
Georgia	paper research	New Mexico	technology developers
Ohio	paper manufacturing	Illinois	gas research
Washington	waste treatment	Texas	biomass conversion
California	engineering consultant	Florida	engineering consultant
Michigan	chemical manufacturing	Illinois	petrochemical manufacturing
Ohio	technology developers	West Virginia	technology information
Nebraska	technology developer	Pennsylvania	environmental engineers
Pennsylvania	chemical manufacturing	New Mexico	technology developers
Illinois	industrial consultant	Minnesota	food processing waste
Texas	chemical manufacturer	Nevada	animal waste
California	electronics manufacturing	Delaware	chemical manufacturing
Washington	municipal waste	Wisconsin	pulp & paper waste
Massachusetts	manufacturing	Nebraska	biomass energy developer
Nebraska	corn utilization	New York	industrial waste treatment
Kentucky	chemical manufacturing	Virginia	engineering consultant
Pennsylvania	environmental engineer	Oregon	environmental engineer
California	oil refinery	California	chemical process research
California	industrial engineering	California	engineering consultant
FOREIGN			
Country	Type of Company	Country	Type of Company
New Zealand	environmental engineer	Switzerland	environmental engineer
Canada	petrochemicals	India	biomass energy developers
Indonesia	engineering consultant	India	engineering consultant
India	engineering consultant	India	manufacturing
Singapore	chemical manufacturing	Malaysia	engineering consultant
Malaysia	environmental engineering	Malaysia	engineering consultant
Malaysia	engineering consultant	Brazil	engineering consultant
Denmark	environmental engineering	Switzerland	technology developers
Netherlands	chemical manufacturing	Italy	wood waste
Germany	slaughterhouse waste	Germany	chemical manufacturing
Australia	engineering consultant	Germany	chemical manufacturing
India	sugar factory		

The benefit to O*O is the demonstration of the technology in an industrial setting. This demonstration is expected to facilitate the marketing of the technology, which, in turns, leads to sub-licensing the technology or sales of equipment or services.

An additional benefit is that the utilization of the Unit should lead to a broader application of TEES. For example, it may be used for demonstrations within the DOE site cleanup programs or the ethanol from biomass program. DOE site requirements could be handled through PNL under subcontract to O*O. The applications of interest to O*O can cover a wide range of industries.

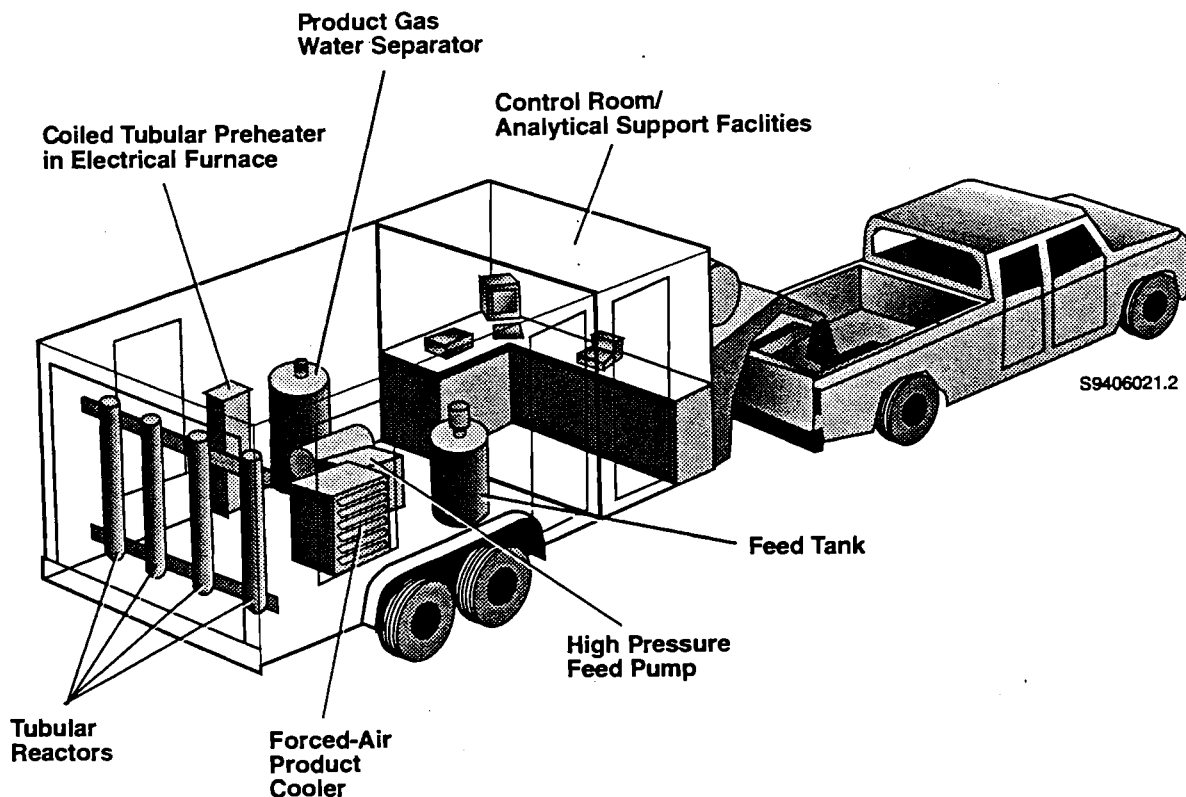


Figure 2. Industrial Onsite Demonstration Unit Available for Demonstrating TEES Process

The PNL contribution to the CRADA includes both the value of the Industrial Onsite Demonstration Unit and staff time and expenses for supporting research and part of the unit. The Unit will be used through this CRADA by O*O to demonstrate the TEES technology in industrial settings and informational programs in a schedule as determined by PNL and O*O. PNL will use a portion of this research project to support operation of the Unit. The support will include bench-scale testing of feedstocks prior to the onsite testing to verify process applicability; detailed analysis of waste streams and process effluents to support operation of the Unit; and operator support in startup of the Unit. Continuation of the CRADA in FY 1996 and FY 1997 is envisioned but is incumbent upon continuing DOE support.

The O*O contribution to this CRADA includes manpower, supporting equipment, and travel expenses (including costs of insurance, advertising, maintenance, and storage). The tests will be for a minimum of 5 days each but may extend to as much as 30 days. In addition to these tests, O*O will present the Unit at industrial expositions and individual company seminars as they are scheduled or available.

In order to get wider participation in the utilization of the Industrial Onsite Demonstration Unit, we prepared a notice for the Commerce Business Daily. The following description was provided:

Pacific Northwest Laboratory is seeking industrial partners to host an Industrial Onsite Demonstration Unit for the TEES® technology for wet organic waste treatment. Operation of the 60 gallon/day unit would be done within a CRADA between PNL and the process licensee,

Onsite*Ofsite, Inc. of Duarte, CA. TEES® (Thermochemical Environmental Energy System) is a unique thermocatalytic gasification concept which converts wet industrial and food processing wastes to methane and carbon dioxide and a purified water stream. The process can also provide cogeneration, waste water treatment, and reduction in solid waste handling. The catalytic system operates at high pressure (140-200 atm) and low temperature (300-350°C) compared to conventional gasification approaches. Many specific industrial wastes (food processing, beverage production, pharmaceutical, petroleum refining, and chemical manufacturing) are in such a form that they cannot be economically incinerated, landfilled, or sewerred. These waste streams consist of high-moisture solids, wet sludges, or highly contaminated wastewater that contain significant amounts of organic carbon which can be converted to a useful fuel form with the TEES® technology. The industrial partner would be expected to work with Onsite*Ofsite to perform demonstration tests of TEES® using the Industrial Onsite Demonstration Unit to process waste from the industrial site. At a minimum, the industrial partner would provide operators for the unit, utilities during the test period, and costs of transporting and setup and takedown of the unit. Dissemination of the results of the tests will be governed by the proprietary information clauses of the CRADA.

However, only about 10 responses were received as a result of this publication.

Operations began in the Industrial Onsite Demonstration Unit just before the end of FY 1994. Initial testing was done at the Onsite*Ofsite facilities. The CRADA contribution from O*O for the tests was expected to be about \$40,000 for four tests with different feedstocks. The tests were undertaken at O*O in lieu of an industrial site test to develop operating capabilities and to develop an operating history for the unit itself. A full program of 3 to 4 industrial site tests is planned for FY 1995.

Future Work

Process development research will continue on TEES in FY 1995. Testing of specific industrial waste streams will focus the process optimization effort. Following successful testing in the bench-scale reactors, onsite demonstration of the process will be the next step in process development. Therefore, during FY 1995, the Industrial Onsite Demonstration Unit will be operated in a CRADA with industry. By FY 1996, sufficient information will be available on a specific industrial waste stream that implementation of the technology by industry will be possible. Operation of the Industrial Onsite Demonstration Unit will facilitate technology transfer by allowing first-hand operation of the technology by the industrial users.

Testing of improved catalyst formulations will continue in FY 1995 as well. Long-term demonstration of catalyst stability will be done in the microreactor systems. New catalyst formulations will be tested as they are identified. Catalyst lifetimes of >6 months are needed for TEES to be economical. Less expensive formulations are also needed.

Commercial viability of the technology may still be limited by lack of a larger-scale operating system which demonstrates the technology at a scale of 1000 gallons/day or greater. Finding the right combination of near-term economical application of the process with industrial need and venture capital availability will be a future goal of this project.

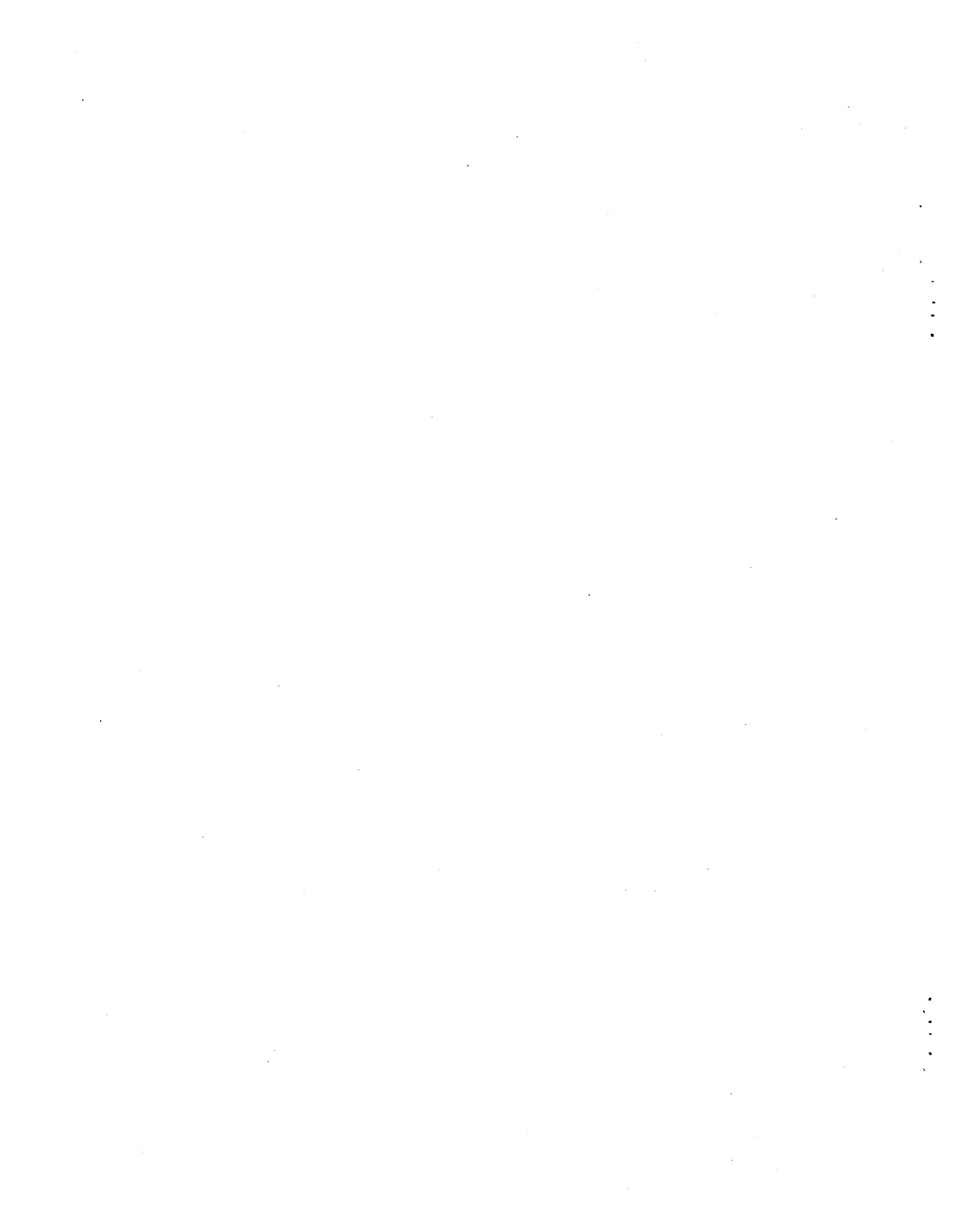
Related Publications

Within this project, during FY 1993 and FY 1994, one presentation manuscript was prepared and published:

- "Development of a Catalytic System for Gasification of Wet Biomass" by D. C. Elliott, L. J. Sealock, Jr., M. R. Phelps, G. G. Neuenschwander, and T. R. Hart. Presented at: *First Biomass Conference of the Americas*, August 30-September 2, 1993, in Burlington, Vermont; published in: *First Biomass Conference of the Americas: Energy, Environment, Agriculture, and Industry*, Proceedings Volume I, pp. 557-570; NREL/CP-200-5768, National Renewable Energy Laboratory, Golden, Colorado.

Several journal articles describing this work were published:

- "Chemical Processing in High-Pressure Aqueous Environments. 1. Historical Perspective and Continuing Developments," by L. J. Sealock, Jr., D. C. Elliott, E. G. Baker, and R. S. Butner, *Industrial and Engineering Chemistry Research* 32, 1535-1541, 1993.
- "Chemical Processing in High-Pressure Aqueous Environments. 2. Development of Catalysts for Gasification," by D. C. Elliott, L. J. Sealock, Jr., E. G. Baker, *Industrial and Engineering Chemistry Research* 32, 1542-1548, 1993.
- "Chemical Processing in High-Pressure Aqueous Environments. 3. Evaluation of Feedstock Effects," by D. C. Elliott, L. J. Sealock, Jr., E. G. Baker, *Industrial and Engineering Chemistry Research* 33, 558-565, 1994.
- "Chemical Processing in High-Pressure Aqueous Environments. 4. Continuous-Flow Reactor Process Development Experiments for Organics Destruction," by D. C. Elliott, M. R. Phelps, L. J. Sealock, Jr., E. G. Baker, *Industrial and Engineering Chemistry Research* 33, 566-574, 1994.
- "Characterization and Catalytic Gasification of the Aqueous By-Product from Vacuum Pyrolysis of Biomass," by C. Roy, H. Pakdel, H. G. Zhang and D. C. Elliott, *Canadian Journal of Chemical Engineering* vol. 72, pp. 98-105, 1994.



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D. K. Kreid	K9-21
T. L. Kuusinen	K3-75
R. C. Locke	K7-02
N. L. Moore	K8-04
G. G. Neuenschwander	K3-69
G. B. Parker	K9-62
M. R. Phelps	K3-75
L. J. Sealock, Jr.	K2-10
L. J. Silva	K2-47
L. J. Snowden-Swan	K3-75
L. C. Schmid	K1-34
S. C. Weiner	(BWO)
T. A. Werpy	K2-40
Publishing Coordination	
Technical Report Files (5)	

