ACCOMPLISHMENTS AND CONCLUSIONS

The primary goal of this research project was to investigate the reaction chemistry and preliminary engineering of a continuous flow, high-pressure aqueous alkali catalyzed water-gas shift reactor. Major accomplishments in support of this goal were:

- Fabrication and successful operation of a continuous flow reactor capable of temperatures up to 350°C and pressures ranging from 600-3000 psia;
- Demonstration of the feasibility of using a variety of aqueous solutions of basic materials, including sodium and potassium carbonates, sodium citrate, and cadmium and ammonium hydroxides to catalyze the water-gas shift reaction;
- Correlation of rate data to develop empirical expressions relating the reaction rate to process temperature and pressure;
- Identification of parameters which might significantly affect the potential costs of building and operating a commercial-scale reactor; and
- Identification and prioritization of future research needs in support of the technology.

Other accomplishments which were less direct in addressing the research goals included the gathering of thermodynamic data for high-temperature aqueous salt solutions and the investigation of alternative process configurations. One of these alternative configurations was the integration of the hot gas quench step with the water-gas shift reactor in order to maximize reaction rates at lower system pressures.

In addition to this report, two publications (Elliott and Sealock 1984; Sealock and Elliott 1984) were generated as a part of this research project. In addition to those two publications, Douglas Elliott presented an Invited Seminar before the Chemical Engineering Department at the Washington State University during January 1985. It is anticipated that one additional paper will be written and submitted to Industrial Engineering Chemistry, Product Research and Development. This paper will deal with the continuous gas processing in the aqueous water-gas shift system and would be part 3 of our series of papers published in the Journal (Elliott and Sealock 1983; Elliott, Hallen and Sealock 1983).

Based upon data gathered during more than 30 experiments (70 hours of operation), several conclusions regarding the use of basic solutions as catalysts for the water-gas shift reaction can be made. These conclusions are delineated below:

- A wide variety of basic solutions may be used to catalyze the water-gas shift reaction and these solutions have a broad range of effectiveness;
- In the normal operating mode, the total system pressure must be maintained at least 500 psi above the vapor pressure of the catalyst solution in order to prevent excessive loss of catalyst solvent;
- The reaction rate is approximately proportional to the partial pressure of carbon monoxide over the catalyst solution;
- Catalyst turnover values for the aqueous catalyzed process fall within the accepted range for homogeneous phase catalysts;
- It may be possible to obtain significant rate increases by feeding hot (above 400°C) gas into the catalyst solution, thereby increasing the interfacial temperature without significantly impacting the bulk fluid temperature (i.e., quench-mode operation);
- Under the conditions studied, mass transfer between the gas and bulk catalyst does not appear to be a significant factor in the observed reaction rate;
- The solubility of sodium carbonate is apparently limited at high temperatures, reducing its ability to lower vapor pressure; and
- The estimated costs of a commercial-scale reactor are strongly dependent upon the total system pressure and number of stages, and are relatively independent of vessel aspect ratio and catalyst temperature over the range 340-360°C.

RECOMMENDATIONS

Based upon the results of this research, it is possible to identify several important areas for future research. While the use of a high-pressure concept for the water-gas shift conversion may not be economically justified at this time, the study of high-pressure water-gas shift chemistry is important and has potential to make significant contribution to improvements in third generation gasification systems. Due to the relatively recent interest in the development of other low-temperature homogeneous catalyst systems for water-gas shift reaction, continued research in this area and recommendations made in this study should be of value to researchers working in this area.

Much of the research originally proposed in this project has not been completed due to early termination of the research (one year). Of the research originally proposed the two general areas of catalyst concentration effects and dilutent gas effects are deemed worthy of further study. In addition, based on our initial attempts of the use of a hot gas feed to the water-gas shift reactor, we believe that the use of the aqueous shift reactor in a hot gas quench is a valuable concept deserving further study. Recommendations regarding these areas and other recommendations resulting from the research findings are discussed below.

Phase Equilibria and Processing Conditions

Our first group of recommendations concerns the influence of phase equilibria upon the reaction system. The direct relationship between carbon monoxide partial pressure and the reaction rate, in conjunction with the limited solubility of carbon monoxide in aqueous solutions, indicates a need to find means of increasing this solubility. Solubility considerations may be important to a broad range of homogeneous catalyst systems. Possible areas of investigation include:

- Co-solvents which are miscible with water, yet readily dissolve carbon monoxide;
- Complexing agents to increase the solubility of CO in solution; and
- Investigation of system pH on the solubility of CO.

In addition to studying the effect of phase equilibrium, it is important to develop an understanding of the process conditions which might increase the partial pressure of CO (and thus its solubility) while maintaining a constant total system pressure. In an aqueous system, the most likely way of doing this is to decrease the catalyst temperature, which has an adverse effect on rate. Other methods might include the use of highly concentrated catalyst solutions to significantly depress the catalyst vapor pressure. This approach would require fundamental thermodynamic investigations of high-temperature aqueous solutions.

Catalyst Concentration Effects

The catalyst concentration effects can be attributed to several phenomena occurring in the aqueous water-gas shift: 1) the carbonate-formate equilibrium; 2) ratio of solution volume to gas volume; 3) the initial amount of catalytic material originally put into the system; and 4) catalyst deactivation and regeneration. These parameters were studied in the batch reactor in our earlier research (Elliott, Hallen and Sealock 1983), and they were found to have significant effects on the rate of water-gas shift. We were not able to perform any continuous reactor tests which address these issues as part of this project. These tests should be undertaken.

Use of Hot Gas Feed

A major process advantage of the aqueous water-gas shift system is the ability to utilize the aqueous bath for a hot gas quench in addition to the water-gas shift reaction. Our experimental reactor as originally designed did not allow for this mode of operation and only a subsequent modification allowed us to attempt to operate in a hot gas feed mode. The preliminary results from these operations encouraged us to try to identify a better method for heating the gas feed than the packed-bed heat exchanger which we fabricated. We believe that useful research could be performed by connecting a pressurized aqueous water-gas shift system to the off-gas stream of any of several pressurized ($\geq$40 atm) research gasifiers which are presently in operation around the country. Such an experimental system could be used to study the use of the aqueous system for combined gas quench and water-gas shift in addition to the gas treatment studies which are also considered important to process development.

The use of hot gas feed and quench mode of operation should also be investigated at the bench-scale. This could be accomplished by passing simulated wet raw coal gas through a preheater of appropriate size and design to prevent plugging. Completing these experiments would prove or disprove the potential of this contacting approach.

Diluent Gas Effects

The effects from diluent gases fall into three main areas: 1) determination of kinetic effects and gas residence times, 2) gas impurity treatment, and (3) catalytic effects due to gas impurities. An additional understanding of the reaction kinetics in the system should be developed by evaluation of the reaction rates in the presence of different amounts of diluent gases in the gas processing stream while maintaining the reactor at constant pressure. Determination of average gas residence time should also be accomplished by continuous monitoring of the flow of trace gases through the system. Treatment of gas impurities in the aqueous water-gas shift system is a major process advantage which remains to be developed. The use of ammonia as the water-gas shift catalyst has been confirmed by this research, but further development is required.

Methodology Changes

These recommendations address themselves to methodological changes which could be implemented in order to improve the quality of data which is obtained during experimentation. These are changes in either experimental equipment or instrumentation which have been indicated by our prior experience and include:

- Use of continuous gas composition monitoring to study the dynamic response of the reactor to changes in inlet flow rate, stir rate, and other process variables;
- Development of a reliable means of controlling the liquid level in the reactor to measure its effect upon the degree of conversion; and

- Development of a practical feed preheater, along with the requisite gas analysis methods to study the behavior of the reactor in the quench mode of operation.

Final - Recommendations

The next group of recommendations is meant to highlight broad research pathways which were identified during the course of this project. Some of these tasks were originally within the scope of this project, but were not completed because they were scheduled for the second year of the project which is not being funded at this time. These research areas include:

- Investigation of catalyst lifetimes;
- Study of the use of aqueous carbonate solutions to accomplish tar cracking/gasification in addition to catalyzing the water-gas shift reaction;
- Study of the use of aqueous carbonate system to carry out H_2S removal and document the effect of this activity on acid gas treatment costs;
- Study the effect of changing the micro-environment at the gas-liquid interface (i.e., by pre-heating the feed gas, use of ultrasonic cavitation, use of surfactants, etc.); and
- Experimental verification of the proposed reaction mechanism.

These recommendations point out areas that are primarily of technical interest. The potential process advantages of the high-pressure advanced aqueous water-gas shift reactor are not sufficient to warrant its continued investigation based on economic merit alone. The ongoing development of third generation gasification technologies, many of which operate at high pressure, points to a time when the disadvantages posed by the high pressure requirements of this system are outweighed by the relative simplicity, versatility, and low catalyst costs inherent in the process. Instead of allowing the development of these later generation gasifiers to be impeded due to a lack of compatible downstream processing technology, the authors' foremost recommendation is to continue the concurrent development of processes such as the high-pressure water-gas shift reactor, so that the potential benefits of high pressure coal gasifiers can be fully realized.

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