# DISCUSSION

Based on our results obtained in this study, we can now evaluate the pressurized, aqueous water-gas shift concept from several perspectives. We can calculate catalyst turnover rates and can present an empirical reaction rate expression for a given range of operating conditions. The extent of processing severity required to produce a given product ratio of hydrogen to carbon monoxide for chemical synthesis can be estimated. Finally, we can review preliminary process economics relative to the concept of aqueous catalyzed water-gas shift.

## Catalyst Turnover Rates

Catalyst turnover rate is often used as a means to numerically evaluate the effectiveness of a catalyst. It is in essence a measure of the amount of feedstock which can be processed with a given amount of catalyst in a set period of time. In a fashion analogous to Figures 9-12, we can calculate the turnover rates as functions of temperature, pressure or flowrates. These rates are plotted in Figures 18-21. In order to place some perspective on these numbers, Table 5 provides typical values of turnover rates for some other catalytic systems for the water-gas shift. The table provides a view of not only the broad range of activity for various catalyst systems which have been reported but also the diverse nature of the catalyst systems themselves. We note that although the temperature range of operation of our aqueous catalyst system is higher than much of the reported catalyst work, it actually lies in the low to middle range of commercial catalyst systems. The activity range which we report here lies in the mid-range of reported catalytic activities though somewhat lower than the commercial catalyst systems.

The various catalysts which we tested also give significantly different turnover numbers as illustrated in Figure 22. The citrate and carbonate are nearly the same even though the citrate possesses half again as much base generating capability since it is a tribasic salt. The cadmium hydroxide is half as active as sodium carbonate in these tests. These comparisons differ

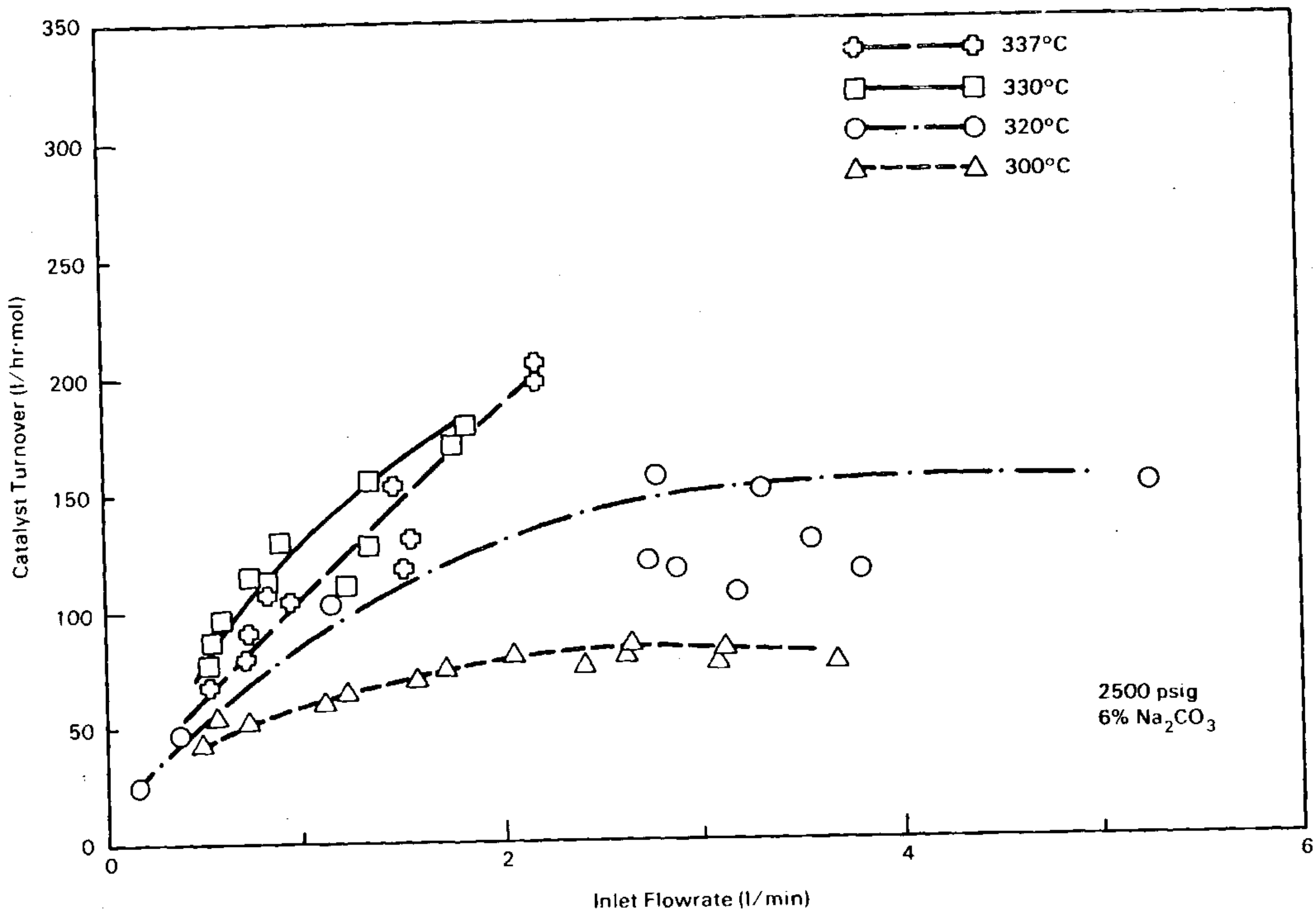

FIGURE 18. Effect of Temperature on Catalyst Turnover Rates at 2500 psig

NOTE: Experiment at 337°C was performed at a lower agitation rate than the other experiments

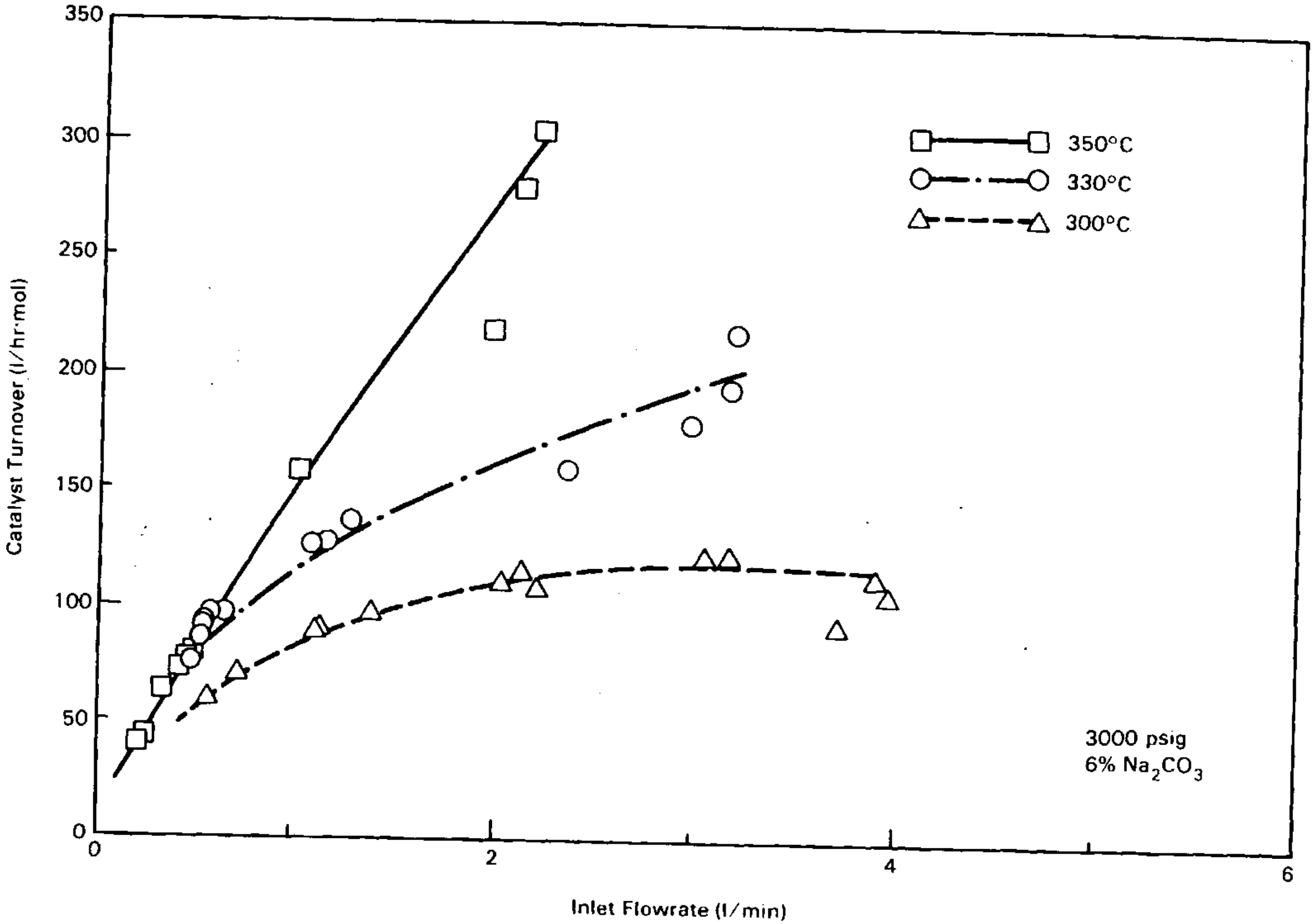

FIGURE 19. Effect of Temperature on Catalyst Turnover Rates at 3000 psig

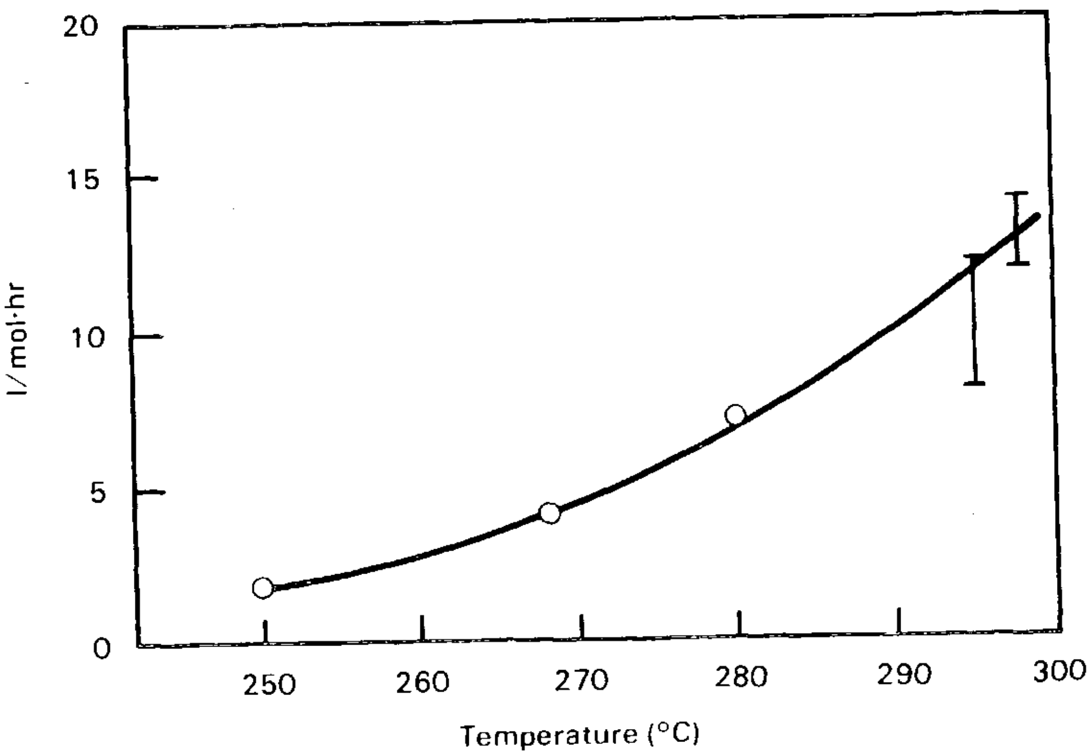

FIGURE 20. Effect of Temperature on Catalyst Turnover Rates at 1500 psig

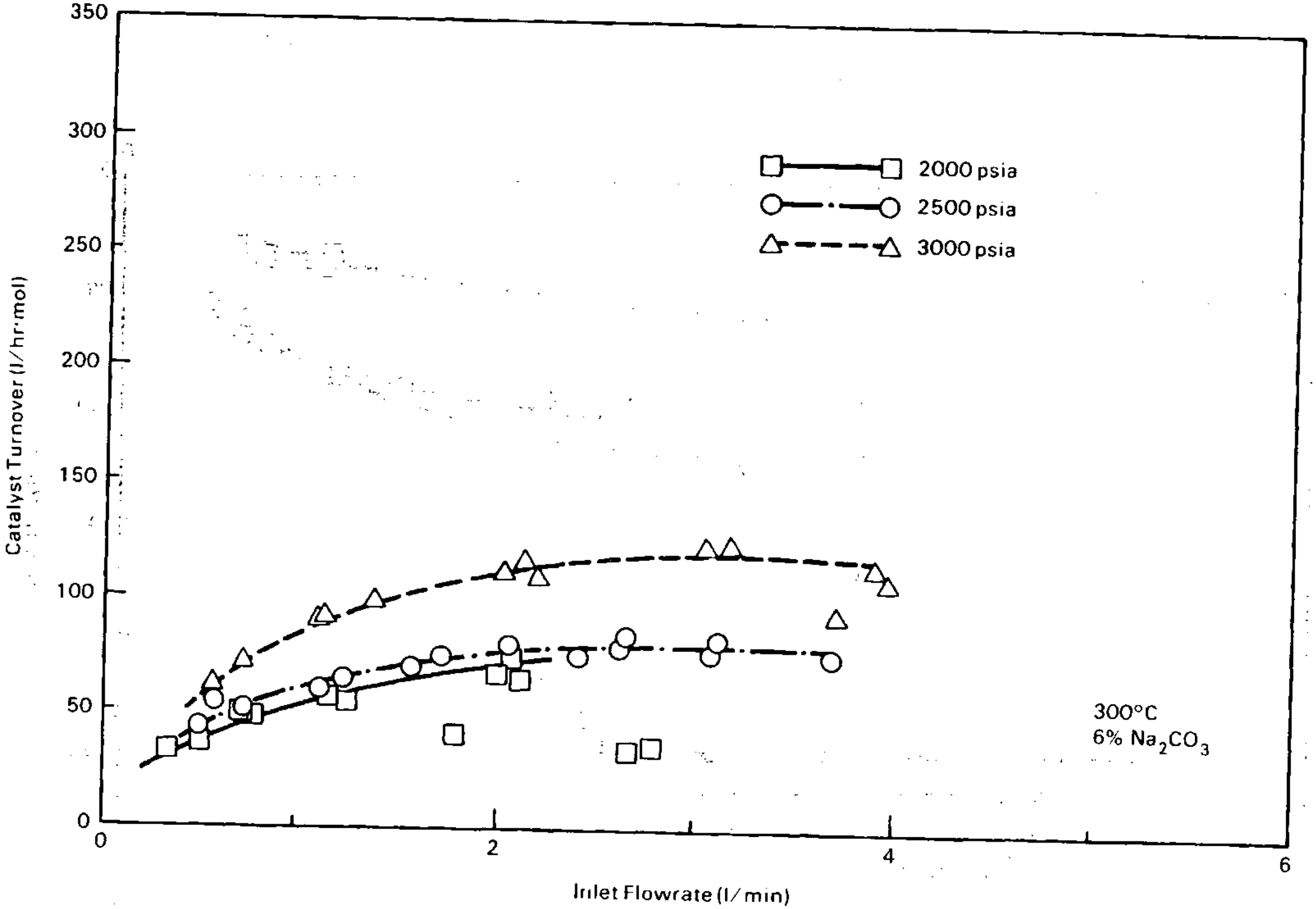

FIGURE 21. Effect of Total System Pressure on Catalyst Turnover Rates at 300°C

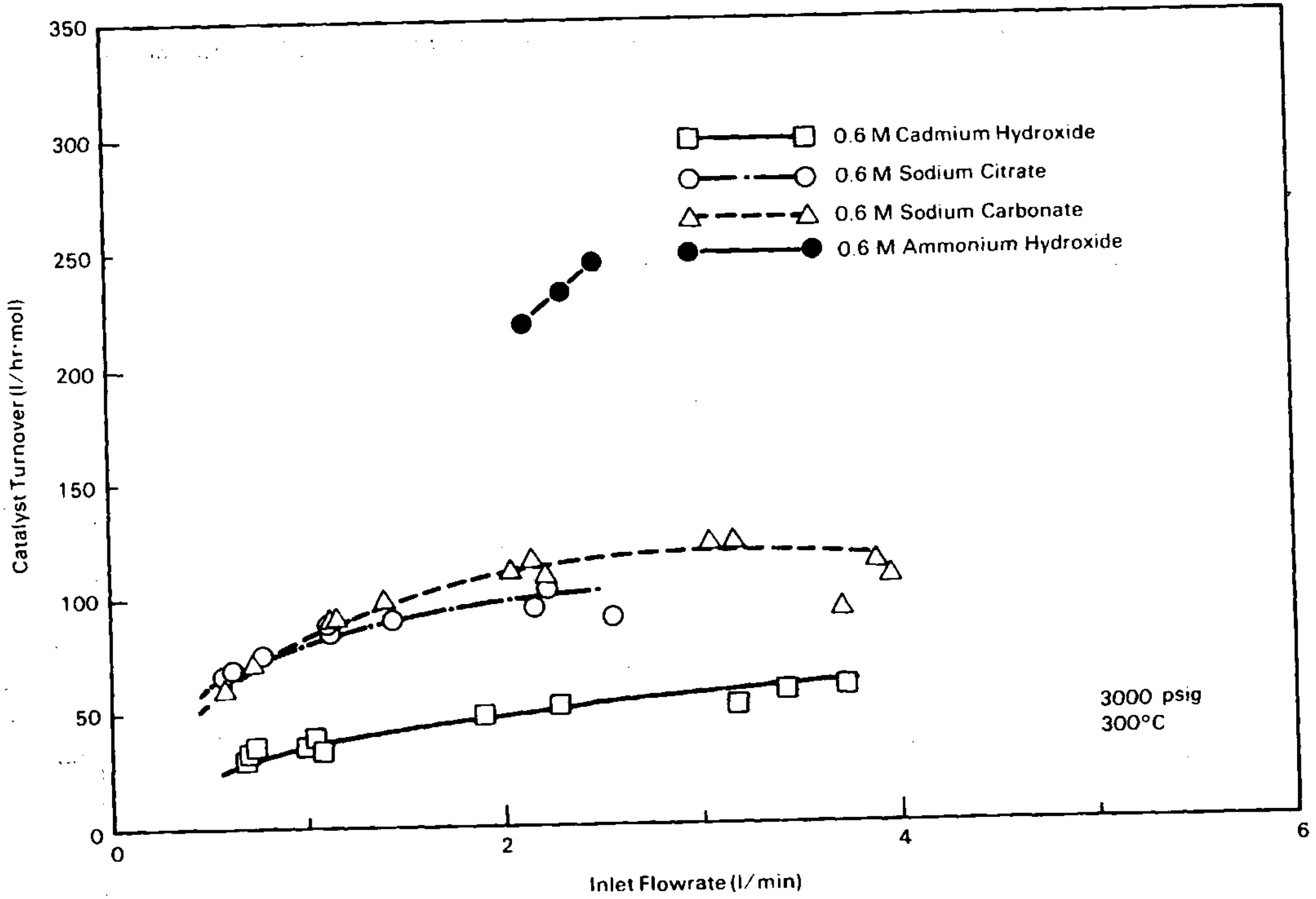

FIGURE 22. Comparison of Turnover Rates for Various Catalysts

sharply from the earlier batch results wherein the citrate and cadmium salts (carbonate and formate) were found to be more active than sodium carbonate. These data suggest that the use of the sodium carbonate, which is plentiful and inexpensive, is the appropriate choice as catalyst in the pressurized aqueous water-gas shift system. An alternate choice would be potassium carbonate which was found to be twice as active as sodium carbonate at low activity conditions (250°C and 1000 psig). Further study is required to determine if an activity improvement at other conditions with the potassium can justify its five-fold greater cost. The data obtained using ammonium hydroxide as the catalyst indicate that it is even more effective than carbonate or citrate. The limited amount of data collected for this catalyst makes comparison with other catalysts somewhat speculative.

## Reaction Rate Expressions

The development of a reaction rate expression can be attempted by several methods, and the resulting expression used in several ways. For reactions which take place by a well understood mechanism, knowledge of the relative rates of each intermediate step can be used to construct a rate equation which expresses the rate of reaction in terms of reactant and/or product concentrations. Alternatively, the "goodness of fit" of a postulated reaction rate expression to experimental data can be used to confirm or deny a proposed mechanism. In either case, reaction rate data is used to further the fundamental understanding of the reactor system. A second, more pragmatic approach which is often used in engineering analysis of reacting systems is to find a "pseudo-rate expression" which, while having no real connection to the actual reaction mechanism, is nonetheless adequate to describe the reaction rate over a limited range of conditions. Due to the complexity of the system, this latter more empirical approach was used to generate a global rate expression for the aqueous water-gas shift reaction. The resulting rate expression was used in subsequent process design and evaluation work which is discussed later.

For most of the experiments performed, it was found that the reaction rate in the aqueous water-gas shift system was approximately proportional to the partial pressure of carbon monoxide in the reactor. If the assumption is made

TABLE 5. Catalyst Turnover Numbers for Water-Gas Shift Catalysts

| catalyst | 1/mole hr | Temp. | Mole Fraction Carbon Monoxide | Reference |
|---|---|---|---|---|
| $H_2FeRu_3(CO)_{13}$, basic | 9.9 | 100°C | 0.9 | Ungerman et al. 1979 |
| $Ir_4(CO)_{12}$, basic | 5.7 | 100°C | 0.9 | Ungerman et al. 1979 |
| $H_2Ru_4(CO)_{13}$, basic | 3.9 | 100°C | 0.9 | Ungerman et al. 1979 |
| $H_4Ru_4(CO)_{12}$, basic | 3.3 | 100°C | 0.9 | Ungerman et al. 1979 |
| $Ru_3(CO)_{12}$, basic | 2.6 | 100°C | 0.9 | Ungerman et al. 1979 |
| $Ru_6C(CO)_{17}$, basic | 1.6 | 100°C | 0.9 | Ungerman et al. 1979 |
| $Fe(CO)_5$, basic | 1.0 | 100°C | 0.9 | Ungerman et al. 1979 |
| $Rh_6(CO)_{16}$, basic | 1.0 | 100°C | 0.9 | Ungerman et al. 1979 |
| $H_3Re_3(CO)_{12}$, basic | 0.1 | 100°C | 0.9 | Ungerman et al. 1979 |
| $Re_2(CO)_{10}$, basic | 0.1 | 100°C | 0.9 | Ungerman et al. 1979 |
| $PtCl/SnCl_3$, acidic | 23.3 | 88°C | 0.5 | Chen and Eisenberg 1978 |
| $[Rh(CO)_2Cl]_2$, acidic | 18.6 | 80°C | 0.6 | Baker et al. 1980 |
| $[Rh(CO)_2Cl]_2$, acidic | 31.8 | 100°C | 0.5 | Baker et al. 1980 |
| $Fe(CO)_5$, basic | 89.6 | 130°C | 0.8 | King et al. 1980 |
| $Fe(CO)_5$, basic | 1867 | 180°C | 0.8 | King et al. 1980 |
| $W(CO)_6$, basic | 607 | 170°C | 0.8 | King et al. 1981 |
| Rh, HI | ≤22 | 185°C | 0.5 | Singleton et al. 1979 |
| Zn/Cu/Cr oxides | 540 | 220°C | 0.03 | Mukherjee et al. 1976 |
| Zn/Cu/Cr/Fe oxides | 563 | 220°C | 0.03 | Mukherjee et al. 1976 |
| $Fe_3O_4$ | 519 | 500°C | 0.4 | Bortolini 1958 |
| Aqueous Base | 2-300 | 250-350°C | 0.2-0.5 | This report |

that the solubility of carbon monoxide in the catalyst solution is described by Henry's law, then this leads to a pseudo-first order rate expression for the reaction.

$$\text{rate} = k(t)X_{(CO)}D_{(sol'n)} \tag{4}$$

where $D_{(sol'n)}$ is the molar density of the catalyst solution. The application of Henry's law leads to:

$$\text{rate} = \frac{k(t)D_{(sol'n)}P_{(CO)}}{H} \tag{5}$$

where H is the Henry's law constant for the solubility of carbon monoxide under the reaction conditions, k is the rate constant expressed in conventional units of inverse time (i.e., $\text{min}^{-1}$), and $P_{(CO)}$ refers to the partial pressure of carbon monoxide over the solution. The notation k(t) was used to emphasize the idea that the reaction rate constant is not a constant in the strict sense of the word; actually it is a function of reaction temperature, independent of reactant concentration. The other constants used [H and $D_{(sol'n)}$] are also expected to be dependent upon temperature. If the density of the solution is replaced by the density of pure water (a reasonable approximation given the dilution of other species in the system) then it may be easily predicted. Figure 23 shows the experimentally determined rate constants obtained with sodium carbonate catalyst as a function of temperature. Due to a lack of gas solubility data under the conditions of the reaction, the rate constant is expressed in units of moles/(liter)(minute)(psia), rather than $\text{minute}^{-1}$ which is customary for first-order reactions.

The usual assumed form of the relationship between the rate constant and temperature is described by the equation:

$$k = k(T) = Ae^{-(Ea/RT)} \tag{6}$$

where A is a constant, R is the ideal gas constant, and Ea is the activation

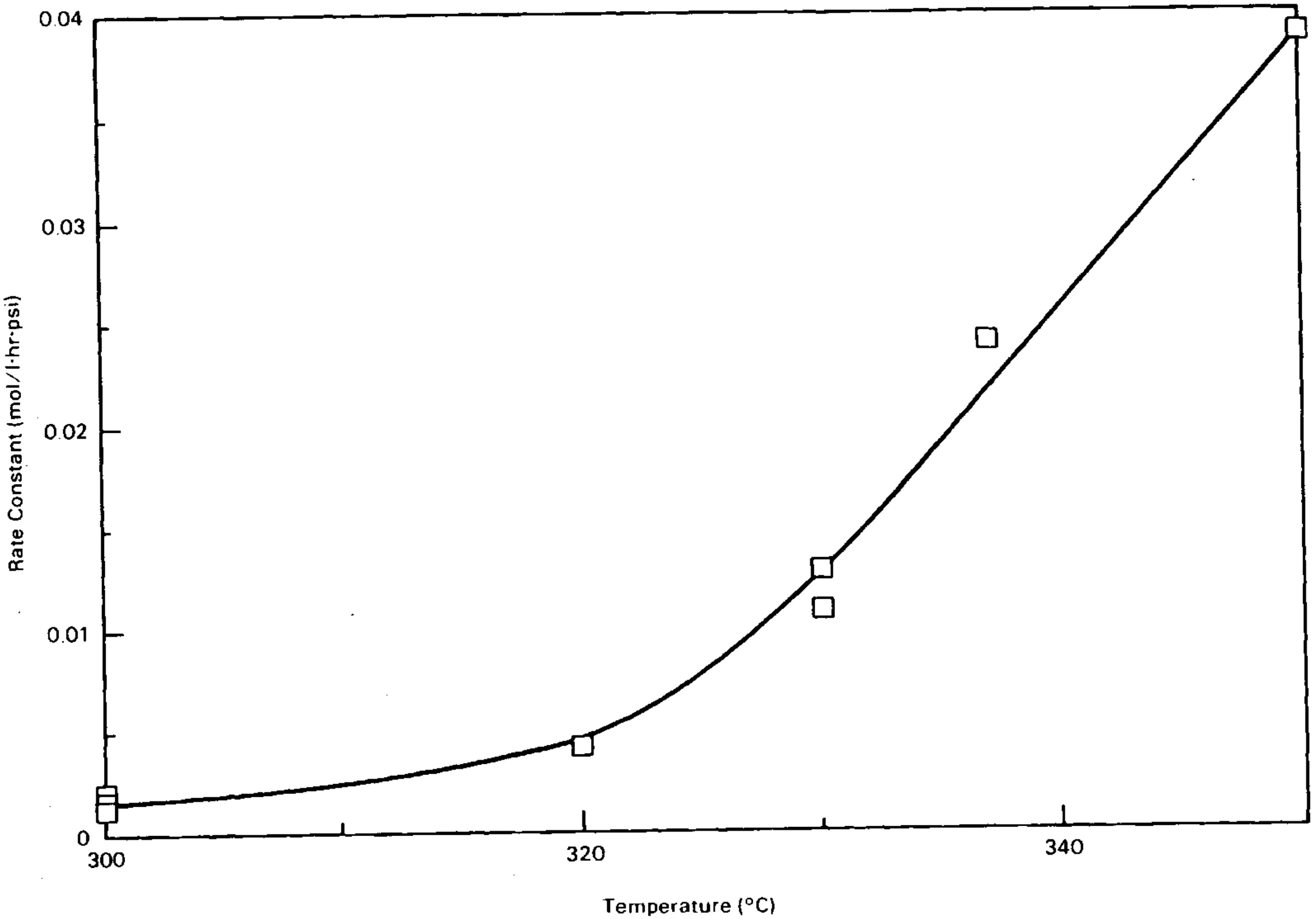

FIGURE 23. Effect of Catalyst Solution Temperature on Measured Average Rate Constant for 6% Sodium Carbonate Catalyst

energy for the rate-controlling step in the reaction mechanism (Hill 1977). This interpretation lends physical significance to the rate constant, relating it to the energy distribution of the reactant molecules through the use of Ea. Manipulation of the previous equation to reflect this change yields the following:

$$\ln(k) = \ln(A)-(Ea/R)\cdot(1/T) \tag{7}$$

Examination of this equation reveals that it should yield a linear plot of the natural logarithm of k versus reciprocal temperature, with a slope of (-Ea/R). Figure 24 illustrates this way of looking at the rate constant. Here, the natural logarithm of the rate constant is plotted versus the reciprocal temperature (expressed in degrees Kelvin). Although the number of data points is somewhat limited, it is clear that the data exhibits the previously described linear behavior. The determination of the activation energy (Ea) from this plot is complicated by the use of a pseudo-rate constant which incorporates the Henry's law constant. This was made necessary by the lack of solubility data for the conditions used during the experiments. Determination of these solubility constants would allow the calculation of Ea, which could be used to gather insight into the mechanism of the reaction.

These reaction rate constants lend little insight into the reaction mechanism. They are useful however, for comparison of the various catalysts tested (see Table 6) and for initial engineering analysis of the reactor system. This is true because the reaction rate is an intrinsic property of a reacting system, unrelated to reactor size or configuration (Hill 1977). Thus, while scale-up of the reactor must consider size dependent factors such as heat and mass transfer effects, the rate expressions developed here may be extended without modification to any applicable reactor size or design.

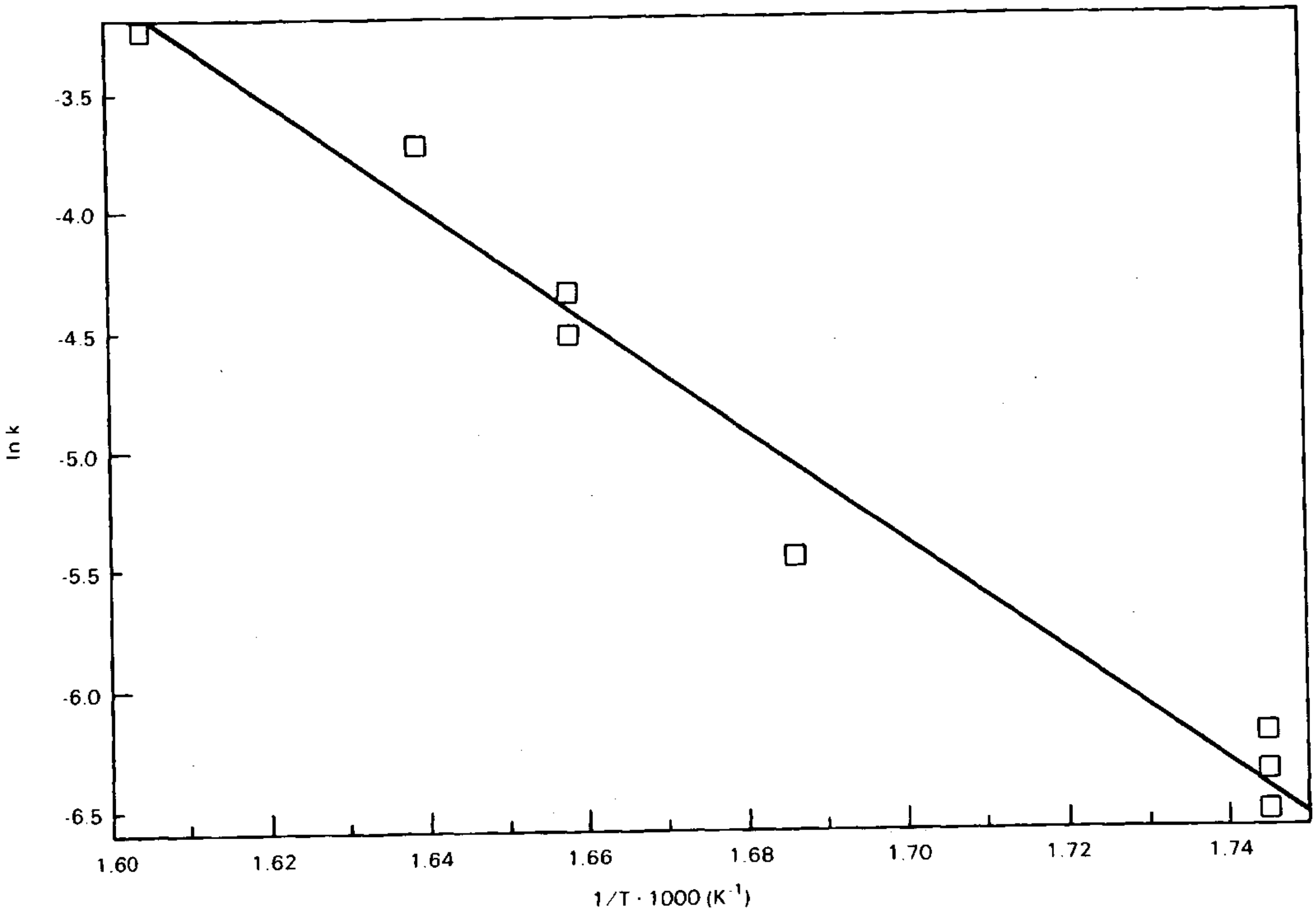

FIGURE 24. Plot of ln(k) versus Reciprocal Temperature

TABLE 6. Rate Constant for Various Catalysts (all at 300°C and 0.6M)

| Run # | Catalyst Type | avg. rate constant (mol/liter·hr·psi) | standard deviation (mol/liter·hr·psi) |
|---|---|---|---|
| 30/31 | ammonium hydroxide | 0.00464 | 0.00069 |
| 25 | sodium citrate | 0.00212 | 0.00056 |
| 22 | sodium carbonate | 0.00201 | 0.00036 |
| 26 | cadmium hydroxide | 0.00059 | 0.00009 |
| 28 | no catalyst | 0.00018 | 0.00003 |

## Product Gas Ratios

It is useful to consider how the results from our water-gas shift reactor can be used to suggest appropriate operating conditions for synthesis gas composition adjustment. Although all of our cold feed gas tests were performed with a pure carbon monoxide feedstock, the kinetics expression developed from this work can be applied to any composition of feedstock. In order to use our kinetic data the composition of the gas feedstock must be known and the desired product composition determined. The data in Table 7 show gas compositions from a pressurized Texaco gasifier which requires shifting to a 3 to 1 hydrogen to carbon monoxide synthesis gas.

TABLE 7. Gas Composition for Pressurized Texaco Gasifier (Bissett 1978)

|  | Feed Gas % | Product Gas % | Dry Product Gas % |
|---|---|---|---|
| CO | 20.73 | 9.47 | 16.22 |
| $CO_2$ | 8.48 | 19.74 | 33.81 |
| $H_2$ | 17.13 | 28.39 | 48.63 |
| $H_2S$ | 0.70 | 0.70 | 1.20 |
| $N_2$ | 0.08 | 0.08 | 0.14 |
| $H_2$ | 52.88 | 41.62 | -- |

Using these compositions and the rate constants presented earlier, the data in Table 8 were generated.

TABLE 8. Process Calculations for Water-Gas Shift at Several Conditions

| Temp. °C | Pressure psig | K mole/l·hr·psi | Pco* psi | CO Converted mole/l·hr | Feed Gas Rate mole/l·hr |
|---|---|---|---|---|---|
| 300 | 2000 | 0.0017 | 128 | 0.22 | 1.94 |
| 300 | 3000 | 0.0020 | 290 | 0.58 | 5.16 |
| 350 | 3000 | 0.0390 | 102 | 3.98 | 35.4 |

* Pco = (operating pressure - vapor pressure of catalyst solution) x mole fraction CO in dry gas

According to our model, the amount of conversion is directly proportional to the partial pressure of carbon monoxide in the reactor, i.e. the amount of carbon monoxide in the product gas. By choosing the operating conditions of temperature and pressure and using the appropriate rate constant, the correct gas feed rate can be calculated. These calculations assume that the catalyst solution is six weight percent sodium carbonate and that the ratio of gas volume to catalyst solution volume remains the same in the experimental system. With these two conditions and the assumption of equivalent gas/liquid contacting these calculations can be used to extrapolate to the required vessel size where the feed gas rate is given in moles of feed gas per liter of catalyst solution volume per hour.

## Engineering Evaluation of the High-Pressure Water-Gas Shift System

A position paper was prepared at the request of METC in July 1984. This paper (included as Appendix B) was prepared to describe the advantages of the pressurized aqueous water-gas shift reaction system and to make available to METC a preliminary evaluation of the concept. This paper included both a qualitative description of the advantages, as well as a preliminary economic comparison to provide an initial quantitative look at the possible economic advantages of the PNL pressurized aqueous water-gas shift process.

The initial technical and economic evaluation of the concept was scheduled to be performed during the end of the second year of the project. Since the second year of the project appears to be unlikely at this time, we felt it was necessary to update this evaluation to include new information obtained since July 1984. This update follows.

Despite some formidable obstacles including higher capital costs and the difficulty of feeding a solid at high pressure to a reactor system (Funk 1983), there is an apparent trend toward increased operating pressure in the new generation of gasifiers (Gall and Johnson 1983). Despite the technical difficulties, this trend continues due to the increased yield and quality of gas that may be obtained under pressurized conditions. Another driving force for the development of high-pressure gasification systems has been the need for gasification technology which is compatible with high-pressure downstream processes such as ammonia synthesis and the manufacture of synthetic natural gas (SNG). Experimental gasification systems have been developed which operate at pressures in excess of 2000 psig (Gall and Johnson 1983) and commercial and pilot scale gasifiers such as the Texaco fluidized bed and the Ruhr 100 fixed-bed gasifier have been built with maximum design pressures in excess of 1000 psig (Schad and Hafke 1983).

The water-gas shift chemistry and the advanced aqueous water-gas shift reactor system described in this report has been studied with this future generation of high-pressure gasifiers in mind. Compatibility with downstream technology was also a consideration. Ammonia synthesis and the production of synthetic natural gas each require that the raw gas from the gasifier undergo a substantial amount of conditioning, including acid-gas cleanup, removal of tars and entrained solids (ash and unreacted carbon), and an increase in the $H_2$ content via the water-gas shift reaction. While the primary purpose of the system under development is to accomplish the latter, it is believed that each of the above objectives may be met to a limited degree by the system. Thus, the incentive for developing this new water-gas shift reactor extends beyond the simple replacement of conventional gas-phase water-gas shift systems.

In this section, we have tried to present an objective review of the engineering factors which must be taken into account when evaluating the water-gas shift system under study. Objective engineering appraisals of a process are generally based upon an economic comparison with the existing process which it is intended to replace. Unfortunately, this often places radically new or innovative processes at a distinct disadvantage, since many of the costs are either unknown or inflated due to development costs which do not exist for established technology. While these economic comparisons are an entirely valid mechanism for planning at the plant and corporate level, their use as the sole criteria for determining research priorities is not justified. It is in this light that we have prepared this section of the report, keeping in mind that cost is an important assessment criteria, but not the sole one.

Design Basis - In order to consider the effect of process parameters upon reactor costs, initial assumptions were made regarding total plant size, throughput, and the degree of conversion required. In this section, reactor sizes are based upon an assumed coal gasifier capacity of 1000 tons per hour, with inlet and desired outlet gas compositions as shown previously in Table 7. Although there is currently no practical technology to produce raw synthesis gas at the pressures employed in this work, the assumption has been made for the sake of these calculations that such a source exists. This is consistent with the design philosophy above. Operational costs have not been addressed at this point.

As one would expect for a plant at this scale, the size and number of reactors required is large. The design of such large reactors (the basis assumed a series of reactors, each containing approximately 25,000 gallons of catalyst solution) based upon bench scale data alone must be approached carefully and somewhat skeptically. Heat and mass transfer effects which are not present in the idealized environment of a one-liter reactor may become significant in a reactor which has been scaled up by 5 orders of magnitude. The problems inherent in such scale-ups have been discussed throughout the literature of chemical engineering (Perry and Chilton 1973; Oldshue 1983). For the approximate nature of these estimates, these problems were considered to be negligible. This is not to say that they were ignored completely. A reactor geometry was selected that would maximize gas-liquid contact time and at the same time be capable of withstanding the high design pressures. The reactor is essentially a sparged tank filled with catalyst solution. The reactor vessel itself is a cylindrical shell, mounted vertically, with a hemispherical lid and bottom. Gas is blown in to distributors at the bottom of the reactor. These distributors consist of a series of perforated tubes which run horizontally across the bottom of the reactor vessel. The perforations help to disperse the gas, insuring good mixing and increasing the surface to volume ratio of the bubbles. The gas leaves the reactor through a flange at the top of the reactor. Entrained catalyst solution is prevented from leaving the reactor by the use of wire mesh screens and baffles near the exit flange. A condenser located outside of the reactor dries the exiting gas, which continues on to be further processed. A catalyst circulating loop allows the catalyst solution to be cooled or heated as needed to control the temperature in the reactor and to remove the heat generated by the exothermic reaction. Axial temperature gradients in the reactor could be reduced as well by this flow scheme.

Reactor size was estimated using correlations of experimental rate data with pressure and temperature. The reactor aspect ratio (the ratio of height to diameter of the shell) was selected to be similar to that which existed for the experimental reactor. Wall and end cap thicknesses were estimated based upon the selection of a low alloy (2.25 Cr - 1 Mo) with an allowable stress of 17000 psi. This material was chosen due to its recommendation for use in a reactor of nearly identical design and environment (Pack, Desrosiers, and Kamali 1985). In order to provide adequate corrosion resistance and protection from hydrogen embrittlement, this reactor must be lined with a resistant alloy such as Inconel or Hastelloy. Allowances for the high costs of these materials were made in the cost estimation. Projected costs were based upon standard correlations of vessel weight (Peters and Timmerhaus 1980) and working pressure. The costs were adjusted from 1979 dollars to January, 1985 dollars by use of the 1985 Chemical Engineering equipment cost index. The total installed costs was estimated by multiplying the base vessel cost times a Lang factor of 4.0 to account for installation, fittings, instrumentation, inspection and site preparation. All welds are assumed to be fully radiographed. Costs for associated equipment (heat exchangers, pumps, etc.) were not included in the estimate.

The reactor dimensions which were calculated were consistent with similar designs (Peck, Desrosiers and Kamali 1985). A maximum practical reactor volume of 100000 liters was selected for most of the design cases. This size reactor corresponds to a vessel which is approximately 46.7 feet tall (including end caps) and 14.0 feet in outside diameter. The estimated wall thickness is approximately 16.5 inches, excluding the cladding. Such a vessel would weigh approximately 500 tons and cost approximately 2.3 million dollars, uninstalled. Reactor vessels of this size have been built for the petroleum processing industry. Because of the unusual requirements with regards to size and maximum allowable working pressure, the cost estimates here should be regarded as approximate, although they are much more detailed (and correspondingly more accurate) than those found in the preliminary design report (see Appendix B).

Sensitivity to Process Parameters - The sensitivity of equipment costs to changes in process parameters and configuration was examined. Pressure, temperature, reactor geometry and reactor volume were each changed while the other parameters remained constant in order to determine their individual impacts upon equipment costs. Time and money did not permit the inclusion of operating costs, or the simultaneous change of more than one related variable to look for synergistic effects.

The variable which had the greatest impact upon cost was reactor pressure. Figure 25 illustrates that the cost of equipment actually increases as the pressure is lowered. This is due to the dependence of reaction rate upon partial CO pressure. At a fixed catalyst temperature, lowering the total system pressure eventually lowers the partial pressure of CO to the point where the total volume required to complete the reaction becomes prohibitive. As the vapor pressure of the catalyst approaches a significant fraction of the total pressure, this rate reduction quickly sends the cost of the reactors upward. In a related manner, there is an optimum temperature for each system pressure, beyond which the increase in reaction rate due to increasing temperature is offset by the increasing vapor pressure of the catalyst solution, which in turn lowers the partial pressure of CO in the system. Figure 26 depicts this effect for one particular set of conditions.

A stage-wise reactor configuration is also possible, and in fact may be desirable for some applications. The advantage of stage-wise conversion lies in the previously mentioned relationship between CO partial pressure and reaction rate. Since the CO partial pressure is determined by the degree of

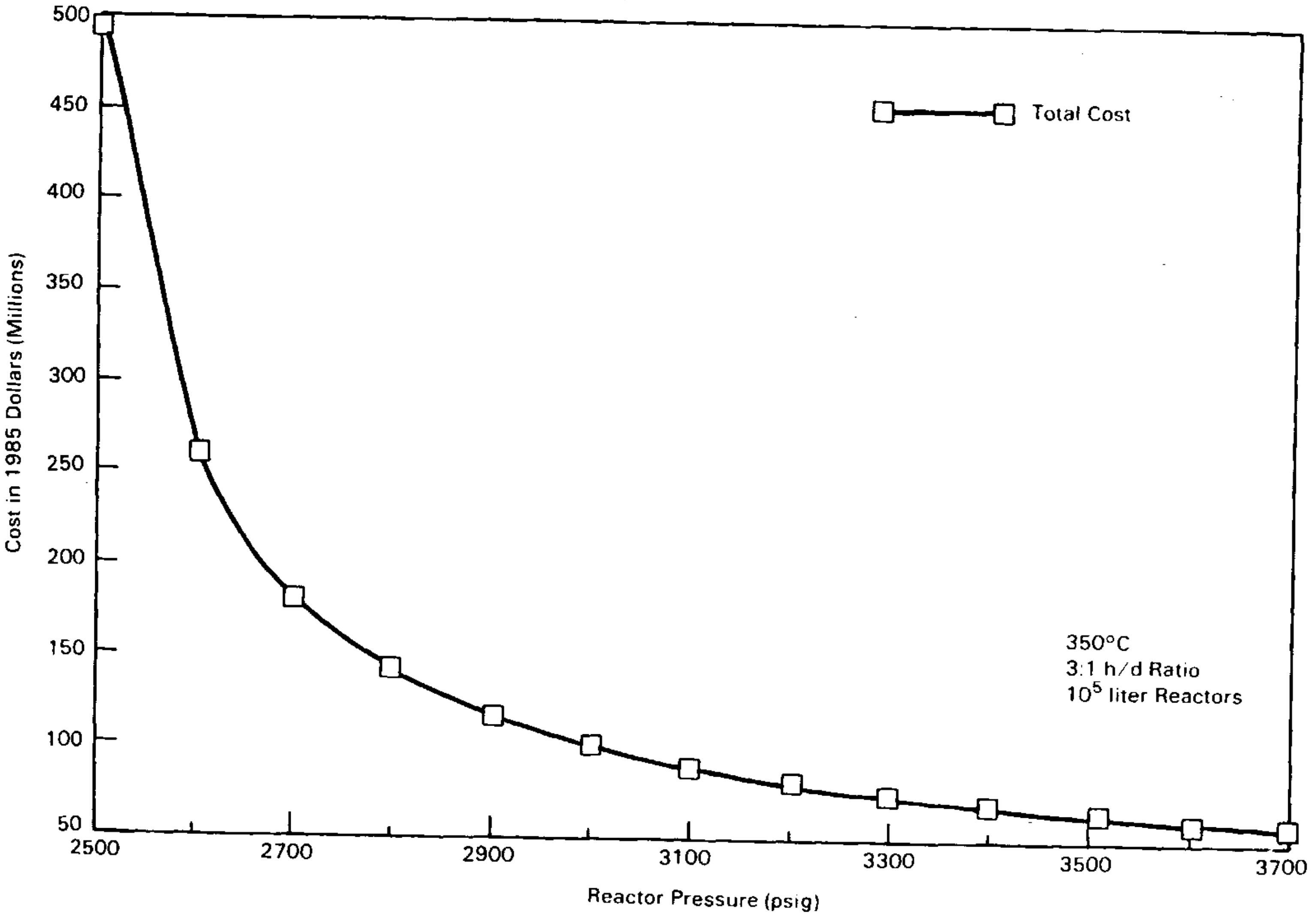

FIGURE 25. Effect of Operating Pressure on the Estimated Cost of Water-Gas Shift Reactors for a 1000 ton per hour Coal Gasification Plant

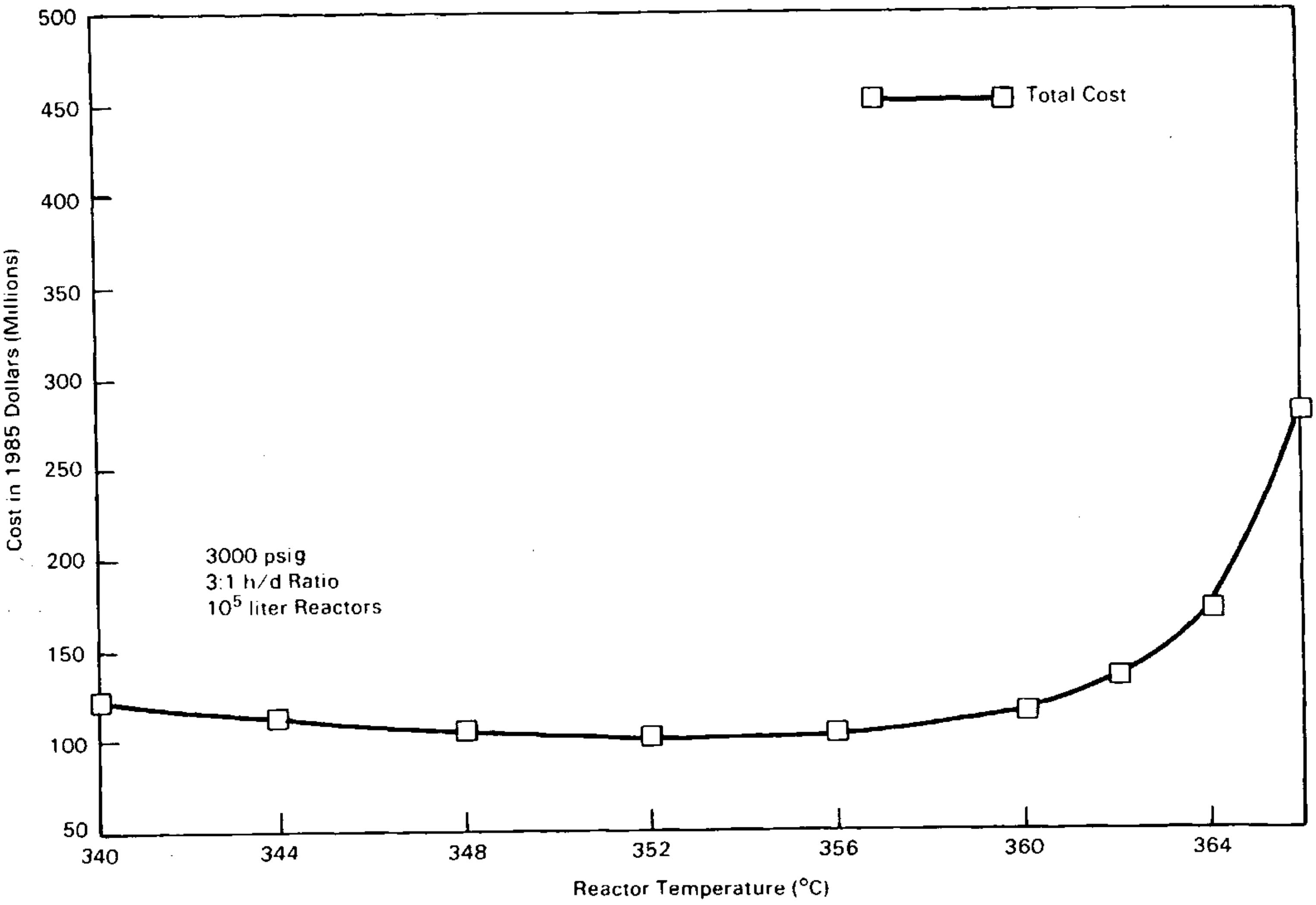

FIGURE 26. Effect of Catalyst Temperature on the Estimated Cost of Water-Gas Shift Reactors for a 1000 ton per hour Coal Gasification Plant

conversion in each stage, it is possible to achieve high reaction rates in the earlier stages of conversion. The dependence of the reaction rate upon the gas-phase CO concentration (partial pressure) is obvious in Figure 27, which presents the total system cost as a function of the outlet gas concentration of CO (on a dry basis). The shifting of the incoming gas to a dry mole fraction of approximately .09 was the basis for this design study. The graph clearly illustrates that the incremental cost for additional conversion is relatively constant down to a CO mole fraction of approximately 0.12%, below which it increases dramatically.

Two other design factors which have lesser impacts upon the cost of the system are geometric in nature. Aspect ratio (Figure 28) and maximum reactor volume (Figure 29) combine to indicate that the least expensive design is to use a few very large, tall columns, as opposed to several reactors with smaller aspect ratios. While the use of vertical vessels is consistent with accepted practice, the volume-cost relationship may be of questionable validity beyond the range shown, due to limitations of the cost estimation formulas employed.

In summary, assuming that compatible coal gasification technology is eventually developed, a reactor can be designed which should meet the requirements for the aqueous water-gas shift catalyst system. Vessel costs and sizes appear to be relatively consistent with the limited data available, and are within the range of existing fabrication technology. Process parameters which are expected to have significant impact upon the equipment costs include pressure, temperature and degree of desired conversion. Reactor size and geometry are also expected to have an impact upon these costs although to a lesser degree. A basic conceptual design of the reactor reveals no inherent difficulties with regards to manufacture or operation.

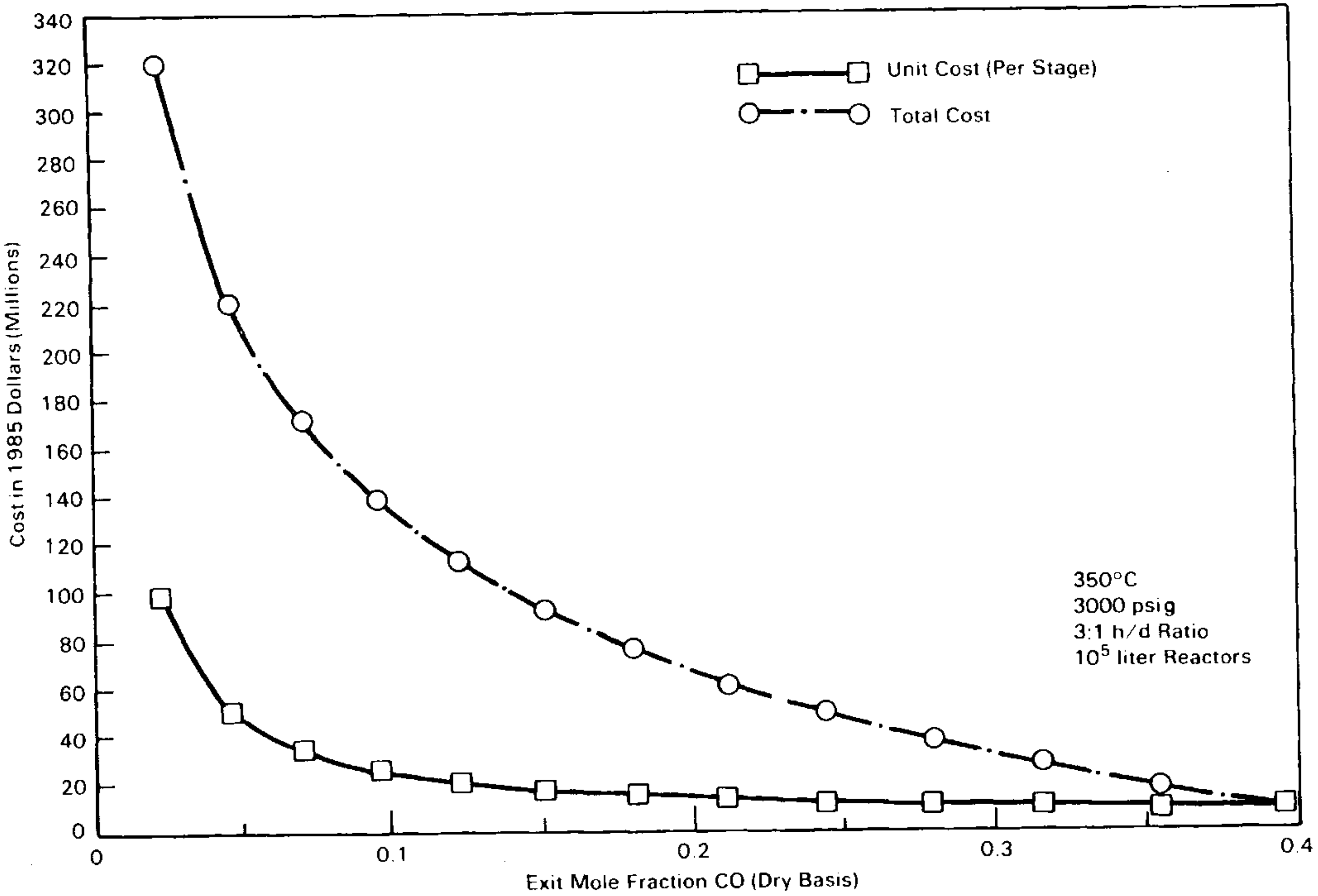

FIGURE 27. Effect of Required Exit Concentration of CO on the Estimated Cost of Water-Gas Shift Reactors for a 1000 ton per hour Coal Gasification Plant

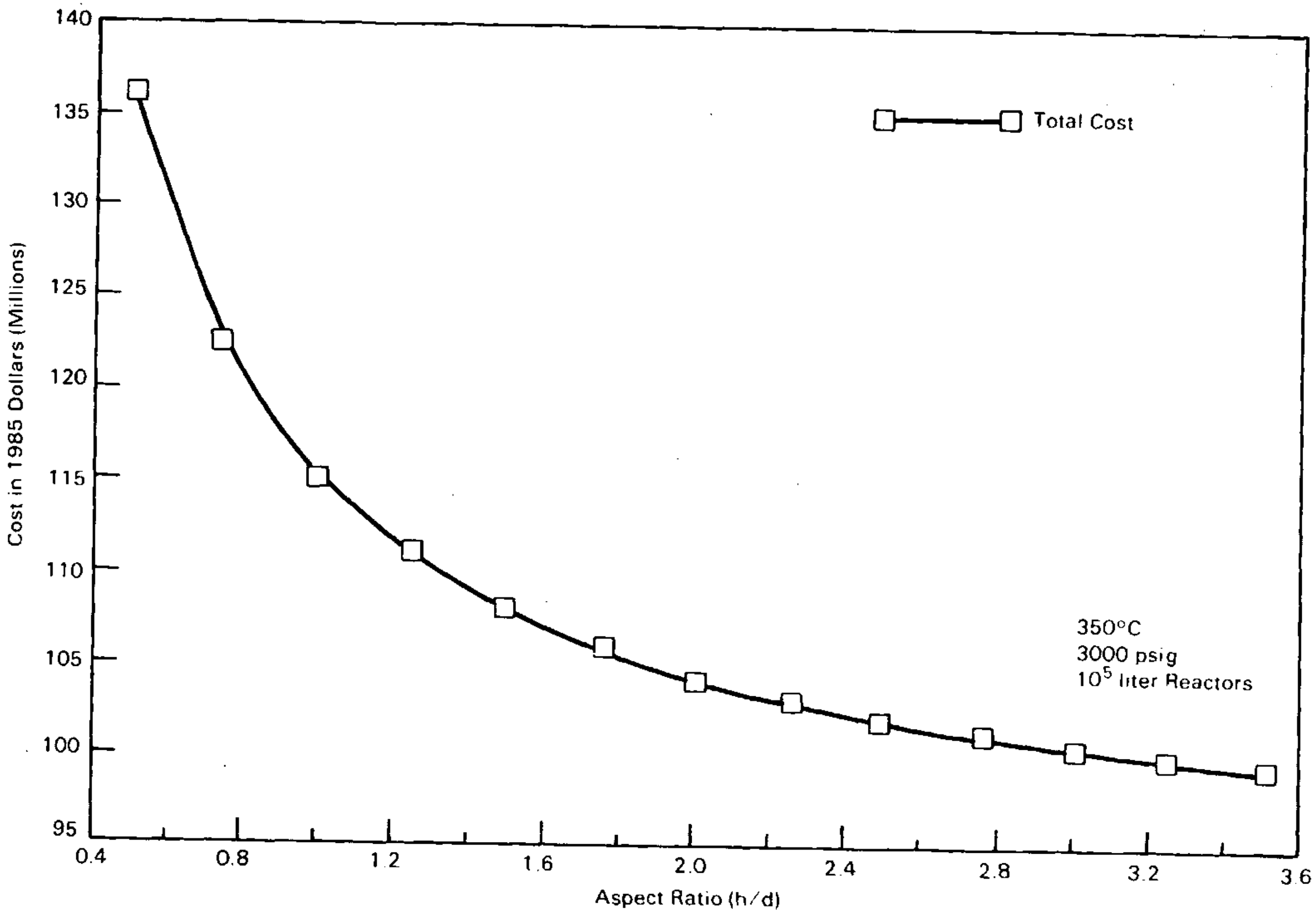

FIGURE 28. Effect of Reactor Aspect Ratio on the Estimated Cost of Water-Gas Shift Reactors for a 1000 ton per hour Coal Gasification Plant

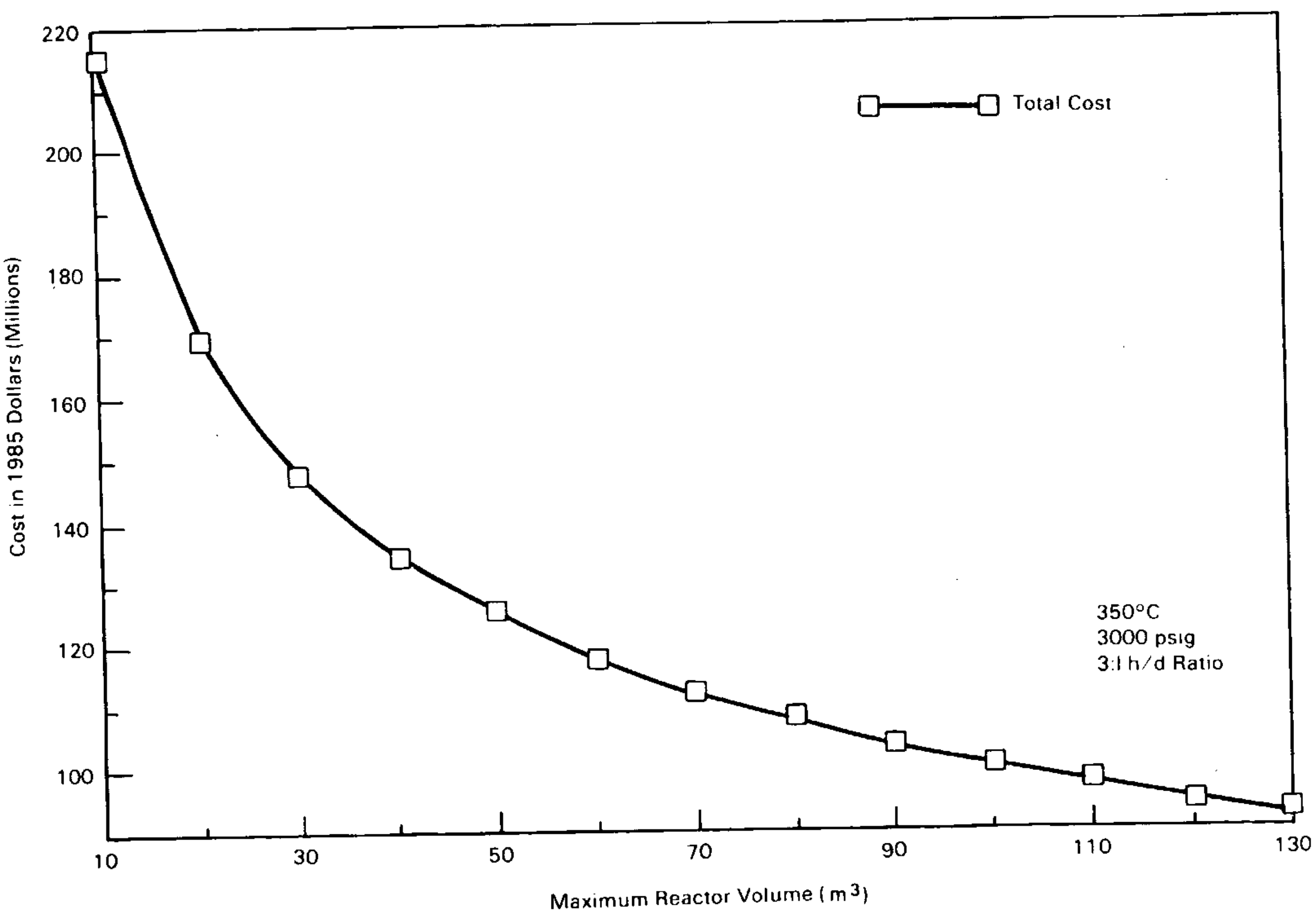

FIGURE 29. Effect of Individual Reactor Volume on the Estimated Cost of Water-Gas Shift Reactors for a 1000 ton per hour Coal Gasification Plant