Low-Temperature Catalytic Gasification of Wet Industrial Wastes

FY 1991-1992 Interim Report

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MASTER

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®),^(a) 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 reactor 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 cheese whey and spent grain, can be processed to >99% reduction of chemical oxygen demand (COD). The estimated residence time is about 7 min at 350°C and 3000 psig, not including 1 to 2 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 level of development of TEES has progressed to the initial phases of industrial process demonstration. Bench-scale testing of industrial waste streams is under way, and engineering-scale testing has begun. Plans for FY 1993 include the fabrication of an Industrial Onsite Demonstration Unit which will be operational in FY 1994. Long-term catalyst testing has verified catalyst lifetimes of at least 6 weeks with reagent chemical feedstocks. Long-term testing of actual industrial feedstocks is planned for FY 1993. New catalyst formulations identified in this research will be produced in larger scales to verify fabrication techniques.

(a) TEES is a registered servicemark of Onsite*Ofsite, Inc., Duarte, California, the process licensee.

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We acknowledge the continuing support of our process licensee, Onsite*Ofsite, Inc., and the president of the company, Mr. Norman Banns.

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Introduction

A catalytic gasification system that operates in a pressurized water environment has been under continued development and refining at Pacific Northwest Laboratory (PNL)^(a) for over 12 years. Initial experiments, performed for the Gas Research Institute, were aimed at developing kinetics information for steam gasification of biomass in the presence of catalysts [Sealock et al. 1981]. In that work, the combined use of alkali and metal catalysts was first reported [Elliott and Sealock 1985] 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 [Elliott et al. 1988]. Extensive batch reactor testing [Sealock et al. 1988] and limited continuous reactor system (CRS) testing [Elliott et al. 1989] were undertaken in the development of this system under sponsorship of the U.S. Department of Energy. A wide range of biomass feedstocks were tested, and the importance of the nickel metal catalyst was identified. Specific use of this process for treating food processing wastes was also studied [Baker et al. 1989a]. The concept application was further expanded to encompass cleanup of hazardous wastewater streams, and results were reported for both batch reactor tests [Baker and Sealock 1988a,b] and continuous reactor tests [Baker et al. 1989b]. Ongoing work at PNL focuses on refining the catalyst and scaling the system to long-term industrial needs.

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 1989-90 interim report [Elliott et al. 1991], which reviewed the results of the studies conducted with a fixed-bed, continuous-feed, tubular reactor. The discussion here provides an overview of experiments on the wide range of potential feedstock materials conducted in a batch reactor; development of new catalyst materials; and tests performed in continuous-flow reactors at three scales. The appendices contain the history and background of the process development, as well as more detailed descriptions and results of the recent studies.

(a) Operated for the U.S. Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830.

Conclusions and Recommendations

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

Conclusions

- A wide range of feedstocks 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, over 6 weeks of operation was verified on a ruthenium on zirconia formulation. Of the nickel catalysts evaluated, only one had demonstrable activity for a period of at least 4 weeks.
- The tubular reactor design has been tested at three scales of operation. Scale-up of the fixed-bed tubular reactor, including heat recovery by exchange between the feed and the reactor effluent, has been demonstrated successfully.

Recommendations

- Continue bench-scale testing of TEES process to include other feedstocks of industrial interest and verify catalyst compatibility.
- Perform long-term tests to evaluate catalyst stability.
- Assemble an Onsite Industrial Demonstration Unit to be used to provide in-plant experience with TEES for potential users.

Catalyst Activities and Lifetimes

This section describes the experiments conducted on several catalysts and support materials and summarizes the results of the tests. The experiments were performed initially in a 1-liter stirred batch reactor. 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 described in detail in Appendix B.

Three types of experiments were performed in the batch reactor. All catalysts were tested in a reduced metallic state. For many of the catalysts, reduction was required. When required, the powdered catalyst was reduced in the batch reactor by preheating in excess hydrogen gas. The standard test of catalyst activity was a 1- to 2-hour test of the powdered catalyst in a slurry with 10 wt% para-cresol 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 3000 psig) for 1 to 6 days, exposed catalyst properties were measured and compared with the fresh catalyst.

A large number of catalysts and catalyst support materials were tested for suitability in TEES. Test totals included 51 catalyst tests requiring 27 additional reduction cycles and 12 long-term catalyst tests. Table 1 summarizes the results. These tests showed that nickel is a very good catalyst for TEES as are ruthenium and rhodium. Other Group VIII, VIB, and IIB metals were oxidized at reaction conditions. Copper (Group IB) stayed reduced but had little activity for the TEES reactions. Nickel metal lost activity over time because of loss of active surface area through crystallite growth. Most commercially available catalyst support materials were unstable at TEES conditions. Many actually hydrolyzed. Loss of physical strength was common. Loss of surface area also occurred. Zirconia appeared to be most stable. The most stable form of alumina was α -alumina, but long-term stability is questionable because of slow hydrolysis. High-surface area carbon is also a possible support, but slow reaction of the support in the presence of the catalytic metal at TEES conditions may lead to catalyst support consumption.

After verification of catalyst activity in the batch reactor, long-term activity tests were performed in continuous-flow reactors. These test results verified the short-term activity of most nickel catalysts and the long-term activity of ruthenium catalysts. One exceptional nickel catalyst was identified which was used for 4 weeks while maintaining a high level of activity, albeit at lower space velocity. The ruthenium catalyst was tested for 6 weeks and maintained high activity throughout.

Table 1. Summary of Results of Tests on TEES Catalysts and Catalyst Supports

<u>Useful Catalytic Metals</u>	<u>Inactive Metals</u>	<u>Metals Oxidized at Conditions</u>
Ru	Pt	Co ^(b)
Rh	Pd	Fe ^(b)
Ni ^(a)	Cu	Cr
		Mo
		W
		Zn
<u>Stable Supports</u>	<u>Unstable Supports</u>	<u>Hydrolyzable Supports</u>
α -Al ₂ O ₃	TiO ₂	γ -Al ₂ O ₃
ZrO ₂	SiO ₂	δ -Al ₂ O ₃
C	Ca/aluminate ^(c)	η -Al ₂ O ₃
	Kieselguhr ^(c)	SiO ₂ /Al ₂ O ₃ ^(c)

(a) Subject to sintering.

(b) Baker and Sealock (1988a,b).

(c) Elliott et al. (1991).

Batch Reactor Studies

This section discusses the batch reactor studies on a wide range of organic (and inorganic) functional types. These batch reactor tests were an important beginning step in developing industrial systems based on this technology. The batch reactor was the same system used for the batch catalyst tests described above. For these experiments a 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 samples were recovered during each test to increase the amount of information gained from each test. These tests are described in detail in Appendix C.

Test results show that TEES is an effective processing system for converting organics in water to fuel gases. A wide range of organic functional types have been treated, including hydrocarbons, both aromatic and aliphatic; oxygenates, such as phenolics, acids, alcohols, glycols, and ketones; chlorinated hydrocarbons; and acid salts and cyanide. The single-carbon components such as carbon tetrachloride, chloroform, and sodium cyanide were found to react noncatalytically at TEES reaction conditions. Mixtures of components were also treated in industrial wastewater streams. In addition, diamine-containing wastewater streams were converted. A related technology of ammonia and organics treatment with nitrate was also demonstrated.

A large number of tests were performed to evaluate the feedstock effects. Thirty-eight experiments were conducted including tests performed with actual industrial waste samples. In order to perform the tests with actual waste samples, we set up a Treatability Test Tracking program in the laboratory. All hazardous waste samples must be logged in upon receipt and tracked through the testing cycle until their final disposal. Tests must be reported to Laboratory Safety, and the information is forwarded to the State of Washington, Department of Ecology.

Industrial input to this research program was an important aspect. For these batch tests, waste samples were received from six different operations both directly and through our process licensee. We acknowledge the support and participation of DuPont-Fibers, ARCO Chemical, Conoco (DuPont), Anheuser-Busch Companies, and Oberti Olive Company. In addition, one industrial concern contracted directly with Battelle to provide feedstock for tests in TEES on a proprietary basis.

Continuous-Flow Reactor Studies

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

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 [Elliott et al. 1991]. The unit consisted of a 6 ft long X 1 in. I.D. tube 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 for catalyst lifetime studies. All the components shown for 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.

A scaled-up reactor system (SRS) was based on the bench-scale design. It was a transportable system designed at a scale of one-half ton per day of wet feed for obtaining engineering data for further scale-up of TEES. Equipped with three 6 ft x 2 in. I.D. fixed-bed tubular reactors and supporting equipment to achieve conversion, the test system's capacity was a one-half ton per day liquid feed with a design flow rate of 5 gal/hr. Design working conditions for the reactors were 350°C at 238 atm. This system is described in detail in Appendix D.

In the SRS tests, the tube-in-tube heat exchanger gave good performances. The heat exchanger was the major process difference, besides scale, between the bench-scale unit and the SRS. Although there were significant losses of heat in the transfer lines between the reactors and the heat exchanger (10°C to 20°C), inside the exchanger there was an effective exchange of heat from the reactor effluent to the feedstock. Data details are given in Appendix D. The exchanger recovered >90% of the heat in the effluent stream with a temperature approach to within <30°C.

The tests in these reactor systems totaled an impressive amount of operating time on stream. The bench-scale reactor was operated in 23 experiments lasting from 1 to 120 hours for a total operating time on stream of 397 hours. Six micro-reactor tests were performed lasting from 108 to 732 hours for a total operating time on stream of 1835 hours. The SRS was operated in 4 tests lasting from 2 to 14 hours for a total on stream operating time of 30 hours.

The TEES process has now been demonstrated in continuous-feed, fixed-bed catalytic reactor systems on three 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 6 weeks of operation with reasonable stability. Ruthenium appears to be a more stable catalyst than nickel in this respect. A wide range of feedstocks have been processed effectively, including oxygenates, chlorinated hydrocarbons, nitrates, food processing wastes, and organic chemical manufacturing wastewaters. Reduced nitrogen in these feedstocks is often converted into ammonia, which is stable at TEES conditions. Inorganic components in these feedstocks have sometimes been deposited in the catalyst bed when compounds were produced at concentrations above their solubility limits.

Future Research

Process development research will continue on TEES in FY 1993. Testing of specific industrial waste streams will focus the process optimization effort. Following successful testing in the bench-scale reactors and the SRS, onsite demonstration of the process would be the next reasonable step in process development. Therefore, during FY 1993, an Industrial Onsite Demonstration Unit will be procured for use in cooperative testing programs with industry. By FY 1994, sufficient information will be available on a specific industrial waste stream that demonstration of the technology with assistance from industry will be possible. Onsite operation of the demonstration unit will facilitate technology transfer by allowing first-hand operation of the technology by the industrial users.

Continued testing of improved catalyst formulations will be ongoing in FY 1993 as well. Fabrication of kg quantities of the new ruthenium catalysts will be undertaken by catalyst manufacturers to allow additional large-scale testing of the catalysts in the bench-scale reactor. New catalyst formulations will be tested as they are identified.

Related Publications

In addition to the references cited here, the following presentation manuscript was prepared and published:

- "Low-Temperature, Catalytic Gasification of Wastes for Simultaneous Disposal and Energy Recovery" by D. C. Elliott, G. G. Neuenschwander, E. G. Baker, and L. J. Sealock, Jr. Presented at: Energy from Biomass and Wastes XV, March 25-29, 1991, in Washington, D.C.; published in: *Energy from Biomass and Wastes XV*, IGT, Chicago: 1013-1021; PNL-SA-18839.

Journal articles describing this work include:

- "Bench-Scale Reactor Tests of Low-Temperature, Catalytic Gasification of Wet Industrial Wastes," by D. C. Elliott, E. G. Baker, R. S. Butner, and L. J. Sealock, Jr. *Journal of Solar Energy Engineering* 115(1):52-56, 1993.
- "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*, accepted for publication, 1993.
- "Chemical Processing in High-Pressure Aqueous Environments. 2. Development of Catalysts for Gasification," by D. C. Elliott, L. J. Sealock, Jr., and E. G. Baker. *Industrial and Engineering Chemistry Research*, accepted for publication, 1993.
- "Chemical Processing in High-Pressure Aqueous Environments. 3. Evaluation of Feedstock Effects," by D. C. Elliott, L. J. Sealock, Jr., and E. G. Baker. *Industrial and Engineering Chemistry Research*, submitted for publication, 1993.
- "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., and E. G. Baker. *Industrial and Engineering Chemistry Research*, submitted for publication, 1993.

The last four articles listed above cover the information in the appendices to this report.

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Appendix A

Historical Perspective and Continuing Developments

Chemical Processing in High-Pressure Aqueous Environments. 1. Historical Perspective and Continuing Developments

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ABSTRACT

Use of high-temperature pressurized liquid water has been investigated as a reaction medium for conducting chemical reactions and conversion. Results of these studies have demonstrated that high-temperature pressurized liquid water, especially in the presence of suitable catalysts, has unique chemical and physical properties. An overview of fundamental investigations and processing considerations in this environment is presented including details regarding the effects of temperature, pressure, and catalysis. The reactivities of various feedstocks tested are discussed along with the development and scale-up of high-pressure reactor systems used to investigate the process chemistry and engineering. Several new processing concepts were developed for gasification, destruction, and gas processing based on these findings.

INTRODUCTION

Researchers at Pacific Northwest Laboratory (PNL) have been investigating chemical reactions and processing in high-temperature, pressurized liquid water for over 15 years. This research has led to a clearer understanding of the reaction chemistry and the discovery of several new processing schemes. Most of the research has centered on catalytic processing for the production of liquid and gaseous fuels from biomass and wastes at lower temperatures and higher pressures than conventionally used. Other studies have investigated new methods for carrying out chemical reactions, separations, and the destruction of hazardous organic materials. All of this research has in common the use of high-pressure, water systems operating at below and above critical conditions.

The goals of the research have focused on understanding the unique chemistry that occurs in high-pressure hot water and developing innovative catalysts and processing systems to take advantage of this chemistry. Typical operating conditions investigated include temperatures of about 300°C to 450°C and pressures to over 35 MPa. Performing research at these conditions has required engineering advancements, specialized reactor systems, and special attention to safety design considerations. Process development activities have spanned fundamental investigations, bench-scale and pilot-scale operations, and commercial design.

The objective of this paper is to present the background and developments associated with our research in chemical processing in high-temperature pressurized water. This information sets the foundation for the more detailed companion articles submitted to this journal. Important processing considerations discussed here include reaction chemistry; temperature effects; catalyst types and activities; and feedstock applications. Along with a decade and a half of research conducted at PNL, this paper also provides a review of related studies conducted by others.

BACKGROUND

The use of high-pressure systems for chemical conversion is well known in the petroleum refining and the petrochemicals industries. However, the use of high-pressure systems is relatively rare outside those fields. One area of growing importance is the exploitation of high-temperature pressurized liquid water as a medium for chemical processing (Siskin and Katritzky 1991). While the field is gaining in interest and application, it remains a relatively untapped area for mechanistic and process development related research.

Work at PNL in this field began in the late 1970s with research in synthetic fuels. Initial work was related to high-temperature gasification (Mudge et al. 1981), the production of liquid fuels from cellulose and biomass (Elliott 1980; Russell et al. 1980; Molten 1980;

Nelson et al. 1984), and the investigation of kinetics and catalysis of producing synthetic gases from biomass (Sealock et al. 1981 a,b; 1982).

The unique reactivity in high-temperature pressurized aqueous media was first realized during our examination of the gasification of biomass (Sealock et al. 1982). Various combinations of alkali metal and alkaline earth carbonates and supported metal catalysts were studied in this environment for gasification and methane production from four biomass model compounds: cellulose, holocellulose, lignin, and Douglas fir wood flour. This work provided the technical background and the impetus to expand our investigations into numerous aspects of chemical processing in high-temperature pressurized liquid water.

Other early work by others in the field of high-temperature pressurized aqueous media includes studies by Modell et al. (1978); Amin et al. (1975); and Modell (1985). Most of this early work consisted of reforming glucose and wood flour in water at supercritical conditions ($>374^{\circ}\text{C}$, density $>0.31\text{ g/ml}$). The work presented some interesting results, which were attributed to the unique properties of the supercritical water system. The use of some catalysts under those conditions was also described. Examination of the results given by Modell and others showed that only limited gasification occurred in their system, and that the catalysts tested had almost negligible effect. Although glucose conversion in some of their experiments was high (approaching 100%), the yield of gas and methane was very low. Only small amounts (18%) of the carbon present were converted to gas with the balance of the carbon remaining in the aqueous byproduct as low molecular weight organics. Methane concentration in the product gas was only 1.5%, demonstrating poor methanation in their system. Results obtained with maple sawdust (without catalyst) were somewhat better, achieving a 39% carbon conversion to gas with a methane concentration of 5% in the product gas after 60 min at 377°C . None of the work reported by Modell and others involved the use of alkali catalysts.

More recent work in the field has been reported by Antal et al. (1987). Their experiments were also performed in supercritical water (385°C to 400°C , 35 MPa) to study acid- and base-catalyzed reactions in a continuous-flow reactor. Ethanol, propanol, and ethylene glycol underwent acid-catalyzed dehydration to the corresponding alkene. Substantial conversion of these compounds was observed after reaction times of less than 1

min. Base catalysis was almost undetectable. In those experiments, supercritical water enabled acid-catalyzed ionic reaction pathways to supplant the free radical pathways existing at higher temperatures. The acid catalyst had negligible effect on acetaldehyde under the same conditions. The yield of gas was not reported for a single noncatalyzed test with glucose (Simkovic et al. 1987) under the same conditions (24 s residence time). Acetol, glyceraldehyde, and formaldehyde were identified as the major products remaining in the aqueous byproduct, while the gas product consisted of 55.7% CO₂, 34.5% H₂, 9.3% CO, 0.2% CH₄, and 0.4% C₂.

Evaluating the properties of supercritical fluids as a reaction medium for destruction technology has been the subject of considerable research. Much of this research has been performed with carbon dioxide, but supercritical water has begun to be investigated more fully because of its unique chemical properties and because it is inexpensive, nontoxic, and relatively easy to separate from most products (Shaw et al. 1991). The use of supercritical water oxidation as a destruction technology has also undergone considerable analysis (Modell 1989; Shanableh et al. 1990; Takahashi et al. 1989). The use of subcritical conditions for wet air oxidation has been developed to the point of commercial application as a waste treatment process (Schaefer 1981; Copa and Gitchel 1986). Use of catalysts for wet oxidation has also been studied (Imamura et al. 1982; 1985; 1986; Ito et al. 1989). Significant further study of the science related to the chemical properties of both pressurized liquid water and supercritical water is expected to occur in support of waste destruction technology development and other new applications of water as a reaction medium. The rest of this paper centers on high-temperature pressurized liquid water reactions, which have certain potential advantages over supercritical water applications.

PROCESSING CONSIDERATIONS

High-temperature pressurized liquid water, especially in the presence of suitable catalysts, has its own set of chemical and physical properties that deserve detailed study. Reactions carried out under these conditions have the potential to be more manageable, less

corrosive, and to have a wider application to industry than supercritical water systems. The liquid water system has several important process advantages and has been shown to have reactivities competitive with those achieved at operation above critical point. A discussion of these findings and the key processing issues follows.

PRESSURIZED LIQUID WATER AS A REACTION MEDIUM

Recent papers have brought to light the fascinating properties of water as a reaction medium. Siskin and Katritzky (1991) have provided examples of many organic molecules previously considered unreactive in liquid water that undergo chemical reactions when the water temperature was increased to 250°C to 350°C. They further describe the dramatic changes in the physical and chemical properties of pressurized water as its temperature rises, citing examples of important changes in density, dielectric constant, and solubility parameter. These changes result in increased solvent properties, the favoring of ionic reactions, increased rates of reaction of the water with other chemical species, and favorable thermodynamic equilibria for desired products. The enhanced rate of reaction in the pressurized liquid water system over supercritical fluid has recently been reported for oxidation of phenol in water (Thornton and Savage 1992).

Siskin and Katritzky (1991) also list previous articles by them and a series of 18 initial publications (*Energy and Fuels* 1990) that describe organic reactions in hot pressurized liquid water. Results of these works indicate:

- (1) water can act as a highly effective acidic or basic catalyst and, indeed, as a powerful acid-base biocatalyst. Such catalyst reactions are often further accelerated by acidic and basic materials such as clays and carbonates;
- (2) ionic chemistry predominates as high-temperature water opens reaction pathways that are alternative to and preferred over thermal (free radical) routes; and
- (3) reactions can be autocatalyzed by water-soluble reaction products.

These articles agree with our experience in high-temperature pressurized aqueous systems, where we found that organic molecules are very reactive in pressurized water between 250°C and the critical point of water.

This chemistry was shown to play an important role in our investigations regarding reactions in high-temperature pressurized liquid water and development of improved methods for the liquefaction (Nelson et al. 1984; Fassbender 1991) and gasification (Sealock et al. 1982; 1988) of carbonaceous materials. The work has involved the use of catalysts and combined catalyst systems (Sealock et al. 1982; 1988) to enhance the conversion (reactivity) and to direct the chemistry towards specific products (selectivity). The rate and selectivity of reactions was shown to be greatly enhanced through the proper use of catalyst and pH. In addition, many organics are very reactive at the conditions tested, which makes the environment ideal for carrying out gasification and destruction reactions. Dramatic effects in conversion have been observed in both liquid and fluid phases.

Much of the work reported in the literature and the technical press dealing with high-temperature water has been done in the presence of air or oxygen in near-critical water (wet air oxidation) and in supercritical water (supercritical water oxidation) to oxidize organic feedstocks and wastes. The majority of our recent work has been below the critical temperature of water and has involved the addition of catalysts to enhance reaction of organics with water followed by methanation of the gaseous products. We have shown that much of the unique chemistry that has been attributed to supercritical water conditions also occurs at temperatures as low as 300°C in our reaction systems. We have not observed significant differences in the results below and above the critical point itself other than increased kinetics at higher temperatures. Instead, we have found that by optimizing the catalysts and operating conditions, the desired reactivity and selectivity can be achieved while maintaining the water in the reactor substantially in the liquid phase.

High-temperature pressurized liquid water can also be used for chemical synthesis and separations. For example, the use of relatively low temperatures (250°C to 350°C) and high partial pressures of water in the presence of selected catalysts result in equilibrium conditions that strongly favor water-gas shift (Elliott and Sealock 1983; Elliott et al. 1983; 1986) and methanation (Sealock et al. 1988) reactions. High-temperature pressurized water can participate in various chemical reactions in several ways, acting as a catalyst, a reactant, or serving as a solvent. Noncatalytic applications of hot pressurized liquid water are also possible and have been shown to break and separate "highly stable" water-oil-solids

emulsions generated in petroleum waste water treatment and other industrial operations (Baker et al. 1991; Sealock et al. 1992).

TEMPERATURE AND PRESSURE EFFECTS

Temperature plays an important role in high-temperature pressurized aqueous conversion from several standpoints. The water must be at a temperature to achieve the improved chemical and physical properties that allow it to serve as an attractive processing medium. The temperature must be high enough that desired reactions take place at a rate that is meaningful from a processing standpoint. The processing must occur at conditions where the desired reaction pathways and products are favored. The use of catalyst in conjunction with temperature and pressures can greatly enhance both the kinetics of the desired reaction, as well as maximizing the equilibrium products.

Temperature has been shown to play an important role in conversion of various carbonaceous feedstocks to liquid (Elliott et al. 1987) and gaseous (Sealock et al. 1981 a,b) products. The increase in temperature from 250°C to 450°C in a pressurized water environment is significant, particularly when no catalyst or less-effective catalysts are present. At the lower end of the temperature range liquefaction occurs to some degree with very limited gasification. As the temperature increases, gas production increases at the expense of the liquids and through additional carbon conversion.

The effect of lower temperatures on conversion and product distribution can be significantly offset by the use of an appropriate catalyst. Liquefaction can be enhanced through the use of alkali catalysts and gasification through the combined use of alkali and reduced metal catalysts (see Scheme 1 below).

An example of the use of catalysts to enhance gasification in high-temperature aqueous water is shown in Figure 1, which addresses the "basic dilemma" for the direct conversion of carbonaceous feedstocks to methane in a single vessel. The "basic dilemma" is the choice between a high-temperature, low-pressure reaction system that favors the breakdown of carbonaceous material to gases but limits methane formation, and a low-temperature, high-pressure system that favors methane formation but is less likely to promote gasification.

Scheme 1. Mechanism for Biomass Conversion

Figure 1. The Basic Dilemma of Single-Step Gasification and Methanation

The use of proper catalyst selection in high-temperature pressurized water has overcome the "basic dilemma" and allowed the direct conversion of carbonaceous feedstocks to methane within a single reactor. Poor conversions typically achieved at low temperature (350°C) can be more than offset by the effect of increased pressure in the presence of an active catalyst system. In essence, gasification conducted at lower temperature with high pressure water can be used to achieve high carbon conversion to methane and to circumvent the formation of char.

A comparison of low-temperature gasification to high-temperature gasification was described by Sealock et al. (1988). Low-temperature gasification differs from conventional gasification in two important respects: reaction mechanism and thermodynamics. These differences are governed by important catalytic enhancements, which are discussed later in this paper.

Carrying out the desired conversion in the liquid phase has several important considerations. The advantages include energy savings of greater than 50% by not vaporizing the water, less cost for reactors and equipment due to lower pressure operation and high fluid density, and more efficient heat recovery by liquid/liquid heat exchange. From an engineering standpoint, the ability to carry out reactions using catalyst in the liquid water, below the critical point, and without adding air or oxygen is also very significant. The reactor can be constructed with thinner walls due to lower pressure operation and out of less-expensive materials because corrosion is dramatically reduced when no air or oxygen is required in the system. The effect of the catalyst helps improve the kinetics of liquid phase processing, minimizing the primary advantage of supercritical water oxidation.

In the gas processing and separation areas, feedstock reactivity typically increases with increasing temperature. Catalyst problems can occur with higher temperatures in the gas processing area, depending on the catalyst and mechanism of conversion. Separation chemistry is dependent on the mechanism of separation, with the separation of water-oil-solids emulsions increasing with temperature up to the critical point. Above the critical point, emulsion separation is difficult in that the fluid tends to re-emulsify on condensation.

CATALYSTS TYPES AND ACTIVITIES

The use of proper catalysts is the key to commercial applications which rely on sustained operation and must meet certain regulations. The processes discussed here have led to new approaches for converting organics feedstocks to useful products (Sealock et al. 1988; Elliott et al. 1991) and destroying hazardous organic chemicals in water (Baker and Sealock 1988b; Baker et al. 1989b).

Understanding the role and function of the catalyst during conversion has seen an increasing emphasis in our work, as catalyst effects and lifetimes become a critical part of commercialization activities. By implementing proper catalysts and conditions, carbon conversions can be achieved at rates similar to or greater than those obtained at more severe supercritical conditions. Initial catalyst investigations have dealt with developing a fundamental understanding of catalyst effects on conversion and on product yields. Catalyst systems were evaluated to determine their ability for breaking carbon-carbon bonds and for enhancing the selectivity and kinetics of gas phase reactions. Catalysts investigated for these applications fall into five general types: alkali metal; alkaline earth; ammonia based; reduced metals; and combined catalyst systems.

Alkaline earth and alkali metal catalysts were tested for their catalytic activity for cellulose gasification in a high-temperature pressurized environment (Sealock et al. 1981a). Catalysts tested included sodium, potassium, lithium, barium, and calcium carbonates and sodium and potassium hydroxides. Gasification of cellulose in the presence of these catalysts resulted in important differences in carbon conversion and in product gas compositions. The alkali metal carbonates were shown to be significantly more effective catalysts for carbon conversion and methane production than the alkaline earth carbonates. The alkali metal carbonates tested (cesium, potassium, and sodium) all functioned at a similar level of catalytic activity in the system. A qualitative ranking of catalytic activity was established, ($K > Na > Cs$), although the differences were not great at temperatures between 350°C and 450°C.

The ability to catalyze the water-gas shift reaction correlated with the gasification catalytic activity, with alkali metal salts being much more effective catalysts than the alkaline earths (Elliott and Sealock 1983). The use of ammonia and ammonium-based compounds as

catalyst for the water-gas shift reaction was also demonstrated. Conversions of hydrogen and carbon monoxide mixtures using aqueous alkali catalysts compared favorably with conventional supported metal oxide catalysts in the reactor system. These results are well described in the literature, along with the proposed mechanism of basic catalysis for water-gas shift and results of continuous gas processing tests (Elliott and Sealock 1983; Elliott et al. 1983; 1986).

The presence of alkali carbonate catalysts was shown to increase the carbon conversion to gaseous compounds in wood component gasification except for lignin gasification at 450°C (Sealock et al. 1981b). The alkali carbonate catalyzed the production of carbon dioxide and hydrogen at the expense of carbon monoxide, methane, and probably water. The production of ethylene at the expense of ethane was also noted, but both these products were inhibited by the alkali. The alkali and nickel appeared to have an additive effect in most cases, which resulted in greater methane production, higher methane concentration, and increased carbon conversion to gas apparently through a complex mechanism, as suggested in Scheme 1.

Alkali carbonates are also well known as important liquefaction catalysts (Elliott and Giacolletto 1979; Molton 1980; Nelson et al. 1984). Nelson et al. (1984) reported that pure cellulose was converted to mixtures of phenols, cyclopentanones, and hydroquinones, as well as other components at temperatures of 250°C to 400°C and pressures up to 20.7 MPa in the presence of sodium carbonate. The use of alkaline catalysts under liquefaction at 300°C was shown to shift the mechanism from one involving liquid pyrolysis (predominantly furan formation) to one incorporating aldol and related condensations. Fassbender (1991) depicted the breakdown of sludge using alkaline digestion at 265°C to 350°C into low weight compounds such as acetone, acrolein, and glycerol. Elliott et al. (1987) reported oil product yields for the alkaline liquefaction of high-moisture biomass similar to those reported for wood liquefaction obtained at Lawrence Berkeley Laboratory (LBL) (Figuerola et al. 1982). LBL also provided a listing of the chemical functional groups contained in high-moisture biomass oil products.

The use of a nickel catalyst plays a substantial role in the production of methane from biomass (Sealock et al. 1982). The catalytic effect was shown to increase with temperature

over a broad range of temperatures up to about 450°C. The highest yield of methane was achieved using a wood flour feedstock in the presence of a nickel catalyst (without alkali) at 450°C. Methane yields of 10% to 20% of the mass of the wood flour feed were obtained at temperatures from 400°C to 450°C. Methane concentrations in the product gas ranged from 23% to 27%, with the remainder of the gas being primarily hydrogen and carbon dioxide. There was evidence that the nickel served a hydrogenation function in converting ethylene to ethane. The nickel catalyst facilitated production of carbon dioxide as well, although the specific mechanism was not determined. On the basis of these limited results, nickel was judged to be a more active catalyst than cobalt, which was also tested, in the low-temperature gasification system (Sealock et al. 1981a).

The use of reduced nickel catalyst was employed to destroy several organic model compounds in water by converting the compounds to methane, hydrogen, and carbon dioxide (Baker and Sealock 1988a,b). In associated tests, reduced iron and cobalt were shown to be ineffective in both their reduced and oxidized states. These data confirmed the nickel-cobalt relationship developed for gasification and documented the importance of the reduced metal state in conversion. The reaction mechanism for organic destruction and methane production using reduced nickel was proposed, along with a discussion of temperature and organic loading effects. The proposed mechanism involved only steam-reforming and gas-phase methanation steps, although a direct methane production mechanism in the high-pressure system has been proposed (Butner et al. 1987b).

Additional work in a continuous reactor system developed reaction order information and established rate constants for the catalytic destruction of p-cresol and methylisobutylketone (MIBK) (Baker et al. 1989b). This work also confirmed that carbon conversions greater than 99% could be achieved for these compounds in 10 min or less at 350°C. In addition, methane concentrations were higher at 350°C than at 400°C with methane concentrations for p-cresol and MIBK being about 60% at 350°C.

Higher methane concentrations using reduced nickel have been substantiated in continuous tests with high-moisture biomass (Elliott et al. 1989) and in a more recent report (Elliott et al. 1991) where methane concentrations in the range of 40% to 48% were achieved. These results are greater than what was achieved in initial batch testing (Sealock

et al. 1988). These increases in methane concentration are likely due to increased reduced nickel to organic loadings in the reactor; efforts to ensure that the catalyst was fully reduced to its most active form; and the use of more stable catalyst supports. These methane concentrations may be further enhanced in future tubular reactor tests and with the implementation of more active and stable catalysts.

In some cases, increased conversion of biomass feedstocks was achieved in the presence of the combined alkali and nickel metal catalyst systems. The alkali and nickel catalysts appear to have an additive effect on conversion and resulted in the greatest methane production, the highest methane concentrations, and increased carbon conversion to gas (Sealock et al. 1982). These increases are likely due to the alkali enhancing the liquefaction of the feedstock to liquids that can then be more easily converted in the presence of reduced nickel, as shown in Scheme 1. In many cases no apparent enhancement is seen by adding alkali, as the feedstocks themselves contain the required catalytic amounts of the alkali (Sealock et al. 1988). Baker and Sealock (1988) found that the addition of alkali was detrimental to the destruction of many liquid organic compounds. Since these compounds are already present in a liquid state, the alkali plays no role in helping the reduced nickel catalyst convert the organic molecule. The alkali evidently inhibits the mechanism by which the liquid organic molecule is converted to gas in the presence of reduced nickel and also traps some of the carbon dioxide product as carbonate in water solution.

The loss of catalyst activity for reduced nickel and other metals was identified during batch (Baker and Sealock 1988) and continuous reactor tests (Elliott et al. 1989). The loss of activity may be due to dissolution of the metal, dissolution or other sources of breakdown of the support, oxidation or poisoning of the reduced metal, and loss of active surface area of the metal or support. These possible causes and other potential deactivation routes for catalyst deactivation, as well as new catalyst formulations, are currently under study. New proprietary catalysts are being developed for application in our high-temperature liquid water environment which have potential to resist the severe conditions at 350°C. Catalyst support information is being developed and catalyst formulations are being investigated that are designed to lead to active catalysts with long-term stability. Details regarding some of these investigations are reported in this journal (Elliott et al. 1993a).

Developing long-lived catalyst systems remains a critical issue for chemical processing in a high-temperature aqueous environment. These problems must be overcome if processing in high-temperature liquid water is going to achieve significant commercial importance.

FEEDSTOCK APPLICATIONS

Feedstock evaluations have played an important role in our investigations of the reaction chemistry of organic compounds in high-temperature liquid water and in the development of new processing concepts. Most of these investigations have dealt with gasification/destruction of the feedstock in the presence of appropriate catalyst. Table I lists some of the many feedstocks tested for gasification (Butner et al. 1987a; Sealock et al. 1988; Baker et al. 1989a), and Table II lists the organic chemicals tested for destruction (Baker and Sealock 1988; Elliott et al. 1991; Elliott et al. 1993b) in our reactor systems.

Table I. Feedstocks Tested for Gasification

<u>Herbaceous</u> (40-60 wt% moisture)	<u>Aquatic</u>	<u>Processed Wastes</u>	
Napier Grass	Hyacinth	Potato waste	Spent grain liquor
Sorghum	Kelp	Spent grain	Vinegar
Sunflower		Grape pomace	Olive water
Corn stover		Cranberry pomace	Chicken processing waste
		Kraft black liquor	Fish processing waste
		Cheese whey	Gelatin manufacturing waste
		Coffee grounds	
		Anaerobic digestion sludge	

Table II. Organic Chemicals Tested for Destruction

<u>Model Compounds</u>		<u>Real Streams</u>
methylisobutylketone	benzene	nylon wastewater
para-cresol	anthracene	acrylonitrile wastewater steams
meta-cresol	biphenyl	fatty acid waste stream
ortho-cresol	polystyrene	ammonium sulfate waste stream
ethanol	polyethylene	sodium cyanide waste stream
phenol	sodium cyanide	polyol wastewater
sodium benzoate	nickel acetate	mixed nitrophenols waste stream
sodium phenolate	ammonium hydroxide	
propylene glycol	hexane	
eicosane	pentadecane	
chloroform	carbon tetrachloride	
chlorobenzene	trichloroethylene	
aniline	pyridine	

Gasification results with biomass feedstocks have shown a wide range of reactivity/convertability based on the composition of the feedstocks. These tests agree with our early investigations regarding the contribution of various wood components to gasification (Sealock et al. 1982). These studies showed that cellulose was the most reactive of the components tested in the system as measured by the rate of carbon conversion to gases. It generally reacted two to three times faster than lignin over the range of catalysts and temperatures studied. Methane production from cellulose was generally greater than that of lignin when the feedstocks were converted in the presence of the nickel catalysts. Experiments using holocellulose produced results similar to the cellulose tests, but the presence of hemicellulosic material appeared to slightly decrease the reactivity.

Lignin was generally the least reactive feedstock studied. However, lignin was shown to be a major source of methane. Sodium carbonate and nickel catalysts individually had

only a slight effect on the rate of conversion of lignin. However, the combination of the two catalysts resulted in a marked increase in the conversion rate. Wood flour was also less reactive than cellulose, apparently because of the contribution of the lignin fraction in the whole wood. Due to this lignin fraction, the wood flour also produced greater amounts of methane when compared with cellulose.

Feedstocks containing high cellulose content such as sunflower, sorghum, and napier grass showed similarly high reactivities as cellulose. Most terrestrial biomasses will fall in that category with some reduction in reaction rate with the increase of lignin in the feedstock. Aquatic feedstocks such as kelp and hyacinths exhibited similar rates of reaction, but produced a larger fraction of unreacted material. Residues from food processing operations, like spent grain and grape pomace, generally react at a slower rate but nearly to completion (Sealock et al. 1988). This lower reactivity is apparently due to these processed biomasses having reduced concentrations of cellulose and carbohydrates. These feedstocks likely consist of complex lignocellulosic materials and proteins, which are apparently less reactive.

Kraft black liquor, peat, and lignite were tested in our reactor system and found to be less reactive than biomass. This lack of reactivity is probably due to a combination of complex aromatic structure and problems associated with the heteroatoms contained in the feedstock. The ash content of the feedstock was also found to act as a catalyst or detriment depending on its chemical makeup.

Tests have also been conducted with organic model compounds (Baker and Sealock 1988) to evaluate their destruction in water. Five organic compounds were tested at 400°C and 35 MPa in the presence of a nickel catalyst. Results of those tests showed over 99% conversion for all of the compounds. Further work has demonstrated similar conversions at 300°C and 21 MPa.

CONCLUSIONS

Because of its reactivity and special chemical and physical properties, high-temperature pressurized liquid water is an excellent reaction medium for conducting synthesis

and conversion of organic compounds. When the proper catalysts are added, the unique chemistry of this reaction medium can be further enhanced with respect to both the rate of conversion and the selectivity of products. Operating conditions of 350°C and 21 MPa appear sufficient to reach the desired conversion conditions that are favorable from an economic and engineering viewpoint to operating at or above the critical point of water.

Studies conducted at the above described conditions have led to the discovery of several new processing approaches to chemical synthesis and conversion. Based on this research, we believe that numerous significant developments in the field of high-temperature pressurized liquid water processing are yet to be discovered and that these new innovations have the potential to lead to several widely accepted commercial enterprises.

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Appendix B

Development of Catalysts for Gasification

Chemical Processing in High-Pressure Aqueous Environments.

2. Development of Catalysts for Gasification

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ABSTRACT

A liquid water processing environment was used at 20 MPa and 350°C to convert organic compounds to methane and carbon dioxide in the presence of catalysts. This paper describes the evaluation of various types of base and noble metal catalysts and numerous support compositions for the process. The feedstock used in these tests was a mixture of para-cresol and water. Nickel, ruthenium and rhodium were identified as active metals for the reaction. Other metals from Groups VIII, VIB, IB, and IIB were inactive or readily oxidized and lost activity. Stable supports in the processing environment included α -alumina and zirconia. Silica and titania did not react chemically, but the tablet forms lost their physical integrity. Alumina forms, other than α -alumina, reacted with water to form böhmite (γ -AlOOH) with significant loss of surface area and physical strength.

INTRODUCTION

A pressurized catalytic gasification process, operated at low-temperature, is available under the trade name TEES® (Thermochemical Environmental Energy System). It is effective for treating organics in water streams to address both environmental cleanup and energy recovery goals. Through a liquid-phase, heterogeneously catalyzed process operated at nominally 350°C and 20 MPa, TEES produces a methane/carbon dioxide product gas from water solutions or slurries of organics. The concept was initially presented (Elliott and Sealock 1985; Sealock et al. 1988) as a biomass gasification process and was specifically developed for processing high-moisture biomasses (high-growth grasses, marine and aquatic biomass, and food processing residues), which are not efficiently gasified in conventional, low-pressure thermal systems. Later studies applied the technology to the destruction of

hazardous organic chemical wastes and organic chemical manufacturing wastewaters (Baker and Sealock 1988; Elliott et al. 1991). Nickel catalysts have been used in the system throughout its development and scaleup.

Part of the continuing development of the TEES technology involves studies on catalyst efficiency and integrity. This paper discusses experiments conducted and catalysts formulated for the purpose of maintaining high conversion and longer catalyst lifetimes in the subcritical, high-temperature, liquid-phase water operating environment of the TEES process. Many conventional catalysts developed for steam reforming, hydrogenation, and methanation, (the chemical mechanisms involved in TEES) were evaluated earlier. Many of these catalysts were found to be active for converting organics to methane and carbon dioxide but were not satisfactory for long-term operation. In this paper, experiments are described which were used to evaluate a wide range of catalyst materials and support compositions. The experiments have been grouped as follows: base metal catalysts, innovative nickel catalysts, conventional supported-nickel catalysts, noble metal catalysts, and catalyst support evaluations.

BACKGROUND

TEES processing involves relatively complex chemistry including pyrolysis, steam-reforming, hydrogenation, methanation and water-gas shift. Specific chemistry varies with the feedstock type. For the para-cresol used in the experiments described here, various reaction pathways are suggested by the products that have been identified:

The overall stoichiometry approximates:

A thermodynamic equilibrium limitation of about 1% residual hydrogen (Sealock et al. 1988) shifts the methane/carbon dioxide product ratio slightly more toward the carbon dioxide than is suggested in the given stoichiometry.

Nickel catalysts are used commercially in steam-reforming of a wide range of volatile hydrocarbons; methanation of synthesis gas mixtures of hydrogen and carbon monoxide; and hydrogenation of numerous organics. Steam reforming of methane and other hydrocarbons using nickel catalysts is a mature chemical process practiced with several commercially proven catalysts. It is performed as a vapor phase reaction over solid, supported-metal catalysts.

Carbon deposition, steaming/oxidation of the catalyst, metal sintering, and support degradation are critical issues related to catalyst stability in reforming processes. These degradation mechanisms are influenced by operating conditions such as H_2O/C feed ratio and operating temperature (Rostrup-Nielsen 1975; Mirodatos et al. 1987; Chen and Chen 1990). Methanation and hydrocarbon synthesis by catalytic hydrogenation of carbon oxides are less utilized industrial processes but have been studied extensively in the laboratory. These reactions are also performed in the vapor phase over solid, supported-metal catalysts. Thermal degradation (sintering) of the catalyst and carbon deposition are major concerns for catalysts used in these systems (Bartholomew and Sorensen 1983; Agnelli et al. 1991). Sintering of these nickel catalysts has been quantified even in operations at $300^\circ C$ to $380^\circ C$ (Kelley et al. 1983). Sulfur poisoning of nickel metal catalysts is a concern in all applications and especially in direct conversion systems (Cox et al. 1975). The use of other Group VIII metals in addition to nickel has also been studied for these types of reactions (Dalla Betta et al. 1974; Vannice 1975). Furthermore, the effect of support type on activity and sintering of nickel catalysts has been investigated (Bartholomew et al. 1981; Varma et al. 1990; Bartholomew and Sorensen 1983).

Past catalyst studies for the TEES concept have addressed contacting (mass transfer limitations) and the active form of the nickel catalyst (Butner et al. 1987). Clear evidence was presented on the need for reduction of the nickel catalyst prior to processing (Baker and Sealock 1988). The reduced effectiveness of other Group VIII metals (compared to nickel),

because of their oxidation (in high-temperature water) or lack of specific activity, was also reported (Baker and Sealock 1988). Evidence of the instability of conventional catalyst support materials when used at the reaction conditions was initially reported by Elliott et al. (1991). Continuous-flow reactor tests indicated that long-term stability of the nickel catalyst was a critical developmental requirement (Elliott et al. 1989; Baker et al. 1989a; Baker et al. 1989b, Elliott et al. 1991).

EXPERIMENTAL

The experiments were performed on a batch basis in a standard 1-liter, stirred reactor fabricated from Inconel by Autoclave Engineers. The reactor system is graphically presented in Figure 1. Further details about the system can be found in Sealock et al. (1988). A unique feature of our reactor is the modified sample recovery system, which allows multiple samples to be removed at reaction conditions.

The feedstock for the test was contained in the reactor within a stainless steel liner. A nitrogen gas over-pressure was used to purge air from the system and test for leaks. Results from three types of tests are described in this paper: catalyst reductions, catalyst activity tests, and long-term catalyst stability tests. If a catalyst required reduction before the feedstock conversion, the powdered catalyst was placed in the liner and sealed in the reactor. The reactor was purged with nitrogen, pressurized with hydrogen to about 1 MPa, then heated slowly to the reduction temperature, which was usually 300°C to 400°C depending on the catalyst formulation. Temperature control was maintained to eliminate an exothermically generated over-temperature condition that might damage the catalyst. After the catalyst was subjected to hydrogen at temperature for at least 3 hours and usually overnight, the reactor was cooled and the excess hydrogen gas vented. At that point, the feedstock of water and 10 wt% para-cresol was added to the liner through a port in the reactor cover. A nitrogen purge was employed to ensure that the freshly reduced catalyst was not exposed to air.

Figure 1. Schematic of Batch Reactor System

The catalyst activity tests were performed in the sealed reactor at 350°C and autogenic pressure from 17 to 23 MPa. The pressure varied based on the amount of gas produced, which depended on the activity of the catalyst. Time zero in a test was measured as the point when the reactor contents had been heated to the reaction temperature (350°C), which usually took about 45 minutes. Gas samples were removed via the gas sampling system beginning at time zero and throughout the test. The composition of the gas was analyzed by gas chromatography for hydrogen, carbon oxides, C₁ to C₄ hydrocarbons, and

nitrogen. The reactor contents were quenched using internal cooling coils after 1 to 2 hours at temperature or after reaction had ceased as evidenced by steady pressure and gas composition.

Long-term stability tests were also performed in the batch reactor using only water as the exposure medium. Organic feedstock was not added as it would be readily destroyed in the reactor and would not be a factor after 1 or 2 hours at temperature. Exposure of the catalyst materials to the high-pressure water/steam environment was the primary concern of these tests, which lasted 10 to 200 hours.

DISCUSSION AND RESULTS

Five groups of tests, described in this paper, involved several different catalyst or support materials. The discussion below gives the description of materials and results specific to each test.

BASE METAL CATALYSIS OF TEES

Various base metals and base metal combinations were tested as catalysts for TEES in the batch reactor system. Table I provides information about the catalysts tested. All of these catalysts were reduced before the feedstock conversion test except the zinc-chromite catalyst, which was received in a reduced and stabilized form from the manufacturer.

The results in Table II show that only the copper-zinc oxide catalyst exhibits any significant activity for the conversion of para-cresol or for methane formation. Essentially no activity is seen for all of the other catalysts despite the range of metal loading and physical properties of the catalysts tested. Table II includes data on the percentage of feedstock carbon converted to gas species (methane, carbon dioxide, ethane). The listed time is for minutes at temperature before the reaction was quenched. Most of the metals oxidized during the short batch test, as shown by x-ray diffraction (XRD) analysis of the spent catalysts; only copper remained reduced at these reaction conditions. Crystallite sizes were

Table I. Base Metal Catalysts Tested in TEES

<u>Base Metal</u>	<u>Catalyst</u>	<u>Manufacturer</u>	<u>Composition as Oxides</u>	<u>BET SA</u>	<u>Pore Volume</u>
Cu/ZnO	C61-1	United Catalysts	33%/65%	NA	NA
Co	Co-0127	Harshaw	39% on kieselguhr	NA	NA
Zn/Cr	Zn-0312	Engelhard	74%/21%	130	0.20
Cr	Cr-0211	Harshaw	19% on Al ₂ O ₃	62	0.30
W	W-0801	Harshaw	on Al ₂ O ₃	NA	NA
Mo	MoO ₃ /Al ₂ O ₃	Strem	11% on Al ₂ O ₃	64	NA
Cu	Cu-2501	Harshaw	6% on SiO ₂	4	0.61
NiW	Ni-4301	Harshaw	6%/19% on Al ₂ O ₃	230	0.37
NiMo	HT-500	Engelhard	3.5%/15.5% on Al ₂ O ₃	200	0.46

NA = not available

Table II. Results of Tests with Base Metal Catalysts

<u>Base Metal</u>	<u>% Carbon Conversion</u>	<u>Product Gas, Vol%</u>			<u>Time, Spent min</u>	<u>Catalyst Form</u>
		<u>CH₄</u>	<u>CO₂</u>	<u>H₂</u>		
Cu/ZnO	0.56	2.7	33.8	52.7	80	Cu metal, 240Å; ZnO
Co	0.08	0.3	1.0	98.7	90	not identifiable
Zn/Cr	0.07	0.0	13.3	83.9	90	ZnO
Cr	0.10	0.0	10.5	89.8	90	Cr ₂ O ₃ , 350Å
W	0.03	0.0	3.1	96.0	90	CaWO ₄ , 365Å
Mo	0.03	0.0	1.9	97.7	90	MoO ₂ , 310Å
Cu	0.02	0.0	1.7	98.2	90	Cu metal, 560Å
NiW	0.02	0.0	0.6	99.0	90	NiWO ₄ , 240Å
NiMo	0.02	0.0	1.0	98.9	90	not identifiable

estimated based on line broadening using the Scherrer equation. Unidentifiable phases probably had very small particle sizes ($< 10\text{\AA}$).

INNOVATIVE NICKEL CATALYSIS OF TEES

Several different forms of nickel catalysts were tested in order to evaluate both their activity and their stability in the TEES operating environment. The forms included unsupported metal and solutions of nickel salts, neither of which were likely to be useful but both of which eliminated the need of a stable support. More useful was the application of Raney® (Grace-Davison Specialty Chemical Company) nickel catalyst technology to the system. This high-surface area form of nickel metal has been widely used commercially. Tests were also made with supported nickel metal catalyst suspended in a basket in the vapor phase of the reactor to evaluate the role of the liquid phase in the chemistry and in support degradation. These different forms of catalyst are described in more detail in Table III.

Of the nickel catalyst forms tested, only the conventional catalyst materials had significant catalyst activity (Table IV). The nickel nitrate solution, which seems to show some activity, actually was serving as a reactant in that the nitrate oxidized a stoichiometric amount of organic and then the reaction ceased. Nickel ion in solution appears to have no catalytic activity, as further supported by other tests with acetate (Elliott et al. 1993a). The different nickel metal forms, although highly divided, are just too limited in surface area to be useful as catalysts. The wire mesh had only about $0.0035\text{ m}^2/\text{g}$ of surface area, while the nickel metal powder (assuming spherical particles) had only about $0.0045\text{ m}^2/\text{g}$ of surface area. For comparison, the Ni-0750 supported catalyst is reported to have $145\text{ m}^2/\text{g}$ of surface area.

The Ni(glycine-fired) was formed as finely divided nickel oxide in a proprietary process developed at Pacific Northwest Laboratory (Chick et al. 1990). The nickel oxide is actually collected as an ash fume from combustion of a glycine and nickel nitrate solution. The material is a relatively high surface area material, but apparently not in the same order of magnitude as the conventional catalysts.

Table III. Innovative Nickel Catalysts Tested in TEES

<u>Catalyst</u>	<u>Form</u>	<u>Comments</u>
Ni-0750 R-S	0.3 cm extrudate	nickel on alumina, powdered and slurried in feedstock
Ni(NO ₃) ₂ ·6H ₂ O	reagent in water solution	nickel in equimolar ratio to supported metal catalyst
Nickel wire mesh	40x40 mesh, wire 0.13 mm diameter	reduced in hydrogen, 19 hr @ 353°C
Nickel metal powder	< 150 μm	slurried in feedstock
Nickel metal powder	< 150 μm	reduced in hydrogen, 2 hr @ 350°C
Nickel on graphite	75% Ni, < 75 μm	reduced in hydrogen, 3 hr @ 360°C
Ni (glycine-fired)	NiO powder	reduced in hydrogen, 17 hr @ 410°C
Ni/ZrO ₂	-40+100 mesh	Ni sputtered on ZrO ₂ , reduced
Ni/2.5% Y/ZrO ₂	-40+100 mesh	Ni/Y sputtered on ZrO ₂ , reduced
Ni/4% Y/ZrO ₂	-40+100 mesh	Ni/Y sputtered on ZrO ₂ , reduced
NiZrO ₃	powder	reduced in hydrogen,
Raney® nickel	powder	activated with NaOH solution
Raney® nickel 5886	pellets	activated by manufacturer
Ni-0750 R-S	0.3 cm extrudates	suspended in stainless steel mesh basket above liquid/gas interface

R-S = reduced and stabilized by the manufacturer

® = registered trade mark of Grace-Davison Specialty Chemical Company

The sputtered-nickel catalysts were nearly inactive. Loading of metal was limited to less than 20 wt%. Crystallite size was reasonable (200-400Å) implying a useful extent of nickel dispersion and surface area, but, apparently, the nickel was not well distributed in the sputtering process and the resulting surface area was low. Addition of the yttrium did not improve the dispersion as the activity was still nearly nonexistent.

Table IV. Results of Tests with Innovative Nickel Catalysts

<u>Catalyst</u>	<u>% Carbon Conversion</u>	<u>Product Gas, Vol%</u>			<u>Time, min</u>	<u>Comments</u>
		<u>CH₄</u>	<u>CO₂</u>	<u>H₂</u>		
Ni-0750 R-S (slurry)	88.63	61.9	34.9	2.4	90	0.74 wt% C on catalyst ¹
Ni(NO ₃) ₂ ·6H ₂ O	27.8	0.0	47.2	0.2	60	NO ₃ ⁻ reduced
Ni mesh (reduced)	0.22	0.0	26.8	72.4	80	no activity
Ni powder	0.09	0.0	57.0	42.3	85	no activity
Ni powder (reduced)	0.01	0.0	6.6	94.3	60	no activity
Nickel on graphite	0.01	0.0	3.4	97.0	60	no activity
Ni(glycine-fired)	0.25	4.0	17.0	79.0	70	
Ni/ZrO ₂	0.12	5.6	13.7	80.5	80	
Ni/2.5 % Y/ZrO ₂	0.22	0.0	2.8	93.9	60	
Ni/4 % Y/ZrO ₂	0.07	0.2	1.5	98.3	90	
NiZrO ₃	0.17	0.6	12.0	87.4	80	
Raney® Ni powder	92.98	64.9	33.3	1.1	90	
Raney® Ni pellets	92.53	58.4	38.6	2.2	105	
Ni-0750 R-S (basket)	78.45	62.3	36.3	0.4	115	1.6 wt% C on catalyst ¹

Raney nickel is an aluminum-nickel alloy with the aluminum leached away by strong caustic to leave a highly porous nickel metal. The Raney nickel catalysts showed strong activity in the TEES environment both for gasification of organic and for methanation. Nearly all the para-cresol was removed from the water phase as indicated by the reduction of chemical oxygen demand (COD) of greater than 99% in both cases, as it was with the Ni-0750 catalyst. The nickel on alumina catalyst (Ni-0750) showed strong activity either

¹ Fresh Ni-0750 catalyst contains 0.35 wt% carbon.

slurried in the feedstock or suspended in the vapor phase. However, the reactivity in the test with suspended catalyst was somewhat inhibited, probably because of mass transfer limitations or because the chemistry in the liquid-phase was not catalyzed. The carbon deposition on the slurried catalyst was only slightly higher than the fresh catalyst, while the suspended catalyst picked up a significant amount of carbon. The carbon deposited on the suspended catalyst may represent either intermediates, which have been incompletely converted, or products of an alternate mechanism favored in the vapor phase.

CONVENTIONAL SUPPORTED-NICKEL CATALYSTS

Numerous conventional supported nickel catalysts have been tested in TEES. As reported earlier (Baker and Sealock 1988; Elliott et al. 1991), reduced nickel is the catalytically active form of nickel. All catalysts were reduced to the metallic state before the catalyst activity tests. Table V describes the various catalysts tested.

The supported nickel catalysts exhibited a wide range of activities in the TEES environment, as shown by the results in Table VI. The Ni-0750 (a hydrogenation catalyst) and the two BASF catalysts, Cat A and Cat B, (methanation catalysts) were the most active for gasification and methanation. The experimental NiZr catalyst (produced by thermal decomposition of a metal salt/glycine solution) and the Ni-6220 catalyst (a hydrogenation catalyst) appear to be nearly inactive. The PK-5 (a methanation catalyst) was not completely reduced in this single batch test, based on hydrogen consumption calculations. Its low activity in the batch test confirms our earlier report of low activity in a continuous reactor test (Elliott et al. 1991). RKNR (a steam reforming catalyst) and C150, G49B, and C11-09-04 (methanation and steam reforming catalysts) have intermediate activities.

The spent catalysts from these tests were analyzed to determine if any significant changes had occurred. In addition, other samples of some of these catalysts were subjected to long-term batch tests in water. These samples were also analyzed to determine changes resulting from exposure to the high-pressure steam/water environment at 350°C. Table VI lists the components identified in the spent catalysts. XRD analysis of the spent catalysts proved that the nickel metal stays reduced; however, there were significant changes noted in the composition of some of the support materials (described later in this paper).

Table V. Conventional Supported-Nickel Catalysts Tested in TEES

<u>Catalyst</u>	<u>Manufacturer</u>	<u>Composition</u>	<u>SA,</u> <u>m²/g</u>	<u>PV,</u> <u>cc/g</u>
Ni-0750 R-S	Engelhard	48% Ni on γ -alumina	145	0.50
Cat A	BASF	NiO on proprietary	NA	NA
Cat B	BASF	NiO on proprietary	NA	NA
C150 R-S	United Catalyst	62% Ni, SiO ₂ /Al ₂ O ₃	200	0.4-0.5
G49B R-S	United Catalyst	50% Ni on kieselguhr	75-175	0.3
RKNR R-S	Haldor Topsoe	25% Ni on MgO/Al ₂ O ₃	30	NA
C11-09-04 R-S	United Catalyst	20% NiO on α -alumina	3-10	NA
PK-5	Haldor Topsoe	25% NiO on η -alumina	250	NA
NiZr(glycine-fired)	PNL	2ZrO ₂ .NiO	NA	NA
Ni-6220 R-S	Engelhard	Ni on SiO ₂ /Al ₂ O ₃	NA	NA

R-S = reduced and stabilized by the manufacturer

NA = not available

The results of these analyses were combined with others following continuous reactor tests to determine the long-term stability of these catalysts in the TEES environment. The details of the continuous reactor tests and the results will be presented in a companion paper (Elliott et al. 1993b). Figure 2 shows the nickel crystallite size for the spent catalysts as a function of time at reaction conditions. Only the BASF Cat A appears to exhibit long-term stability for at least 4 weeks after an initial increase in crystallite size. Catalytic metal crystallite size has been correlated with loss of active surface area and, hence, catalytic activity (Pearce and Patterson 1981). It is apparent from these results and those in our earlier report (Elliott et al. 1991) that most commercial nickel catalysts cannot maintain their original crystal size when exposed to the TEES environment.

Table VI. Results of Tests with Various Supported Nickel Catalysts

<u>Catalyst</u>	<u>% Carbon Conversion</u>	<u>Product Gas. Vol%</u>			<u>Time. Spent min</u>	<u>Catalyst Form</u>
		<u>CH₄</u>	<u>CO₂</u>	<u>H₂</u>		
Ni-0750 R-S	88.63	61.9	34.9	2.4	90	Ni, AlOOH (böhmite)
Cat A	73.53	58.2	37.0	3.5	90	Ni,
Cat B	68.62	60.8	34.5	3.7	90	Ni,
C150 R-S	54.21	57.9	36.1	4.1	100	NA
G49B R-S	38.37	55.2	36.4	6.5	100	NA
RKNR R-S	24.30	29.8	29.6	38.8	80	NA
C11-09-04 R-S	5.24	15.2	32.5	50.3	100	Ni, α -alumina
PK-5 (2/3 reduced)	4.44	13.2	39.8	46.0	110	NiO, Ni, α - & η -alumina
NiZr(glyc-fired)	1.67	1.6	28.5	69.6	80	Ni, ZrO ₂
Ni-6220 R-S	0.82	3.1	24.2	70.4	75	Ni, amorphous support

NA = not available.

Figure 2. Crystallite Size Data for Various Metal Catalysts

SUPPORTED NOBLE METAL CATALYSTS

Recently we have begun testing noble metal catalysts for TEES. Particularly interesting are rhodium and ruthenium as these metals have been found by others to be useful methanation catalysts (Vannice 1975). Catalyst formulations with these metals typically contain much lower levels of metal because of their high cost. The catalysts tested are described in Table VII. Several types of support materials are also represented in the collection. Results of batch tests with these catalysts are shown in Table VIII.

Table VII. Noble Metal Catalysts Tested in TEES

<u>Catalyst</u>	<u>Manufacturer</u>	<u>Form</u>	<u>SA.</u> <u>m²/g</u>
5% Ru/ γ -Al ₂ O ₃	Engelhard	powder	NA
5% Ru/ δ -Al ₂ O ₃	Engelhard	1/8" star ext.	NA
5% Ru/ZrO ₂ -D	Engelhard	1/8" extrudate	NA
3% Ru/ γ -Al ₂ O ₃	Engelhard	1/8" star ext.	NA
5% Ru/carbon R-D	Johnson-Matthey	powder	1000
1% Ru/carbon R-D	Engelhard	granule	NA
5% Ru/ α -Al ₂ O ₃ D	Engelhard	powder	NA
5% Rh/carbon	Engelhard	powder	NA
1% Rh/ γ -Al ₂ O ₃ R-D	Johnson-Matthey	powder	300
1% Rh/ α -Al ₂ O ₃ R-D	Johnson-Matthey	powder	10
5% Pt/ γ -alumina R-D	Engelhard	65 μ m	125
5% Pd/ γ -alumina R-D	Engelhard	65 μ m	125
2% Pd/carbon	Degussa	granule	NA

R = reduced.

D = dried.

NA = not available.

Table VIII. Results of Tests with Various Noble Metal Catalysts

<u>Catalyst</u>	<u>% Carbon Conversion</u>	<u>Product Gas, Vol%</u>			<u>Time, min</u>
		<u>CH₄</u>	<u>CO₂</u>	<u>H₂</u>	
5% Ru/ γ -Al ₂ O ₃	89.1	58.9	38.8	1.0	90
5% Ru/ δ -Al ₂ O ₃	43.5	55.2	35.9	7.7	120
5% Ru/ZrO ₂ (reduced)	28.5	49.0	35.6	13.4	90
3% Ru/ γ -Al ₂ O ₃	18.8	40.9	37.3	20.6	120
5% Ru/carbon	21.4	24.1	58.6	10.2	110
1% Ru/carbon (reduced)	17.3	40.4	42.3	8.4	125
5% Ru/ α -Al ₂ O ₃ (reduced)	0.01	0.5	0.6	98.5	120
5% Rh/carbon (reduced)	26.6	57.5	36.3	2.3	125
1% Rh/ γ -Al ₂ O ₃ (reduced)	7.06	42.1	39.1	14.4	110
1% Rh/ α -Al ₂ O ₃	1.54	12.7	32.9	52.5	105
5% Pt/ γ -alumina	1.29	26.9	63.1	3.9	90
5% Pd/ γ -alumina	0.42	11.0	29.3	59.8	95
2% Pd/carbon (reduced)	1.20	7.2	56.3	35.2	90

The ruthenium and rhodium catalysts demonstrated significant activity for the conversion of para-cresol to methane and carbon dioxide in the TEES processing system. The COD conversion was >99% for the ruthenium on γ -alumina catalyzed test, suggesting that the carbon gasification measurement may under report the actual amount of gasification. The result is at odds with our earlier report (Elliott et al. 1991). Specifically, we have retested the 1% ruthenium on carbon after reducing the catalyst and found it to be active. Apparently the reduction done by the manufacturer was of a limited extent, as has been now confirmed by a manufacturer representative. We conclude that well-reduced ruthenium is an excellent catalyst in TEES, but that partially reduced ruthenium, i.e., a suboxide form, is not usable without hydrogen available for further reduction and activation.

The platinum and palladium results shown in Table VIII confirm our earlier reports of the lack of activity in TEES of palladium (Elliott et al. 1991). Extensive carbon deposition was found on these catalysts after just the 90-minute batch test. The carbon wt% was 4.3 for platinum and 6.8 for palladium on alumina-supported catalysts. That amount of carbon represents 7% to 10% of the carbon in the feedstock.

Another distinct characteristic of noble metal catalysts in TEES is their stability toward the hydrothermal conditions. Crystallite growth was observed for nickel catalysts, but ruthenium crystallite growth was not observed after 250 hours of exposure in TEES. These results are shown in Figure 2.

CATALYST SUPPORT EVALUATIONS

Numerous types of catalyst support materials have been tested in the TEES environment. These materials were chosen from commercially available support materials. Table IX provides a description of the supports before and after exposure to the TEES reaction conditions. These materials are in addition to those already tested in TEES, as described in an earlier publication (Elliott et al. 1991).

Extensive reaction with water has been discovered for most of these materials. All forms of alumina, except α -alumina, react to form γ -AlOOH, böhmite. The reaction of γ -alumina to böhmite results in a significant loss in physical integrity, as shown by the crush strength for Ni-0750 in Table IX. The conversion of δ -alumina to böhmite resulted in a dramatic loss in surface area from 147 m²/g to 15 m²/g. The stability of the α -alumina may also be tenuous since we are actually operating just outside the α -alumina range (and in the böhmite range) in the phase diagram reported in the literature (Ervin and Osborn 1951). The monoclinic form of zirconia appears to be quite stable at these conditions, and tablets made of this material seem to maintain their integrity. Silica also is unreactive, but the dissolution of some of the material probably explains the destruction of the extruded pellets. Titania also appears to be unreactive at these conditions. One form of tableted titania, similar to the zirconia tablet, lost its physical strength after processing at TEES conditions.

Table IX. Catalyst Supports Tested in TEES

<u>Support</u>	<u>Manufacturer</u>	<u>Product</u>	<u>Description</u>	
			<u>New</u>	<u>Used</u>
γ -Al ₂ O ₃	Engelhard	Ni-0750	γ -Al ₂ O ₃ 15 lb/in crush	AlOOH (böhmite) 9 lb/in crush
δ -Al ₂ O ₃	Engelhard	star cat	147m ² /g	AlOOH (böhmite), 15m ² /g
η -Al ₂ O ₃	Haldor Topsoe	PK-5	η -Al ₂ O ₃	AlOOH (böhmite), α -Al ₂ O ₃
α -Al ₂ O ₃	Engelhard	CS-5F	1.3m ² /g	α -Al ₂ O ₃ , 1.6m ² /g
α -Al ₂ O ₃	United	C11-09-04	α -Al ₂ O ₃	α -Al ₂ O ₃
ZrO ₂	Engelhard	Zr-0304	cubic/monoclinic	monoclinic
ZrO ₂	PNL	oxidized Zr	monoclinic	monoclinic
SiO ₂	Engelhard	712A-5-448	pellet	SiO ₂ , soft mush
TiO ₂	Degussa	P-25	powder	TiO ₂ 70/30:rutile/anatase
TiO ₂	Engelhard	Ti-0720	anatase 220Å, pellet	anatase > 1000Å, w/graphite, soft mush
carbon	J-M	--	with 5% Ru	methane, carbon dioxide
A	BASF	Cat A	proprietary	chrysotile (asbestos)
B	BASF	Cat B	proprietary	unchanged

A carbon-supported ruthenium catalyst was evaluated for long-term stability in the batch reactor with only water present. Formation of small amounts of carbon dioxide and methane suggests that the ruthenium metal would catalyze the destruction of its support at a slow rate. Extrapolation of the gas production rate for 65 hours suggests a 542-day lifetime for the carbon granule.

No correlation of the changes in the supports with nickel or ruthenium crystallite growth was discernible. The composition of the BASF catalyst supports is proprietary; however, it seems contradictory that the support that underwent almost no change (Cat B) carried nickel that underwent extensive increase in crystallite size (see Figure 2), while the

support that did change (Cat A) carried nickel that did grow initially but then stabilized. Apparently, nickel migration can be affected by the support composition, and the nickel agglomeration does not require either a chemical or physical change in the support.

CONCLUSIONS

Catalytic conversion in high-pressure, hot water systems requires specific catalyst properties that have not been previously evaluated. Many commercial catalysts provide short-term activity, but these catalysts lose activity readily in almost all cases because of reaction with water. Use of TEES to break down organics in water to produce gas requires an active metal catalyst which appears to be limited to the use of nickel, ruthenium, or rhodium. Ruthenium has a demonstrated long-term stability to crystallite growth at TEES conditions. All nickel catalysts lose activity readily because of crystallite growth and resulting loss of active surface area, although the loss is not significant in a few cases. The crystallite growth varies with support material. Most conventional catalyst support materials react with water at TEES conditions. Zirconia appears to be a potentially useful support material because of its stability.

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Appendix C

Batch Reactor Process Development Experiments for Organics Destruction

Chemical Processing in High-Pressure Aqueous Environments. 3. Batch Reactor Process Development Experiments for Organics Destruction

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ABSTRACT

A high-pressure (20 MPa) and high-temperature (350°C) liquid water processing environment was used to treat various wastewaters and model compounds. Organics were converted to methane and carbon dioxide in the presence of catalysts. Functional types included hydrocarbons, both aliphatic and aromatic; phenolics and other oxygenates; chlorinated hydrocarbon solvents; and sodium salts of organic acids. Tests with aqueous nickel ion showed negligible catalytic activity. Noncatalytic hydrolysis of sodium cyanide, carbon tetrachloride, and chloroform was also demonstrated. Ammonium destruction was proven by reaction with nitrate at these processing conditions. Several examples of test results with actual industrial waste streams showed that this process can be effectively used with catalysts to clean wastewater and recover waste organics as useful fuel gas.

INTRODUCTION

A high-pressure (up to 20 MPa) and high-temperature (250°C to 350°C) liquid water processing environment can be used to treat contaminants in process waters by converting the organics to gases. This system can be adapted for both environmental cleanup and energy recovery. Under the proper conditions, concentrated organics can be converted to useful fuel gas and dilute hazardous organics can be destroyed. Known as the Thermochemical Environmental Energy System (TEES®), this system is operated as a liquid-phase, heterogeneously catalyzed process at nominally 350°C and 20 MPa to produce a methane/carbon dioxide product gas from water solutions or slurries of organics. TEES is a registered trademark of Onsite*Ofsite, Inc., of Duarte, California, who holds the commercial license.

The concept was initially presented (Elliott and Sealock 1985; Sealock et al. 1988) as a biomass gasification process and was specifically developed for the processing of high-

moisture biomasses, which are not efficiently gasified in conventional thermal systems. The technology was later applied to hazardous organic chemical wastes and other organic chemical manufacturing wastewaters (Baker and Sealock 1988; Elliott et al. 1991). This paper reports the results of batch reactor studies on a wide range of organic (and inorganic) functional types. These batch reactor tests were an important beginning step in developing industrial systems based on this technology.

BACKGROUND

Use of nickel catalysts in a pressurized water reactor for reforming and methanating dissolved organics is a relatively novel concept. Nickel catalysts are used commercially in gas-phase steam-reforming of a wide range of volatile hydrocarbons to produce carbon monoxide and hydrogen (Rostrup-Nielsen 1984). Different nickel catalysts are used at lower temperatures and in high-pressure reactors for methanation of carbon monoxide/hydrogen synthesis gas (Sirohi 1975). A single-step reforming and methanation for conversion of coal to methane was studied in the early 1970s as a synfuels development project (Cox et al. 1975). Our process development activities have taken the concept one step further and utilized a higher pressure liquid water environment for processing wet feedstocks.

High-pressure liquid water processing of organics has received limited study. Production of liquid fuels from biomass/water slurries has been tested in a number of laboratories (Appell et al. 1975; Elliott 1980; Beckman and Elliott 1985). Coal conversion chemistry in aqueous systems has also been developed (Ross et al. 1990). However, gas production in high-pressure water systems has had little attention. Early catalytic work was unsuccessful in producing useful gas products (Modell et al. 1978), and interest shifted to oxidation systems (Modell 1982). There have been useful developments both in subcritical processing (Siskin and Katritzky 1991; Copa and Gitchel 1989) and in supercritical processing (Modell 1989) by oxidation, but recovery of the energy value of the organics as a useful fuel is not accomplished by reacting the organics with oxidants.

Noncatalytic, nonoxidizing reactions of organics in hot water have been investigated for a number of functional types. Experiments with cyanides (Tan and Teo 1987) and chlorofluorocarbons (Jeffers et al. 1989) have been reported. Hydrolysis rate constants were reported in both instances. Work in the supercritical phase has also been reported by Simkovic et al. (1987). In related work, competitive ionic and free radical reactions were described for aldehydes, alcohols, and polyols (Antal et al. 1987). Recently, the ZnCl_2 -catalyzed decomposition of quinoline in supercritical water was reported (Li and Houser 1992).

EXPERIMENTAL

The equipment and procedures designed for batch testing of high-pressure aqueous-phase organics destruction are described below.

EQUIPMENT

Gasification tests were carried out batchwise in a 1-L, Inconel® (Huntington Alloys, Inc., Huntington, West Virginia), bolted-closure, high-pressure autoclave (reactor). A schematic representation of the reactor is shown in Figure 1. The reactor vessel was fabricated by Autoclave Engineers, Inc., who also manufactured the magnetically coupled stirrer assembly and the reactor furnace. Pressure and temperature were monitored remotely. The temperature inside the reactor was monitored by a Type K thermocouple.

The entire experimental system, except for certain valves and the instrumentation, was located inside a 0.25-in.-thick plate steel barricade, which was built to ensure the safety of the operators while the system was at working pressure. A rupture disk was located on a line leading from the reactor to a 1-in. pipe, which served to vent the reactor contents to the outside of the laboratory in the case of reactor overpressure. The system was also configured with pressure and temperature monitoring devices (alarms), which turned off the furnace if the pressure or temperature exceeded preset limits.

Figure 1. Schematic of High-Pressure Reactor Used for TEES Conversion

The reactor was equipped with ports for sampling the contents at any time during experimental operation. The valves had extended handles, which allowed samples to be taken by operators outside the protective barricade without exposure to the pressurized reactor. The sampling system recovered a sample volume of about 10 mL. The sampling procedure developed for these tests resulted in negligible pressure drop and no discernible change in temperature. The batch reactor system and the sampling system are described in detail by Sealock et al. (1988).

PROCEDURES

For these experiments, 200 to 300 g of 10 wt% organic and water feed mixture were measured into a stainless steel liner along with nickel metal catalyst (Harshaw Ni-0750). The Ni-0750 catalyst was first ground into a powder to improve its dispersion in the reactor.

The liner and its contents were inserted into the reactor, which was then sealed. The reactor was purged, leak checked, and pressurized with a cover gas (nitrogen or argon, depending on whether or not nitrogen was expected as a product gas). The stirrer was started, and the reactor and its contents were heated to the desired temperature with a 1.7-kW electrical heater. Typically, about 60 min were required to heat the aqueous feedstock and catalyst to 350°C. The aqueous feedstock, product gases, and catalyst were rapidly mixed inside the reactor by the stirrer. An analog temperature controller maintained the temperature at the desired level once the contents reached the correct temperature. Typically, gas samples were withdrawn when the reactor reached the target temperature and then, usually, every 15 to 20 min. Other sampling schedules were used, as required, to monitor the reactions. At the end of the experiment, usually after 60 to 120 min, the contents of the reactor were rapidly cooled by running cold water through a cooling coil of stainless steel tubing attached to the inside of the reactor lid (see Figure 1).

After the reactor contents were fully cooled, the volume of the gas remaining in the reactor was determined by venting the gas through a wet test meter. A gas sample of the reactor contents was taken for chromatographic analysis. The liquid and solid materials left in the reactor were also examined and weighed so that a mass balance around the entire reactor could be made.

Elemental Analysis

A Perkin-Elmer (P-E) 240B analyzer was used for analysis of carbon deposits on the catalysts. The P-E 240B determines carbon, hydrogen, and nitrogen by detecting and measuring their combustion products (CO_2 , H_2O , and N_2). Combustion occurs in pure oxygen under static conditions, and the products are analyzed by thermal conductivity. Helium is used to carry the combustion products from the combustion furnace through the reduction tube (which reduces any NO_x) and through the series of detectors and traps. The

instrumental readout was in millivolts, which was used to calculate the composition based on reference compounds.

Gas Analysis

Gas analysis was performed by gas chromatography (GC) using a Carle AGC. The AGC configuration No. 0158A was used to detect low molecular weight gases, including hydrogen. This AGC uses a set of three columns (80% Porapak N + 20% Porapak Q, 50/80 mesh; Molecular Sieve 13X, 80/100 mesh; and 8% OV-101 on Chromosorb W AWD MCS, 80/100 mesh) with automatic switching controls to separate hydrogen, carbon dioxide, carbon monoxide, methane, ethane, ethylene, oxygen, and nitrogen. Propane and butane were detected in the backflush from the columns. A thermal conductivity detector was used in the AGC. Hydrogen was determined through the use of the Carle hydrogen transfer system, a metallic membrane for hydrogen separation by diffusion. The GC signal was processed in a Spectra-Physics 4290 integrator, which plotted the signal, integrated peaks, and determined retention times; it then printed a table of data including peak identifications and gas composition based on previously analyzed standard gas mixtures. A 0.7-cm³ gas sample was used for analysis.

Calculation of Gas Composition and Carbon Conversion to Gas

Following the analysis of the gas samples from the experiments, calculations were made to determine the composition of the actual gas product and to determine the conversion of organic to gases as a function of time. The gas sample was first calculated to an air-free composition to correct for air leakage into the sample during transfer from the sample line into a syringe and then through the septum into the GC. The correction was straightforward based on the subtraction of all the oxygen in the analytical result and subtraction of a portion of the nitrogen in a mole ratio of 78/21 to the oxygen as is found in air. The gas composition was further corrected to a cover gas-free basis to determine the actual composition of the gas generated from the organic.

The air-free gas composition of the samples was used to determine the carbon conversion to gas. The gas production was determined by the amount of pressure increase in the reactor at the sampling time. Calculations were made for each of the gas samples

recovered during the experiment. Carbon conversion to gas was then calculated on a mass basis for the carbon in the product gases as a percent of the carbon in the feedstock.

Aqueous Byproduct Analysis

The aqueous byproducts were analyzed for ammonia, chemical oxygen demand (COD), and pH. The ammonia analytical procedure involved the use of an ammonia-specific gas sensing electrode (ORION 95-12). The electrode was calibrated with a series of ammonium chloride solutions. All samples were pH adjusted to $\text{pH} > 11$ by adding 10M NaOH. The COD method used was the dichromate closed reflux colorimetric method, No. 5220D (American Public Health Association 1992). The pH was measured by an electrode calibrated against buffered pH 4.0 and 7.0 solutions.

RESULTS AND DISCUSSION

A range of feedstocks were tested in the batch reactor in a TEES processing environment. Various model compound reactions were investigated, which are described below. In addition, several industrial process water streams were also tested to provide an initial indication of the applicability of TEES as an energy recovery and wastewater cleanup process.

Generally speaking, at 350°C and 20 MPa, hydrocarbons and oxygenates react with water to produce CH_4 and CO_2 in nearly stoichiometric yields. A small amount of H_2 (< 5 vol%) is present in the product gas, suggesting a thermodynamic equilibrium concentration (Butner et al. 1987). Highly oxygenated organics produce more CO_2 and less CH_4 than hydrocarbons.

HYDROCARBONS

In an earlier report (Baker and Sealock 1988), conversions were discussed for hexane, benzene, and naphthalene at 400°C and 36 to 38 MPa with a nickel catalyst. Conversions of 99% or greater were achieved in 45 min or less (at temperature). Lower temperature (subcritical) processing is reported here for several hydrocarbons.

As shown in Figure 2, the conversion of several hydrocarbons varied widely. We interpret this variation as a function of molecular weight. Significant conversion of some of the feedstocks is apparent at less than the operating temperature of 350°C, as shown by the amount of conversion achieved at time zero (the point at which the reactor reached operating temperature from a cold startup).

Figure 2. Conversion of Hydrocarbons to Gas in TEES

The low conversion of the higher molecular weight materials (eicosane, polyethylene, and polystyrene) can be attributed to some extent to the low solubility and volatility of these materials. In all cases some of the feedstock was recovered as a lump of material floating on top of the water after the experiment, even though the material was fed as a powder. The catalyst in the polyethylene test (and to a lesser extent in the eicosane test) appeared to have little interaction with either the feedstock or the minimal amount of gas product produced. There is only a small amount of carbon deposit on the catalyst despite the large amount of

residual carbon in the condensed phase, and there is only a limited level of methane synthesis.

The product gas contains a relatively larger amount of methane than carbon dioxide (Table 1), as would be predicted based on the highly reduced character of the feedstock. Carbon buildup on the catalyst was inversely related to the amount of conversion; i.e., the lower the conversion, the more carbon that was left on the catalyst.

Based on these and earlier results (Baker and Sealock 1988), it is clear that hydrocarbons can be reformed and methanated in a high-pressure water reactor system incorporating a nickel metal catalyst. A distinct relationship between molecular weight and reaction rate is also apparent. Aromatic hydrocarbons of one or two rings are readily gasified at temperatures as low as 350°C. Higher molecular weight materials will require extended residence times or more efficient methods of contacting the catalyst with the feedstock. Residence times in the batch reactor reported here are relatively comparable, but actual conversion rates in continuous-flow, fixed-bed reactors are expected to be significantly faster, as found with other feedstocks in our related research in continuous-flow, bench-scale reactor systems (Elliott et al. 1993b).

OXYGENATES

Para-cresol was used as a model compound for hazardous waste in the initial development of TEES (Baker and Sealock 1988). It has also been used extensively in the more recent research on catalyst development (Elliott et al. 1993a). Conversions of 99% or greater have been achieved in 45 min or less in the presence of active catalysts at temperatures of 350° to 400°C. In this paper, the testing is extended to the other two cresols (ortho- and meta-), as well as other oxygenates: propylene glycol, vinegar (dilute acetic acid), and ethanol.

As shown in Figure 3, the conversion of oxygenates was achieved readily at 350°C. Significant conversion of some of the feedstocks is apparent at less than the operating temperature of 350°C, as shown by the amount of conversion achieved at time zero (the point at which the reactor reached operating temperature from a cold startup). The data of Baker and Sealock (1988) for methylisobutylketone (MIBK) is also plotted for comparison.

Table 1. TEES Conversion of Hydrocarbon Feedstocks

	<u>Benzene</u>	<u>Biphenyl</u>	<u>Anthracene</u>	<u>Polystyrene</u>	<u>Hexane</u>	<u>Pentadecane</u>	<u>Eicosane</u>	<u>Polyethylene</u>
Gas Yield, L/g	1.84	1.80	0.69	0.59	0.49	0.36	0.20	0.05
Gas Composition, %								
Methane	61.4	63.4	51.3	57.0	64.8	62.6	39.7	0.9
Carbon Dioxide	34.2	35.2	40.0	34.9	22.5	23.6	28.2	54.3
Hydrogen	4.1	1.3	8.7	8.0	6.2	13.5	31.8	44.6
Ethane	0.2	0.09	0.04	0.1	0.4	0.2	0.1	0.1
Time @ Temp., min	100	100	100	80	100	100	60	88
Carbon on Catalyst, %	0.4	0.1	2.0	5.2	0.01	0.34	0.12	0.2

Although a different nickel catalyst was used in the earlier test (Harshaw Ni-1404), the results appear comparable.

Figure 3. Conversion of Oxygenates to Gas in TEES

For comparison, a second test with vinegar was performed without the addition of the nickel catalyst. In that case, conversion of the carbon in the acetic acid to gas was only 1.5% after 90 min at temperature. The product gas was primarily hydrogen, 62.6%, with smaller amounts of carbon dioxide, methane, and ethylene, 28.6%, 5.9%, and 2.3%, respectively. This result is in line with the Baker and Sealock (1988) report that only 1.2% of MIBK and only a trace amount of p-cresol were converted to gas at 400°C without a nickel catalyst.

The product gases contain substantial amounts of methane (Table 2). The ratio of methane to carbon dioxide in the product gas can be predicted based on the extent of

oxidation of the feedstock. Carbon buildup on the catalyst was again inversely related to the amount of conversion.

Table 2. TEES Conversion of Oxygenate Feedstocks

	<u>p-Cresol</u>	<u>m-Cresol</u>	<u>o-Cresol</u>	<u>Propylglycol</u>	<u>Ethanol</u>	<u>Vinegar</u>	<u>MIBK^a</u>
Gas Yield, L/g	1.84	1.49	1.39	0.87	0.98	0.68	0.95
Gas Composition, %							
Methane	61.4	58.6	57.9	63.8	74.9	39.1	49.9
Carbon Dioxide	34.2	37.3	37.6	30.3	21.7	46.2	30.2
Hydrogen	4.1	2.4	2.9	5.5	3.1	14.4	3.3
Ethane	0.2	0.4	0.5	0.5	0.2	0.2	0.8
Time @ Temp., min	100	80	80	90	80	90	75
Carbon on Catalyst, %	0.4	0.4	0.1	0.4	0.3	NA	5.8

^a Baker and Sealock (1988)

Based on these and earlier results (Baker and Sealock 1988), it is clear that a range of oxygenates can be reformed and methanated in a high-pressure water reactor system incorporating a nickel metal catalyst. Without the catalyst, reforming of the oxygenates is very slow. Residence times reported here are relatively comparable, but actual processing rates in fixed bed reactors are significantly faster (Elliott et al. 1993b).

HALOGENATES

Chlorinated hydrocarbons react similarly to hydrocarbons except the chlorine is converted to HCl. At one extreme, carbon tetrachloride is converted to HCl and CO₂. Other chlorinated hydrocarbons produce CH₄ and H₂ as well. Trichloroethylene and chloro-

benzene were used as model compounds for hazardous waste early in the development of TEES (Baker and Sealock 1988). For this paper, the testing was extended to two other halogenates, chloroform and carbon tetrachloride. These tests were performed at relatively low concentration, just above the solubility limit of the halogenates in water at room temperature.

As shown in Table 3, the conversion of these materials was achieved readily at 300°C. Carbon tetrachloride appears to react more readily than chloroform. A number of catalyst materials were tested, but good conversion of the halogenates was achieved without any catalyst. The composition of product gases is affected by the catalyst, suggesting some effects on the chemical mechanisms. The product gases contain substantial amounts of carbon dioxide. Carbon monoxide is also a significant product except in the presence of the nickel catalyst, which must convert it to methane. Chloroform yields larger amounts of carbon monoxide than does carbon tetrachloride.

Table 3. TEES Conversion of Halogenate Feedstocks

Catalyst	<u>CCl₄</u> Ni-0750	<u>CCl₄</u> γ-alumina	<u>CCl₄</u> none	<u>CHCl₃</u> γ-alumina	<u>CHCl₃</u> none
Product Gas Composition					
Methane	2	0	4	0	0
Carbon Dioxide	70	78	36	45	27
Hydrogen	28	17	58	12	34
Carbon Monoxide	0	6	2	42	39
Final Solution Conc.					
CCl ₄ , ppm	ND	0.4	0.6	<.01	<.01
CHCl ₃ , ppm	0.36	0.7	1.4	10	5

1000 ppm initial concentration of halogenate in water.

60 min @ 300°C +/- 5°C; autogenic pressure = 8 to 10 MPa.

ND = not detected.

Based on these results and those reported for continuous reactor testing in a companion paper (Elliott et al. 1993b), it is clear that noncatalytic hydrolysis of single-carbon halogenates can be achieved in a high-pressure water reactor system at reasonable rates at temperatures as low as 300°C.

AQUEOUS SALT SOLUTIONS

Aqueous salt model compounds were tested both as representative hazardous waste components and as potential homogeneous catalysts. For this paper, the testing included sodium phenolate, sodium benzoate, sodium cyanide, nickel acetate, and nickel nitrate (with p-cresol). The phenolate and benzoate can be compared to other organics, while the cyanide is considered individually, and the nickel nitrate and acetate test results reflect attempts at homogeneous catalysis of the conversion of the organics to gases.

As shown in Figure 4, the conversion of the sodium salts of phenol and benzoic acid was relatively slow, for example, compared with p-cresol or benzene (p-cresol and phenol have been shown to have similar reaction rates, see Elliott et al. 1991). The rate of carbon gasification is shown as determined by two methods: by direct measurement of gas production and in a corrected mode that allows for the carbon dioxide product gas uptake in the aqueous phase as bicarbonate of the sodium liberated from the organic salts. As shown in Table 4, the product gases contain primarily methane, carbon dioxide, and hydrogen, with small amounts of ethane.

The sodium inhibition of the gasification of the organics has been reported earlier for p-cresol and MIBK (Baker and Sealock 1988). No speculation of the mechanism has been made. Methane formation inhibition in the presence of sodium has also been noted (Sealock et al. 1982, 1988; Elliott et al. 1991). The reduced level of methane production has been attributed, at least in part, to increased competition of the water-gas shift reaction as catalyzed by base with the gas-phase synthesis of methane.

Sodium cyanide conversion was also tested by catalytic processing. Because of the high ratio of sodium to carbon in the feedstock (1 to 1 atomic ratio), there is almost no recoverable gas production. Based on stoichiometry, all the hydrolysis product of carbon dioxide could be trapped in the aqueous phase as bicarbonate. The nitrogen balance around

Figure 4. Conversion of Sodium Salts to Organics in TEES

Table 4. TEES Conversion of Aqueous Salt Feedstocks

	Sodium Phenolate	Sodium Benzoate	Sodium Cyanide	Nickel Nitrate ^a	Nickel Acetate
Gas Yield, L/g	0.67	0.30	0.06	0.87	0.01
Gas Composition, %					
Methane	48.5	33.5	19.3	0.1	16.8
Carbon Dioxide	26.7	51.4	16.4	99.4	41.7
Hydrogen	24.4	14.9	23.0	0.2	41.0
Ethane	0.4	0.1	0.4	0.0	0.0
Ethylene	0.0	0.0	0.0	0.0	1.7
Carbon Monoxide	0.0	0.0	0.0	0.3	0.3
Time @ Temp., min	91	90	95	90	90

^a With 10% para-cresol.

this test was not good, but a large fraction of the nitrogen was measured as ammonia in the aqueous phase (1380 ppm by gas sensing electrode). Elemental analysis indicated that there was approximately 0.1% nitrogen in the aqueous effluent compared with 1.0% in the feed. Some nitrogen gas product was also recovered, although it is not reported in Table 4 since the gas product is listed on a nitrogen-free basis. Residual cyanide was measured at 90 ppm by a silver nitrate titration. Noncatalytic tests by others (Tan and Teo 1987) at lower temperatures suggest that this high conversion of cyanide in water may be achievable by simple hydrolysis.

The nickel nitrate and nickel acetate tests were both performed without a supported nickel metal catalyst. The nickel nitrate was added to a 10% p-cresol solution to test the oxidation of the organic with the nitrate ion. Analysis of the aqueous effluent indicated that < 100 ppm nitrate remained of the 10 wt% nitrate solution used as the feed. However, the conversion of the p-cresol was far from complete but reflects a stoichiometric reaction with the nitrate. This result contrasts strongly with the nearly complete conversion of p-cresol in the presence of a supported nickel metal catalyst. In the case of the nickel acetate, the carbon conversion to gas was almost nil (0.94%), compared with the high conversion of acetic acid (vinegar) with supported nickel catalyst. From these two tests it is clear that nickel ion does not catalyze the reaction of organics with water as does supported reduced nickel metal. However, the reaction of nitrate with organics proceeds rapidly even without the supported nickel catalyst.

INDUSTRIAL WASTE TREATMENT

Batch reactor tests have been undertaken with numerous industrial waste streams to determine the applicability of TEES to the cleanup problem (Baker et al. 1989; Sealock et al. 1988). The tests reported here include nylon manufacturing wastewater, polyol manufacturing wastewater, and olive processing waste. These streams represent relatively dilute hazardous to benign chemical wastes and nonhazardous food processing wastes.

Nylon Manufacturing Wastewater

Wastewater from a commercial nylon manufacturing plant was processed in several batch tests to compare catalytic effects. The results of the tests are given in Table 5. Of the

three tests, two were done with a commercially available nickel catalyst and the third was done with a proprietary catalyst being developed in our research program. The wastewater was nominally 0.6% hexamethylenediamine in water with 0.1% cyclopentanone. Over time of storage of the sample, a noticeable amount of precipitate formed (apparently the carboxylate salt), which was remixed with the water for sampling particularly in the last two tests. The balances of the gas compositions were primarily C₂s to C₄s; NO and N₂O were not detected. The product water was consistently at 50 to 55 mg/L of COD compared with our measurement of 1200 mg/L on the process water, as received. The pH of the water dropped from 10.7 to 6.9 in the processing.

Table 5. Results of Tests with Nylon Manufacturing Wastewater

<u>Catalyst</u>	<u>CH₄</u>	<u>CO₂</u>	<u>H₂</u>	<u>N₂</u>	<u>COD Conv.,%</u>	<u>Time</u>
Ni-0750	12.4	32.1	53.6	1.8	96.0	120
Proprietary	7.6	5.8	76.5	9.9	95.4	90
Ni-0750	0.6	37.2	55.0	7.1	95.9	120

Ammonia analysis of the effluent from nylon wastewater processing showed that nearly all of the diamine portion of the wastewater was converted to ammonia in the reaction. Additional tests were made of potential ammonia treatment processes to destroy the ammonia in the final process effluent. The treatment included both the reaction of nitrate ion with the ammonia to produce nitrogen gas and the direct catalytic dissociation of the ammonia.

The product from TEES treatment of the nylon wastewater was simulated by a solution of 8 mL of NH₄OH (reagent grade, 29.1%) in 2 L of water; 300 mL of this solution were then mixed with 1 mL of concentrated nitric acid (feed solution analysis: 830 ppm NH₃, 1100 ppm NO₃-N). The results of these tests are given in Table 6. Nitrogen product gas is produced in a ratio of about 10 to 1 in relation to N₂O product gas. Ammonia destruction is

not favored in the presence of the nickel catalyst. The uncatalyzed tests show a strong temperature effect on the rate of ammonia reaction with nitrate between 300°C and 350°C. An explanation of the difference in the results of Experiments 2 and 3 could be that slightly less nitric acid was added in Experiment 2 (only a few percent difference in the 1 mL aliquot of acid could account for the difference) such that all the nitrate was exhausted before all the ammonia was consumed. A slightly larger amount of nitrate in Experiment 3 could have allowed the reduction of the ammonia to a lower level while resulting in a higher residual nitrate.

Table 6. Results of Ammonia Treatment Tests

	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>
Catalyst	Ni/Al ₂ O ₃	none	none	none	Fe ₂ O ₃ ^a
Temperature, °C	350	350	350	300	350
Nitrate added	yes	yes	yes	yes	no
Product Analysis					
NH ₃ , ppm	880	87	26	520	580
NO ₃ -N, ppm	75	0.8	41	750	---

^a No nitric acid added.

As shown by the results of Experiment 5 in Table 6, the iron oxide ammonia dissociation catalyst, without addition of nitrate, cannot effectively catalyze the dissociation of ammonia reaction at temperatures as low as 350°C, even in the presence of high-pressure water.

Polyol Manufacturing Wastewater

Two wastewater streams from polyol (polypropylene glycol) manufacturing have been tested (Table 7). The pH of the polyol wastewaters dropped from about 12.5 to about 7 in

the processing. This effect suggests that the potassium in the stream is reacting with carbon dioxide product gas to reduce the basicity of the solution. A coordinated analytical program performed by the manufacturer showed low residual levels of polyol. The "B" stream contained less polyol and more monomer (which is readily gasified by TEES, as shown above), and, therefore, a higher COD destruction percentage was achieved while a lower percentage of the polyol was gasified.

An uncatalyzed test of the "A" polyol wastewater produced very little gas; < 10% of the carbon assumed to be in the feed was recovered as gas. The pH was reduced slightly from that of the starting material (10.1 vs. 12.2). Polyol analysis provided by the manufacturer showed significant polyol destruction during this test. We conclude that the polyol is hydrolyzed to a great degree by a noncatalytic mechanism, yet final gasification is only achieved at useful rates by catalysis.

Table 7. Polyol Treatment Test Results

<u>Feedstock</u>	<u>CH₄</u>	<u>CO₂</u>	<u>H₂</u>	<u>C₂</u>	<u>Destruction of COD, %</u>	<u>Product COD, ppm</u>	<u>Destruction of polyol, %</u>
Polyol A	20.8	42.4	36.1	0.9	85.3	650	97.7
Polyol B	10.0	65.8	24.0	0.1	97.2	160	90.5
Polyol A	1.9	3.8	78.7	1.7 ^a	<5(est.)	7250	86.4

^a Uncatalyzed test product gas also contained 13.8% propane.

Olive Processing Wastewater

An olive processing wastewater was also tested. In a single batch test, 98.7% destruction of COD was attained with a 95.5% recovery of carbon as gas product. The wastewater had an initial COD of 26,500 ppm and was reduced to 360 ppm. Apparently, the

organic components incorporated into the wastewater from olive processing are easily treated in the TEES process.

CONCLUSIONS

These test results show that TEES is an effective processing system for converting organics in water to fuel gases. A wide range of organic functional types have been treated including hydrocarbons, both aromatic and aliphatic; oxygenates, such as phenolics, acids, alcohols, glycols, and ketones; chlorinated hydrocarbons; and acid salts and cyanide. These same types of components can also be treated in mixed organic industrial wastewater streams. In addition, diamine containing wastewater streams can be converted. A related technology of ammonia and organics treatment with nitrate has also been demonstrated. Common to all these chemistries is the use of a pressurized liquid water reaction environment at 300°C to 350°C and 10 to 20 MPa.

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Appendix D

Continuous-Flow Reactor Process Development Experiments for Organics Destruction

Chemical Processing in High-Pressure Aqueous Environments. 4. Continuous-Flow Reactor Process Development Experiments for Organics Destruction

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ABSTRACT

A high-pressure (20 MPa) and high-temperature (350°C) liquid water processing environment was used to treat various wastewaters and model compounds. Organics were converted to methane and carbon dioxide in the presence of a fixed bed of nickel or ruthenium catalyst. Nitrates were destroyed by reaction with methanol in the presence of a nickel catalyst. Noncatalytic hydrolysis of carbon tetrachloride and chloroform was also demonstrated. Three scales of continuous-flow reactors were used in these tests. Extended tests to demonstrate catalyst lifetimes were also performed. Several examples of test results with actual industrial waste streams showed that this process can be effectively used with appropriate catalysts to clean wastewater and recover waste organics as useful fuel gas.

INTRODUCTION

A high-pressure (up to 22 MPa) and high-temperature (250°C to 350°C) liquid water processing environment can be used to treat contaminants in process waters by converting the organics to gases. This system can be utilized for both environmental cleanup and energy recovery. Under the proper conditions, concentrated organics are converted to useful fuel gas and dilute hazardous organics are destroyed. Known as the Thermochemical Environmental Energy System (TEES®), this system is operated as a liquid-phase, heterogeneously catalyzed process at nominally 350°C and 20 MPa to produce a methane/carbon dioxide product gas from water solutions or slurries of organics. TEES is a registered trademark of Onsite*Ofsite, Inc., of Duarte, California, who holds the commercial license.

The history of the development of the TEES concept was recently reviewed (Sealock et al. 1993). This article is the fourth in a series describing the most recent results in the developmental effort. The earlier papers addressed 1) the processing environment (Sealock

et al. 1993); 2) catalyst systems for this environment (Elliott et al. 1993a); and 3) batch reactor tests with various organic chemical components and waste streams (Elliott et al. 1993b). Here we report the results of continuous-flow reactor studies with fixed beds of catalyst in a tubular reactor. These tests demonstrate the scale-up of a useful reactor configuration for industrial application of the TEES technology.

BACKGROUND

The use of high-pressure liquid water at elevated temperatures as a processing environment has recently been reviewed (Sealock et al. 1993). One application of this processing environment is for catalytic gasification of organics. In this application, which we call TEES, catalysts accelerate the reaction of organics with water and produce methane and carbon dioxide from the product gases. TEES has been reported both as a means of recovering useful energy from organic-in-water streams and as a water treatment system for dilute organic contaminants. Batch reactor test results have demonstrated process applicability to a wide range of organic components (Sealock et al. 1988; Baker and Sealock 1988; Elliott et al 1993b). Development of catalysts for this processing environment has also been an important factor in making this processing technology viable (Elliott et al. 1993a). Previous reports of continuous reactor tests of TEES were primarily short-term processing results (Baker et al. 1989a,b; Elliott et al. 1991). This article provides additional results with other feedstocks and with longer-term and larger-scale operations.

EXPERIMENTAL

The equipment, procedures, and catalysts described below were used for the continuous reactor testing of high-pressure, aqueous-phase destruction of organics by gasification.

EQUIPMENT

Gasification tests were carried out in three scales of fixed-bed catalytic tubular reactor.

Bench-Scale Operation

The bench-scale unit, shown schematically in Figure 1, was described in detail in an earlier report (Elliott et al. 1991). The unit consisted of a 1.83 m long X 25 mm I.D. (6 ft x 1 in. I.D.) 304SS tube which 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.

Figure 1. Schematic of Bench-Scale Reactor System

Micro-Scale Operation

A microtubular version of this reactor system was used for catalyst lifetime studies. All the components shown in Figure 1 for 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 0.3 m of 13 mm (1/4 in.) 316SS tubing. In addition to the reactor, there was a preheater section consisting of 2.1 m of 3.2 mm (1/8 in.) tubing. Both the reactor and the preheater were contained in the electrical resistance reactor furnace.

Engineering-Scale Operation

The scaled-up reactor system (SRS) was based on the bench-scale design. It was a transportable system designed at a scale of one-half ton per day of wet feed for obtaining engineering data for further scale-up of TEES. The SRS was mounted on a single 2.44 m X 3.05 m (8 ft x 10 ft) skid platform that could be transported on a single flat-bed truck. Equipped with three fixed-bed tubular reactors and supporting equipment to achieve conversion, the test system's capacity was a one-half ton per day liquid feed with a design flow rate of 22 L/hr. Design working conditions for the reactors were 350°C at 24 MPa.

As diagrammed in Figure 2, the aqueous organic feedstock was either loaded into or prepared for processing in feed tanks at the front end of the process. Each of the 300 L tanks was constructed of mild steel, lined with a chemical-resistant epoxy, and had a centrifugal pump to circulate and agitate the tank's contents. These pumps were also used to transfer feedstock from one tank to another or from the feed tank to the high-pressure feed pump. A hinged lid on the mixing tank provided access for either loading or preparing feedstock, and the feed tank was completely sealed. Feedstock could be loaded into the feed tank from the mixing tank, or it could be directly pumped in from an outside source.

Once prepared, the feed stream was pumped through the tube side of the preheater by a positive displacement pump. This pump was a standard Kerr KD 1250B fitted with a 16-mm (5/8 in.) plunger and a half-stroke crankshaft. Constructed of mild steel, the pump was capable of delivering 38 L/hr at 27.6 MPa. The preheater was a double-tube type heat exchanger that was constructed of 316SS tubing. The tube side was 9.5 mm (3/8 in.) O.D. X 1.2 mm (0.049 in.) wall. The shell was 19 mm (3/4 in.) O.D. X 2.1 mm (0.083 in.)

Figure 2. Schematic of Scaled-Up Reactor System

wall. Pressure in the heat exchanger was limited by the shell side, which had a maximum allowable working pressure (MAWP) of 23.4 MPa at 350°C. With a total length of 15 m, the preheater could bring the feedstock to within 30°C of the final operating temperature.

The final heating of the feed was accomplished in the preheater vessel which was enclosed in a 1.45 m X 0.4 m X 0.4 m cabinet fitted with ceramic furnaces. The preheater vessel (H-1) was 1.8 m (6 ft) long and had a 76 mm (3 in.) O.D. with a 51 mm (2 in.) I.D. High Pressure Equipment Company manufactured the vessel out of 304SS and rated it to 23.40 MPa at 350°C. The furnace assembly contained three sets of tube-type ceramic heaters. Each set operated independently of the other two, thereby creating a three-zoned furnace. The furnace was rated at 538°C with power requirements of 7500 W at 230 V.

After heating, the feed was routed to the two reactor vessels (R-1 and R-2). Flow could be directed through the reactors in either a series or parallel configuration or through

only R-2. The system has been run only in the series configuration because of inconsistent flow characteristics in parallel operation. Each reactor was fitted with two sets of ceramic-tube-type external furnaces to provide makeup heating of the feed stream. The first set of heaters, located on the bottom third of the reactors, was 46mm (18 in.) long and rated at a total of 2200 W at 230 V. The reactors were of a tubular fixed-bed design with volumes of 3.7 L each. The preheater vessel was of the same design and size as each of the reactors and, if filled with catalyst, could serve as a third reactor. After leaving the reactor(s), the product stream was routed through the outer tube of the double-tube heat exchanger to provide heat for preliminary heating of the feed stream. After passing through the exchanger, the product stream entered a liquid/gas cooler that fed a liquid/gas separator tank where process water was reclaimed and combustible gases were vented.

Pressure in the system was regulated to approximately 20.8 MPa by a back-pressure regulating valve capable of yielding a 41.5-MPa pressure drop across its restriction piston. One rupture disk assembly and two pressure relief valves were incorporated in the system to ensure system pressure never exceeded 23.5 MPa. The rupture disk assembly, located at the front end of the system between the feed pump and the heat exchanger, was equipped with a disk rated at 21.8 MPa. The first pressure relief valve, located at the top of the preheater vessel, was set to relieve at 23.5 MPa. The second pressure relief valve, located at the top of the preheater vessel, was also set to relieve at 23.5 MPa. The rupture disk vented feedstock from the feed pump into the feed tank. A check valve between the rupture disk assembly and the heat exchanger ensured that the remainder of the system did not depressurize through the rupture disk assembly. Both pressure relief valves went through a catch pot and into a vented catch barrel located outside the west wall of the operations facility.

PROCEDURES

For these experiments, the test was preceded by a period of heating of the catalyst bed in hydrogen to ensure reduction of the catalyst. Actual startup of the experiment usually required an hour or more to bring operating conditions to the desired levels. Startup of the

SRS required in excess of 4 hr. Operating data were recorded, and data windows were defined based on steady-state (or near steady-state) operating conditions.

Elemental Analysis

A Perkin-Elmer (P-E) 240B analyzer was used for analysis of carbon deposits on the catalysts. The P-E 240B determines carbon, hydrogen, and nitrogen by detecting and measuring their combustion products (CO_2 , H_2O , and N_2). Combustion occurs in pure oxygen under static conditions, and the products analyzed by thermal conductivity. Helium is used to carry the combustion products from the combustion furnace through the reduction tube (which reduced any NO) and through a series of detectors and traps. The instrumental readout was in millivolts, which was used to calculate the composition based on reference compounds.

Gas Analysis

Gas samples were withdrawn from the smaller two systems by an automated sampler and manually. Automated samples were withdrawn typically every 5 min and manual samples every 20 to 30 min. However, in the longer-term tests, the automatic procedure was limited to once every 60 min, and manual samples were withdrawn twice a day. The gaseous stream was composed principally of CO_2 , CH_4 , H_2 , and C_2 + hydrocarbons, as well as water vapor.

The online gas analysis equipment was able to measure concentrations of carbon oxides, hydrogen, methane, and C_2 hydrocarbons with reasonable accuracy and precision on a near-continuous (real-time) basis with a very short (<5 min) turnaround. A thermal-conductivity detector was used.

Manual gas analysis was performed by gas chromatography (GC) using a Carle AGC. The AGC used a set of three columns (80% Porapak N + 20% Porapak Q, 50/80 mesh; Molecular Sieve 13X, 80/100 mesh; and 8% OV-101 on Chromosorb W AWD/MCS, 80/100 mesh) with automatic switching controls to separate hydrogen, carbon dioxide, carbon monoxide, methane, ethane, ethylene, oxygen, and nitrogen. Propane and butane were detected in the backflush from the columns. A thermal conductivity detector was used in the AGC. Hydrogen was determined through the use of the Carle hydrogen transfer system, a metallic membrane for hydrogen separation by diffusion. The GC signal was processed in a

Spectra-Physics 4290 integrator, which plotted the signal, integrated peaks, and determined retention times; it then printed a table of data including peak identifications and gas composition based on previously analyzed standard gas mixtures. A 0.7-cm gas sample was used for analysis.

Calculation of Carbon Conversion to Gas

Following the analysis of the gas samples from the experiments, calculations were made to determine the composition of the actual gas product and to determine the conversion of the organic feedstock to gases. For the manual GC analyses, an air-free gas composition correction was used. Carbon conversion to gas was then calculated on a mass basis for the carbon in the product gases (from either the direct online analysis or the manual analysis corrected to air-free basis) as a percent of the carbon in the feedstock. In those cases in which the mass balance was deficient, the gas yield was normalized to a 100% recovery.

Aqueous Byproduct Analysis

The aqueous byproducts were analyzed for ammonia, chemical oxygen demand (COD), and pH. The ammonia analytical procedure involved the use of an ammonia-specific gas sensing electrode (ORION 95-12). The electrode was calibrated in 10M NaOH. The COD method used was the dichromate closed reflux colorimetric method, No. 5220D (American Public Health Association 1992). The pH was measured by an electrode calibrated against buffered pH 4.0, 7.0, or 10.0 solutions.

CATALYSTS

The catalysts used in these experiments were acquired from commercial catalyst manufacturers. The available information on their compositions and properties is given in Table 1.

Table 1. Conventional Metal Catalysts Tested in TEES

<u>Catalyst</u>	<u>Manufacturer</u>	<u>Composition</u>	<u>SA,</u> <u>m²/g</u>	<u>PV,</u> <u>cc/g</u>
Ni-0750	Engelhard	48% Ni on γ -alumina	145	0.50
BASF	BASF Corporation	NiO on proprietary	NA	NA
Raney® 5886	Grace/Davison	pellets	NA	NA
C150	United Catalyst	62% Ni on SiO ₂ /Al ₂ O ₃	200	0.4-0.5
5% Ru/ δ -Al ₂ O ₃	Engelhard	1/8" star extrudate	NA	NA
5% Ru/ZrO ₂ -D	Engelhard	1/8" extrudate	NA	NA
3% Ru/ γ -Al ₂ O ₃	Engelhard	1/8" star extrudate	NA	NA

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RESULTS AND DISCUSSION

The experiments yielded information on catalyst effects and lifetimes and use of the TEES process with various industrial-related feedstocks.

EVALUATION OF CATALYSTS

Several metal catalysts have been evaluated in the TEES continuous reactor systems. Based on catalyst screening in batch reactor tests (Elliott et al. 1993a), the focus of these evaluations was on the use of nickel and ruthenium as the catalytic metal. Catalyst support effects are also an important consideration, and several different support materials and unsupported Raney nickel catalyst were evaluated.

Short-term test results (< 8 hr), given in Table 2, show the variation in catalyst activity attained in TEES with nickel catalysts. The Ni-0750 and BASF catalytic results are nearly equivalent. The Raney nickel test is slightly different because only a limited amount

Table 2. Short-Term Experimental Results with Nickel Catalysts

	<u>Ni-0750</u>	<u>BASF</u>	<u>Raney</u>	<u>C150</u>
Feedstocks	p-cresol	p-cresol	p-cresol	p-cresol
<u>Results</u>				
Gasification	99.4	97	99.9	68.6
Carbon, %				
Reduction	99.994	99.9	99.8	97.3
COD, %				
Feed, L/hr	1.6	1.6	1.1	1.1
LHSV, L/L/hr	2.7	2.8	2.8	1.8
Gas Yield, L/hr	41.6	40	30.9	21.1
Effluent COD, ppm	3	76	105	1300
Effluent pH	4.3	4.8	3.5	4.0
Gas Composition, volume %				
Methane	62	55	57	61
Carbon Dioxide	36	44	30	33
Hydrogen	1.5	1.2	12	4.0
Ethane	0.2	0.2	0.2	0.4
Backflush	0.4	0.4	0.7	1.7
Btu/SCF	644	577	640	688

Catalyst bed conditions: 350°C to 360°C and 20 to 22 MPa.

Organic loading of 1.8 wt% in water as feedstock.

was available for the test. With the smaller catalyst bed, the lower feed rate achieves an equivalent space velocity for comparison with the Ni-0750 and BASF catalysts. The lower feed rate results in a lower gas yield. The higher hydrogen content in the product gas is attributable to the higher temperature in the preheat zone (284°C vs. 227°C for BASF), also

because of the lower feed rate. The fourth catalyst, C150, is noticeably less active even at a lower space velocity.

More important is the long-term activity of the catalyst. As shown by the results in Table 3, the long-term operation of Ni-0750 shows a definite loss of activity over time. The

Table 3. Extended-Time Experimental Results with Nickel Catalysts

	<u>Ni-0750</u>	<u>Ni-0750</u>	<u>BASF</u>	<u>BASF</u>
Feedstocks	p-cresol	p-cresol	p-cresol & phenol	p-cresol & phenol
Time on Stream, hr	38	72	240	620
<u>Results</u>				
Gasification of Carbon, %	99.1	23.4	101.4	89.2
Reduction of COD, %	99.94	68.2	99.8	97.6
Feed, L/hr	1.6	1.6	0.036	0.017
LHSV, L/L/hr	2.7	2.7	1.2	0.8
Gas Yield, L/hr	41.5	8.9	1.1	0.5
Effluent COD, ppm	30	14900	95	1710
Effluent pH	3.9	4.7	NA	NA
Gas Composition, volume %				
Methane	61	45	59	59
Carbon Dioxide	36	41	39	37
Hydrogen	1.6	6.2	0.4	0.7
Ethane	0.4	1.4	0.5	0.7
Backflush	0.6	5.7	1.0	1.7
Btu/SCF	646	669	634	666

Catalyst bed conditions: 350°C to 369°C and 21 to 22 MPa.

Organic loading of 1.8 wt% in water as feedstock.

long-term loss of activity is apparent even when stable short-term activity has been demonstrated as shown in column 1 of Table 3 (see also Elliott et al. 1993c). The loss of activity is evident in the reduced level of COD destruction, lower gas yields, and shift in gas composition away from methane to hydrogen and higher hydrocarbons. The BASF catalyst shows much better long-term stability than the Ni-0750. Note that Table 3 is a combination of bench-scale results for the Ni-0750 catalyst and microscale results for the BASF catalyst, so the gas yield results cannot be compared directly from one catalyst to the other.

Changes in the catalyst resulting from exposure to the TEES environment is the primary explanation for the loss in activity. As illustrated in earlier tests (Elliott et al. 1993a), the composition of the catalyst support can be chemically changed and the metal can become agglomerated, limiting its active surface area. Long-term results presented here further demonstrate the effect of the change (and lack of change) in catalysts upon exposure to the high-temperature liquid water.

Metal agglomeration is a primary concern for catalysts used in TEES. Catalytic metal crystallite size has been correlated with the loss of active surface area and, hence, catalytic activity (Pearce and Patterson 1981). Figure 3 shows that different catalysts exhibit different rates and amounts of agglomeration. For example, the Ni-0750 catalyst shows a nearly straight line growth in crystal size, while the BASF catalyst shows an initial growth of crystal size followed by a stable period which has been demonstrated for up to 4 weeks. The change in the Raney nickel is more nearly like the Ni-0750 than the BASF catalyst. The data in Figure 3 are derived from tests in all three scales of continuous-feed reactor system. There is no significant difference in catalytic metal agglomeration that can be correlated to any of the scales of operation.

Changes in the catalyst support contributed to the activity changes. The BASF catalyst support was converted to a hydroxide form and crystal growth paralleled the metal crystal growth, as shown in Figure 4. As reported in our earlier publication (Elliott et al. 1993a), high-surface-area γ -alumina, as used in the Ni-0750 catalyst, was readily converted to böhmite (AlOOH), which has a much reduced surface area. The change to böhmite may have allowed the water to interact more strongly with the nickel and caused the nickel agglomeration that was seen in the Ni-0750 catalyst.

Figure 3. Catalyst Metal Crystalline Growth Over Time in TEES

Figure 4. Relation of Crystallite Growth in Nickel Metal and Catalyst Support Material in the BASF Catalyst

A different situation was found with ruthenium. Ruthenium showed no evidence of crystal growth. As seen in Figure 3, even a slight reduction in crystal size was apparent (although the change is just at the limit of the experimental error of the analysis). There was little evidence of an effect of the support on crystal growth. The ruthenium did not agglomerate when supported on the δ -alumina (which is also readily converted to böhmite), as is shown in Figure 3, or zirconia. Analyses of the ruthenium on zirconia showed no sign of growth as the crystallite size of much less than 10 nm for several samples recovered during 6 weeks of operation. Zirconia was relatively stable in the TEES environment (Elliott et al. 1993a). X-ray diffraction (XRD) analysis of the zirconia support showed no significant growth of the crystallite size after the first 2 days of operation.

Table 4 provides results of TEES processing with several ruthenium catalysts. There was a noticeable improvement in processing rate achievable with the 5% ruthenium catalyst compared with the 3% ruthenium (both on high-surface-area alumina supports). The 5% catalyst showed a significant loss of activity over a 9-month period between tests resulting from unknown effects in handling and storage. The ruthenium on zirconia was tested only in the microreactor system. It showed good activity but was tested at a lower space velocity.

Table 5 provides results of long-term tests for comparison of two ruthenium catalysts. These tests showed good maintenance of conversion over time for both catalysts. COD destruction remained high with good gas yield. The alumina-supported catalyst showed significant loss of activity after 10 days of operation as evidenced by the lower space velocity required to maintain conversion levels. A shift away from methanation was noticeable toward the end of a 6-week test with the zirconia-supported ruthenium, while the level of conversion remained high.

EVALUATION OF FEEDSTOCKS

A variety of feedstocks have been tested in the continuous reactor systems. This discussion focuses on the testing in the following order: bench-scale reactor tests with chemical model compounds; processing tests with actual waste streams in the bench-scale system; and test results at the engineering development scale in the SRS.

Table 4. Short-Term Experimental Results with Ruthenium Catalysts

	<u>3% Ru</u>	<u>5% Ru</u>	<u>Reused 5%</u>	<u>Ru/ZrO₂</u>
Feedstocks	p-cresol	p-cresol	p-cresol	phenol
<u>Results</u>				
Gasification	100.4	99.9	96.3	101.2
Carbon, %				
Reduction	99.8	99.95	99.7	99.4
COD, %				
Feed, L/hr	1.4	1.95	1.2	0.03
LHSV, L/L/hr	2.4	3.6	2.0	1.0
Gas Yield, L/hr	36.1	47.3	30.0	0.8
Effluent COD, ppm	80	20	118	300
Effluent pH	3.1	2.8	3.1	NA
Gas Composition, volume %				
Methane	61	60	65	64
Carbon Dioxide	36	38	33	35
Hydrogen	1.6	1.8	1.1	0.5
Ethane	0.6	0.1	0.1	0.1
Backflush	0.8	0.0	0.3	0.0
Btu/SCF	659	616	676	654

Catalyst bed conditions: 350°C and 20 to 21 MPa.

Organic loading of 1.8 to 2.0 wt% in water as feedstock.