6.0 GASIFICATION RESEARCH

6.1 Production of Hydrogen and By-Products from Coal

CATALYTIC COAL GASIFICATION FOR HYDROGEN PRODUCTION PILOT PLANT DATA AND SCALEUP CONSIDERATIONS

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by

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1.0 INTRODUCTION AND SUMMARY

This is the final semiannual report for a six-year program conducted by the Energy and Environmental Research Center (EERC) exploring the effects of catalytically enhanced reactivity of coals to accelerate gasification rates for the production of hydrogen and hydrogen-methane mixtures. As a companion volume (1), released concurrently with this report, a brief Executive Summary report will cover the entire project chronologically and summarize the salient conclusions. This semiannual is essentially a topical report, presenting detailed analysis of pilot-scale studies conducted over the past year, which has been cited in the preceding semiannual report (2).

The effort of the past six months has consisted primarily of analyses of earlier 1-lb/hr continuous pilot-scale tests, done in the final weeks of the preceding period, and the development of some correlations between laboratory and pilot data, leading to some cautious conclusions regarding the design of gasifiers to realize, as far as is possible, the economic advantages of catalytically enhanced coal-char gasification. This report presents this most recent experimental results in enough detail for critical scrutiny by those who wish to draw on them in support of plans for more extensive pilot efforts and commercial-scale feasibility studies.

In summary, a wealth of determinations by thermogravimetric analysis (TGA) of coal-char reactivity indicates that impressive enhancement of initial reaction rates, up to two orders of magnitude, is possible by addition of impregnated alkali catalysts. TGA is the established method of defining and comparing the reactivity of [illegible] which determines the reaction rate of devolatilized char and stea[illegible] duce hydrogen. Reactivity is defined in detail in Appendix A, taken [illegible] earlier report for a parallel project (3). Continuous pilot plant studies during the past year, in different units, at throughput rates from 1 to 40 lb/hr, have indicated more uncertainty as to the effects of catalytic enhancement of reaction rates than is apparent from TGA data alone. Correlation of TGA-defined (batch) reactivities with effective continuous process reaction rates would make TGA data far more useful as a preliminary design input.

The number and duration of both large (40 lb/hr) and small (1 to 4 lb/hr) pilot-scale tests were limited because pilot plant equipment was in various states of modification and/or in use for similar but different purposes. Notwithstanding such constraints, the data have provided significant insights as to the nature and definition of char reactivity and support some specific recommendations on the design of coal gasification systems to realize the benefits of enhanced reactivity through catalysis. In summary, these conclusions can be summarized qualitatively as follows. Their order of presentation is generally random and is not a measure of relative importance. Specific recommendations are highlighted:

- Impregnation of Wyodak coal with potassium hydroxide, at a potassium to fixed carbon ratio of around 0.2 or greater, roughly doubles the gasification reaction rate in fluidized beds of limestone. Soluble potassium, in any convenient form, is recommended as a rate-enhancing catalyst, subject to supply costs and efficiency of recovery by leaching. This confirms earlier studies (by Exxon and others) using different coals.

- In a fluidized bed of taconite, the reaction rate enhancement by potassium impregnation appears at least as great as in a limestone bed. This was not predicted from TGA measurements, which indicate that limestone makes a small but significant contribution to reactivity, while taconite alone has essentially no rate-enhancing properties.

- Reactivity coefficients defined by continuous test results are a different but closely related property and are over an order of magnitude lower than standard TGA-determined reactivities numerically, but appear consistent in the ranking of feed-bed-catalyst conditions by reaction rate.

- The most useful result from the continuous process unit (CPU) is determination of specific capacities, defined as pounds per hour of fixed carbon converted per volume of reaction vessel. This property shows excellent correlation with CPU-derived reactivities by an empirical, exponential function, or by an approximate straight line function for the upper half of the range measured. This defines reactor volume for known sets of conditions and desired degree of fixed carbon conversion.

- The above TGA-determined reactivities of the bed content in two runs were numerically nearly identical to the corresponding specific capacity, defined above, within normal experimental scatter. In future work, if in-bed TGA-determined reactivities, in 1/hr, can be demonstrated to be essentially equal to specific capacity, in (lb/hr) per cubic foot, the direct applicability of TGA data to gasifier design will be increased tremendously, bypassing much of the more costly CPU testing. It is recommended that all future CPU and larger-scale continuous pilot runs include TGA tests of bed material, to add to an effective reactivity database.

- The CPU-determined reactivities increase consistently with temperature and are relatively insensitive to pressure, within the range studied, and steam/carbon ratio. While a limited experimental matrix covered different values of the latter two variables, differences were no greater than experimental scatter. The form of reactivity variation with temperature is consistent with that observed for TGA-determined reactivities.

- Potassium impregnation clearly enhances reaction rates, but, in a practical process, will require an efficient leaching step for potassium recovery to be economically viable. Ash-leaching studies, associated with the tests reported here, indicate that potassium recoveries over 95% can be easily achieved.

- Earlier TGA results suggest that a weight ratio of potassium to fixed carbon of roughly 0.4 will give maximum reactivity enhancement. It is believed that at this K/FC ratio active sites ($-COO^-$) on the coal structure are saturated with K^+ ions. Further increasing the K/FC ratio results in no further rate enhancement. This is based on data for bituminous coal and wood, but has not been confirmed for lignite and subbituminous coals. It is recommended that TGA saturation test series be done on any candidate coal for catalytic gasification.

- For these CPU tests, control over the actual degree of potassium impregnation during feed impregnation proved more difficult than expected, apparently leaving a lot of the KOH catalyst free (nonion-exchanged) and subject to segregation during handling and feeding, as well as in the gasifier itself. The level of catalysis thus became another process parameter subject to random variation during the tests.

- Ash analyses and potassium balances for these tests indicated striking, consistent, but unexplained differences in the chemical state of the potassium between beds of limestone, taconite, or coal ash alone. The mobility of the potassium, and, hence, its catalytic effectiveness, appears to be substantially enhanced or limited by its reactions with other inorganic components in the bed or coal ash. This is based on presumed inorganic equilibrium, achieved over many hours at steady state, and cannot be observed by TGA data. It is recommended that future fundamental efforts in alkali catalysis include detailed studies on catalyst-mineral reactions, paralleling the level of effort at the EERC applied to equivalent reactions during combustion. Significant testing in this area can be done in the EERC's 1-lb/hr CPU.

- The fact that most of the taconite tests showed at least equal reactivities at significantly lower potassium level than the limestone tests makes taconite's equal or slightly superior performance still more impressive. Taconite is recommended as a bed material for gasifier design, site-specific supply costs permitting. Its potential for promoting methane formation or for sulfur capture is neither demonstrated nor refuted by the data reported here. In addition to at-least-equal catalytic effects, taconite is harder than limestone and should, therefore, require lower rates of bed replacement.

- Simple theoretical considerations reveal that standard TGA-determined reactivities reflect only initial slopes of generally first-order reaction curves. After longer reaction times, at reduced levels of fixed carbon, the difference in reaction rates indicated by TGA data is much less, accounting generally for the less striking reactivity differences in CPU data.

- For the above reason, design of fluid-bed (completely mixed) gasifiers requires a rapidly increasing residence volume and capital cost for increasingly complete carbon consumption. It is, therefore, recommended that overall plant designs should feed all coal, fines included, into gasifiers and use residual char for on-site boiler fuel.

- TGA tests on both feed and bed overflow product indicated that there is no significant decrease in reactivity as remaining carbon is depleted, which agrees with basic theory. This refutes a hypothesis that the effective reactivity of a coal may reflect a composite of reactivities of different macerals within the sample.

- The CPU was operated at feed rates normally used for mild gasification (pyrolysis) testing, which resulted in generally higher levels of residual carbon than would be acceptable in a practical gasification process. This enabled more meaningful measurements of reaction rates, which was a major objective of these tests, than would be possible at near-complete carbon conversion.

- As to product gas composition, variation with pressure and steam-carbon ratio was generally less than the experimental scatter, while averages of all gas yield data showed a variation with temperature consistent with theory.

- The CPU, at 1- to 4-lb/hr capacity, represents the bare minimum scale on which gasification process evaluation can be of significant value. Due to heat losses, inaccurate gas flow measurements, and possibly irregular fluidization, experimental scatter exceeded the range of gas yield and composition variables of interest. It is recommended that any future tests on this unit should involve longer runs, multiple replications of material balance periods, and multiple samplings of all products during each in order to provide statistical credibility.

- In all gas samples, H_2S levels fell below the detectable analytical limit, precluding any observation of sulfur capture potential for the conditions studied. This is consistent with the use of low-sulfur (S = 0.63% maf) Wyodak coal.

- To augment TGA and CPU methods for feed-catalyst-condition screening, a new research tool, the integrated bench-scale gasifier (IBG) has completed preliminary shakedown testing and shows a very good possibility of essentially replicating TGA data on a larger scale, of 200-300 grams, as compared with 20-50 milligrams for the TGA. Unlike TGA, this unit can provide samples of residual char and condensible liquid coproducts large enough for complete analysis, and multiple or replicate gas samples. Extensive use of this unit is presently scheduled for two related projects.

- Data from the last successful, weeklong run by EERC's continuous 40-lb/hr process demonstration unit (PDU), for Wyodak coal in a bed of limestone, were reviewed for comparison with the CPU data reported here. Specific capacity data, lb of fixed carbon converted per hour, per cubic foot of reactor volume, were over twice as great for the PDU as for the CPU, establishing the CPU data as a conservative basis for preliminary gasifier design.

- It must not be forgotten that process heat for the CDU is provided electrically, so that gas yields and concentrations of hydrogen or methane are unrealistically high. Future interpretation of CPU data should include calculation of the amount of additional coal that would be consumed to supply process heat in a real-world gasifier, assuming various heat utilization efficiencies.

- Results from this and parallel studies are still inconclusive regarding the potential use of sodium as an economical alternative to potassium as a gasification catalyst. Large PDU-scale tests are needed to determine whether preimpregnation of sodium or potassium on feed coal, as homogeneous catalysts, will result in the agglomeration problems observed with heterogeneous (cofed) trona and nahcolite earlier in this project. Because of the very small bed size, the CPU is not recommended for studying mechanical factors affecting bed fluidization.

- For firm engineering design data and identification of operating problems, future pilot plant efforts should be done on a significantly bigger capacity scale than the EERC PDU system described here. Such a facility must be built for and dedicated to the single purpose of hydrogen/methane production, on a budgetary scale large enough to ensure complete shakedown operation and extended runs of at least a week on each set of conditions considered, with several replications of all runs showing promise for commercial-scale designs.

- EERC has on hand nearly all the components to assemble a substantially larger pilot gasifier system than the PDU used in this project. The vessel, partial feed system, and gas cleanup train may be suitable for up to twenty times the PDU capacity at near ambient pressures, with further increases possible at pressures to possibly 35 atmospheres. The vessel is large enough to accommodate multiple bed and feed configurations.

- As an alternative approach to further process development, small demonstration gasification projects should be considered, preferably integrated with utility plants to minimize capital and fixed operating costs of facilities and auxiliary systems. If/when such a system is in operation, relatively inexpensive tasks would be to vary the bed material and impregnate batches of feed coal, for several weeks of operation, with potassium or other catalysts. The first step along this route would consist of site-specific feasibility studies to establish the costs and benefits of such demonstration plants.

2.0 BACKGROUND

Since the mid-1970s, the United States has been in a state of apprehension over the next energy crisis and in eager anticipation of the next generation of energy supplies. While still unresolved, it appears reasonably certain that, for decades to come, the U.S. will, or should, rely increasingly on coal, simply because it is cheap, and we have an abundance of it. It is also apparent that somewhere within the continually shifting, multiple scenarios predicted, there will be an expanded market for hydrogen, either as an end product or an essential intermediate. This observation is summarized in Figure 1, showing the full array of potential markets for hydrogen from coal. The most economically proven source of hydrogen is reformation of natural gas, itself a valuable commodity and of potentially limited supply. In any scenario of complete energy independence, natural gas is too ideal a fuel for domestic heating and short-term emergency utility and industrial uses to deplete for massive hydrogen production for any extended (multidecade) period. Efficient electrolytic hydrogen production using wind or solar power is still decades of development away from economic feasibility. Therefore, any medium-term policy to significantly accelerate commercial production for the markets noted in Figure 1 must depend upon coal. In order for the potential of coal as a hydrogen source to be realized, valid process data must be generated, from which process options and gasifier designs of maximum yield and minimum capital and production cost can be identified.

The emphasis of this project has been on the effects of catalysis, to reduce reaction severity and reduce capital costs, with gasifier and process design of interest only to realize on a practical scale the benefits of catalysis as indicated by TGA data. As an overall program rationale, the increasing scale of catalyst screening at the EERC, in terms of size and research cost, is indicated by Figure 2. TGA screening is well established as a standard evaluation tool, is relatively inexpensive, and has provided most of the useful data to date, indicating the substantial increases in the reaction rate between coal char and steam to produce hydrogen that are possible through catalysis. The IBG (integrated bench-scale gasifier) system allows larger-scale batch testing, providing gas, solid, and liquid product samples large enough for thorough analyses. This device was completed too recently to generate significant data within the funded period of this project, although some shakedown tests will be discussed briefly in this report, to demonstrate its potential as a research tool.

The CPU (continuous process unit) system is a minimum-scale, "near-simulation" of continuous, fluid-bed process conditions, falling short of achieving full-scale process conditions only in that it is externally (electrically) heated, so that product gases are unrealistically rich, being undiluted by the CO_2 from the burning of extra feed to provide internal process heat. Most of the data presented in this report were generated by CPU tests. This unit was designed primarily for char production (mild gasification), rather than for complete gasification, somewhat limiting its usefulness. However, the incomplete consumption of char, in effect, allowed study of the catalyzed gasification reactions under conditions of varying carbon levels in the fluidized bed. Finally, the PDU (process demonstration unit) is a complete process simulation, capable of generating process engineering data and realistic material balances for selected process conditions.

Earlier in this project, the PDU was operated successfully, generating an array of useful data, until it was shut down, modified, and semi-integrated into pilot facilities for mild gasification and pressurized fluid-bed combustion. Following this renovation, a substantial amount of time and funding was required to bring the unit to full operational status. Consequently, there was little useful, steady-state data on catalytic steam gasification, and scheduled runs were scaled down to the CPU level, producing most of the conclusions of this report. (As a note on nomenclature, the PDU and CPU definitions apply to this report and EERC work during the past two years. Some earlier EERC reports (4) refer to the 40-lb/hr unit as a CPU.)

By way of broader background, some earlier PDU data and some proposed plant design concepts from this and parallel projects will be discussed, relative to the conclusions drawn from the data presented here. Detailed TGA and prerenovation PDU results have been published earlier (4,5), as well as has a marketing study of commercial hydrogen from a hypothetical, commercial-

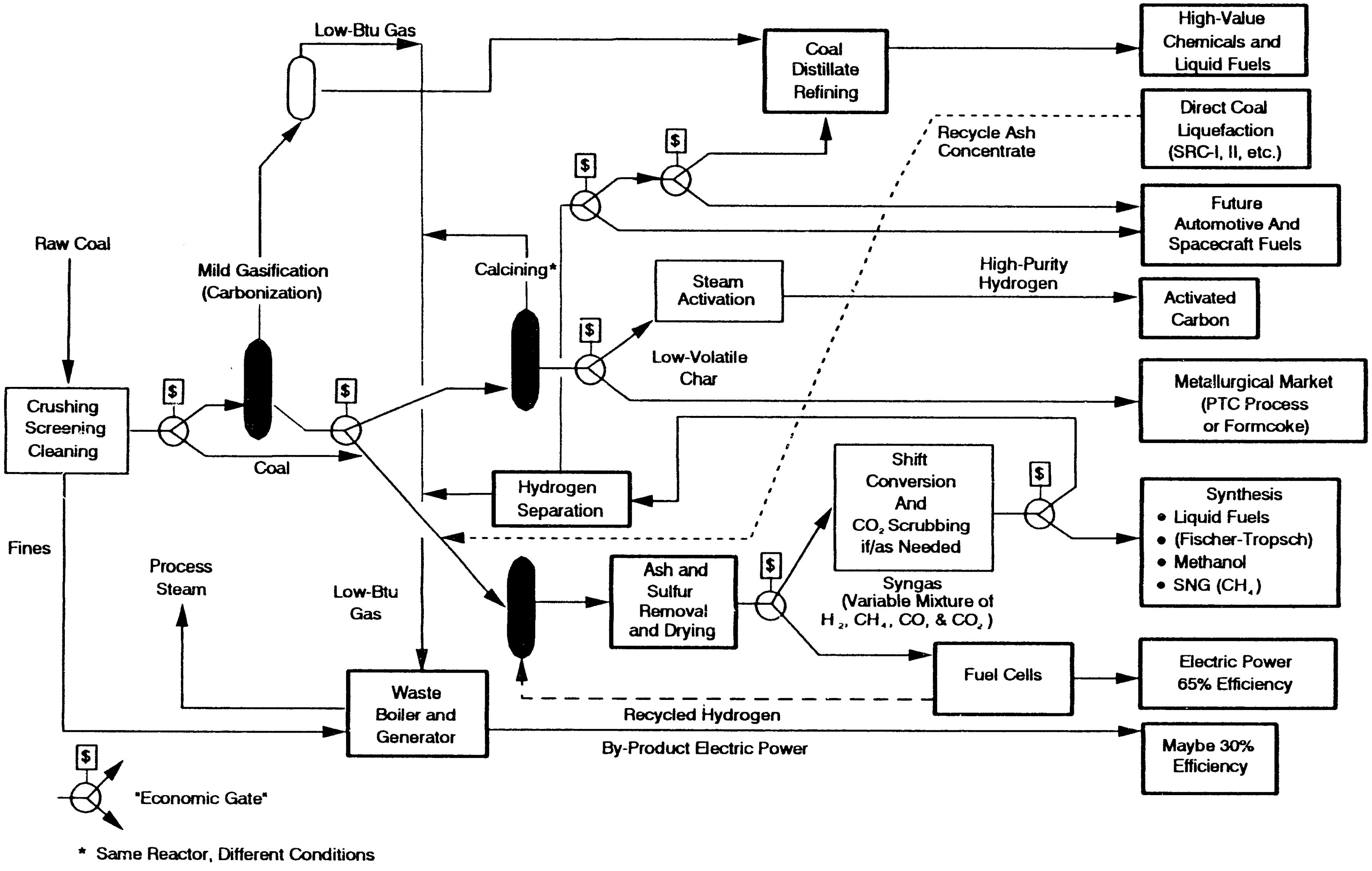

Figure 1. Emerging markets for hydrogen from coal.

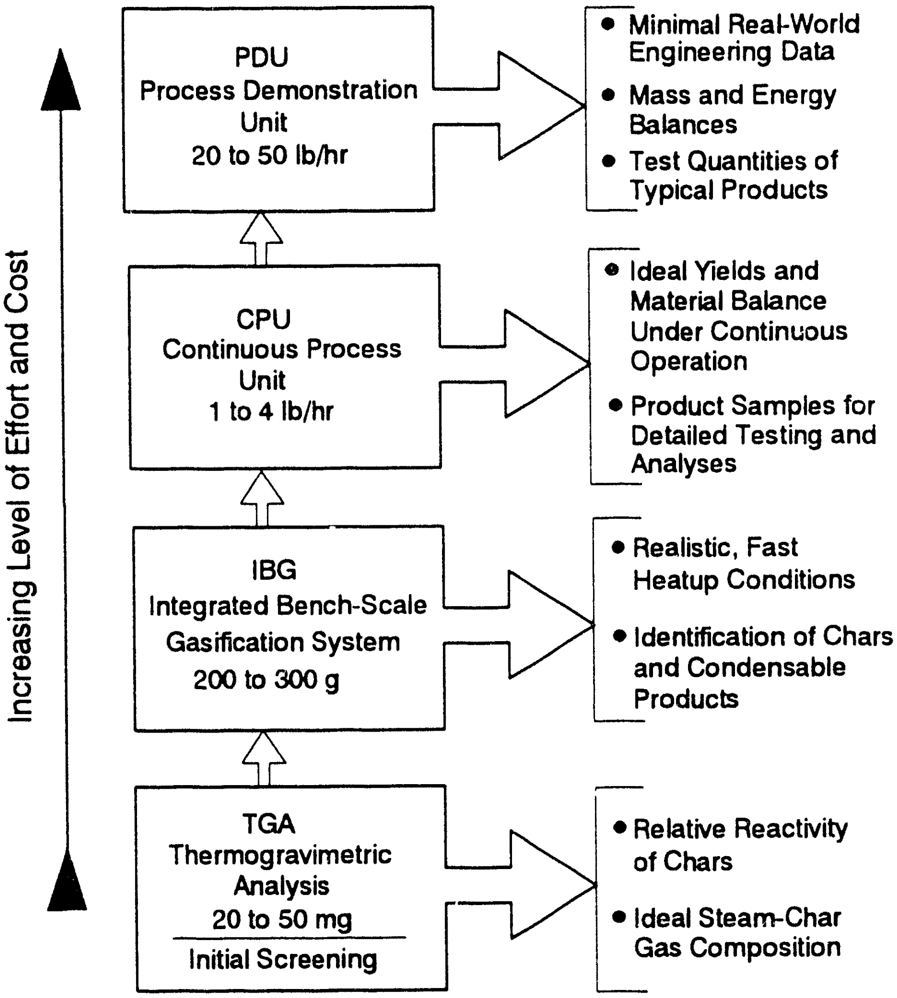

Figure 2. Scaled gasification capabilities at the EERC.

scale plant (6). The PDU data were used as the basis for an outside subcontractor, Black and Veatch (B&V), to do an engineering feasibility study (7) based on the best available set of PDU operating data. That study assumed a straightforward, though inefficient, gasification process design, with alternatives for hydrogen, methanol, or electricity via fuel cells as the end products. That study assumed a western subbituminous coal in a limestone bed, with no other catalyst. An earlier, definitive study by Exxon (8) considered a process using an eastern bituminous coal, catalyzed by potassium impregnation, to produce a gas high in both hydrogen and methane, followed by shift conversion for methane (synthetic natural gas) production. An ongoing, parallel study by the EERC (experimental) and Fluor-Daniel Engineers (F-D), under subcontract to Energy Research Corporation (ERC), assumes an eastern bituminous coal to produce hydrogen-methane mixtures for advanced fuel cells, which, in turn, may produce electricity at overall efficiencies approaching

60%. This study has also addressed the use of potassium-impregnated bituminous coal. It has so far produced a multioption engineering cost study (9), by F-D, assuming the same bituminous coal (Illinois No. 6) in a limestone bed. Though beyond the scope and budget of this report, these studies should be reviewed in the light of the experimental conclusions reported.

3.0 OBJECTIVES

3.1 Project Objectives

The broadly defined objectives of this report are as follows:

- To determine gasifier operating conditions and catalyst selections to maximize the production of hydrogen, methane, condensible products, marketable char and activated carbon
- To develop kinetic models, based on empirical data, to predict product yields under real-world conditions
- To explore the potential for in-bed sulfur capture by selection of bed and catalyst material
- To apply the above objectives primarily to lignite and subbituminous coals, with extensions to bituminous coals where convenient

3.2 Process and Plant Design Objectives

All indications are that significant enhancement of throughput capacity, and possibly of hydrogen and methane yields is possible by catalysis, but is of little practical utility until reflected in viable commercial-scale plant designs. Any process design, even a preliminary one for rough economic feasibility evaluation, must assume the best selection possible of catalysts and design of a gasifier to realize the maximum advantages indicated by experimental data available, however marginal or incomplete. While the data reported here are not sufficient as a basis for reliable gasifier plant designs, they are reported with the plant design application in mind to assist those interested in the practical (economic) application.

3.3 Report Objectives

With the completion of this project, the goal of this report is to extract the maximum useful content from the recent pilot-scale data at the EERC, both from the viewpoint of preliminary process design and of fundamental understanding of the kinetics of steam-coal reactions in a fluidized-bed environment. A secondary goal is to preserve, through documentation and the discussion of data, the various "loose ends" of unanswered questions, to be addressed in any follow-on efforts.

4.0 THEORETICAL: BATCH AND CONTINUOUS REACTIVITIES

The overall purpose of this project has been to identify catalysts to substantially enhance the reactivity of coals and to improve gasifier efficiency, through lower reaction severity, for the production of hydrogen and methane. Thermogravimetric analysis (TGA), on which the definition and measurement of reactivity is based, has demonstrated that coal reactivity can be increased by as much as two orders of magnitude by the proper selection of catalysts. A detailed definition of reactivity and a description of how it is measured (3) is included as Appendix A. Table 1 shows an array of standard reactivities for a variety of coals, with and without various catalysts, from TGA tests at the EERC over the past seven years, done under a number of different projects. The salient conclusion from these data is that low-rank coals (lignites and subbituminous) are more reactive than high-rank (bituminous) coals and that the use of some catalysts greatly enhances the native or intrinsic reactivity. To be of practical value, it is essential to predict to what extent this enhanced reactivity of all ranks of coal may be achieved in continuous gasifiers.

For TGA data to be truly relevant to catalyst evaluation, it is essential to determine the degree to which TGA-determined reactivities can be correlated with measured reaction rates in continuous systems.

The dominant reaction in coal gasification, whose rate determines the overall rate of conversion to gases, is the steam-char reaction: $C + 2H_2O \rightarrow 2H_2 + CO_2$. "C" in this case refers to the nonvolatile carbon, which is approximated by the fixed carbon, FC, as reported in the standard proximate analysis, which is the variable actually measured during standard TGA tests. The larger weight of total carbon, as reported in a standard ultimate analyses, is not used here, since the difference is included in the volatile fraction, which pyrolyses quite rapidly at gasification temperatures. The overall rate of carbon consumption is dominated by the slower steam-char or steam-carbon reaction. This reaction can usually be represented by a first-order reaction rate, which is determined by the differential equation:

$$-(dC/dt) = k_o C^n$$

and its exponential solution, for n = 1, which is:

$$C(t) = C(0)\ e^{-k_o t}$$

where C(t) is the amount of fixed carbon in the reaction zone at any time, t, in hours. The exponent, n, is the reaction order, generally assumed equal to 1 as a simplifying approximation. The initial weight of carbon, not a weight or mol fraction, is defined as C(0), at t = 0. In a batch reaction, such as the TGA analysis, at the moment the reaction starts, the rate or slope of carbon decrease is at its maximum:

$$dC/dt = -k_o t, \quad \text{or} \quad C(t) = C(0) - k_o t, \text{ at } C(t) \rightarrow 0$$

and decreases as the carbon is consumed, much like a fire dying down. In a standard TGA analyses, the approximate or standard reactivity, k, with no subscript, is defined as the average rate of the first 50% of the carbon consumed. Figure 3 shows a normalized exponential curve, C(t), for an arbitrarily assumed value of $k_o = 2.0$, the initial slope, $-k_o t$, and a tangent line, representing the reduced rate of carbon loss when C = 50%. Added to these is a hypothetical straight line, connecting the initial (100%) and the 50% points, which is used to define standard reactivity, k. Note that it shows a slope intermediate between the absolute or true reactivity, k_o, and

TABLE 1

Reactivities (K, 1/hr) of Raw and Catalyzed Coals by Thermogravimetric Analysis

Temperature, °C		650	700	750	800
Velva (ND) Lignite					
No Catalyst		0.30	1.35	2.10	3.55
10% K_2CO_3		1.35	4.06	8.17	34 80
10% Trona (Na_2CO_3)		1.92	6.05	16.46	
10% Limestone		0.48	0.81	6.49	15.50
20% Limestone		0.55	5.00	8.76	15.00
10% Taconite			1.33	1.63	2.85
10% Taconite, 4% Trona			3.56	8.46	
Wyodak (WY) Subbituminous					
No Catalyst	a*	0.37	1.16	1.31	3.05
10% K_2CO_3	a	1.25	4.30	8.24	13.48
10% Trona, 10% Taconite	a		1.00	3.33	7.65
No Catalyst	b		0.70	1.20	2.70
10% K_2CO_3	b		4.00	5.20	7.20
No Catalyst	c			2.34	
2.8% K	c			2.81	
5.6% K	c			2.86	
8.4% K	c			4.74	
11.2% K	c			4.55	
14.0% K	c			5.67	
15,8% K	c			7.93	
No Catalyst	d		0.84	0.94	2.23
10% K_2CO_3	d		9.87	11.13	13.07
No Catalyst	e		1.33	3.28	7.33
Limestone	e		1.26	3.01	3.86
CaO (6% Ca^{++})	e		3.80	6.36	15.74
$CaSO_4$ (6% Ca^{++})	e			2.77	
$Ca(C_2H_3O_2)_2$ (6% Ca^{++})	e			4.55	
Illinois #6 Bituminous					
No Catalyst			0.07	0.14	0.33
10% K_2CO_3				4.36	
10% Wood Ash, Cold Leach.			0.95	2.60	8.54
10% Wood Ash, Hot Leach.			0.61	3.01	5.15
20% Limestone				0.59	1.45
20% Dolomite				0.25	0.90
18% Limestone, 2% K_2CO_3				0.36	
15% Limestone, 5% K_2CO_3				0.89	
12.6% Limestone, 7.4% K_2CO_3				3.55	
10% Limestone, 10% K_2CO_3				5.38	
15% Taconite, 5% K_2CO_3				0.15	
10% Taconite, 10% K_2CO_3				4.97	
5% Taconite, 15% K_2CO_3				4.17	
Indiana Bituminous					
No Catalyst			0.18	0.16	0.31
CaO (6% Ca^{++})			0.21	0.58	1.26
$CaSO_4$ (6% Ca^{++})			0.17	0.32	1.17
$Ca(C_2H_3O_2)_2$ (6% Ca^{++})				0.66	

* a-e indicate test series on five different Wyodak coals, some from different mines, indicating variation in coal type.

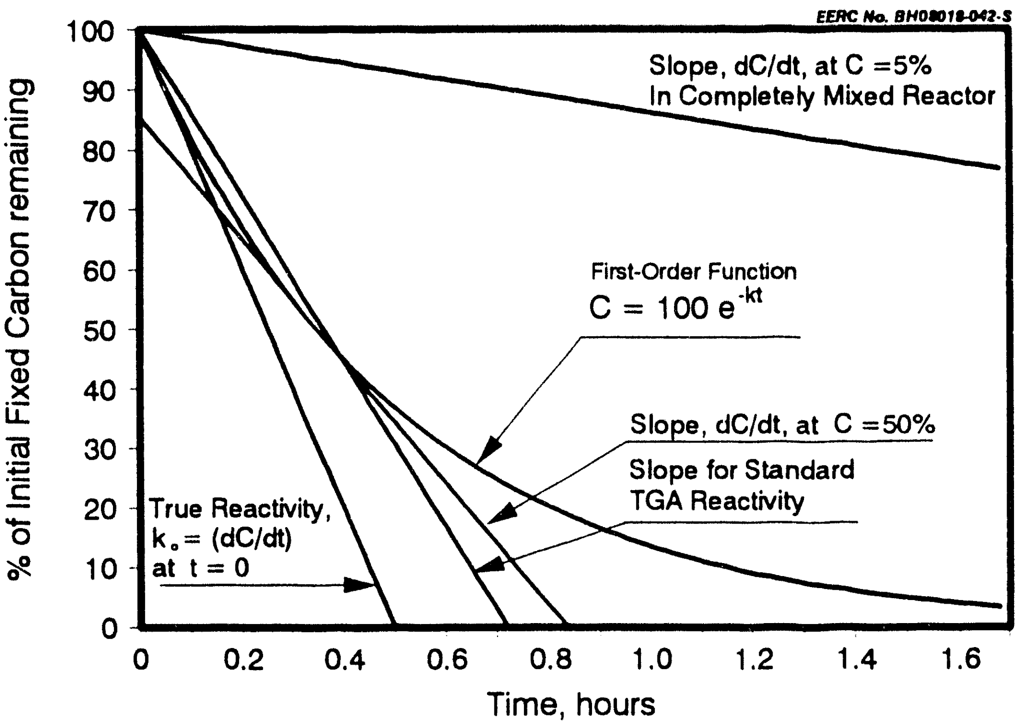

Figure 3. Standard and "true" reactivities for steam-char reaction.

50% tangent line. In a typical set of TGA data, the distinction between the k line, the k_0 line, and the exponential curve is generally not obvious in this range, due to the combined effects of experimental scatter and minor deviations from first-order behavior. The standard definition of reactivity, k, without subscript, is thus based on this easy-to-read line on experimental data plots, such as the several examples shown in Appendix A.

Throughout this study, analyses of data assume first-order behavior. TGA data indicate, however, that heavily alkali-catalyzed reactions tend to have lower order reactivities, with $n < 1.0$, which results in a faster $-dC/dt$, which tends less to slow down as carbon is depleted. In this respect, all conclusions that can be drawn from this work, regarding throughput or gasifier size, will err on the conservative side. Real-world reaction rates are thus expected to be a bit faster.

To relate the TGA-derived, standard reactivity, k, to the absolute reactivity, k_0, note that k is the slope of a straight line = $50/t_{50}$, where $t_{50} = -\ln(0.5)/(-k_0)$ is the time at which $C(t) = 50\%$. By rearranging the normalized exponential function above and setting $C(0) = 1$, $k = 0.7215k_0$ or $k_0 = 1.386k$. This difference is relatively insignificant, compared with the differences in reactivity with temperature and for different coals and catalysts, shown in Table 1.

Returning to Figure 3, the 50% tangent line roughly represents the reaction rate that the hypothetical coal or char is experiencing when it is 50% depleted by the reaction. Consider next a fluidized-bed gasifier, with a continuous bed overflow, as is the case of the continuous process unit described below. If the overflow, at steady-state conditions, contains 50% of the fixed carbon entering the system, it may be valid to say that this slope dC/dt, determined by a material balance, equals the reaction rate at C = 50%. Recombined as the above differential equation, the reactivity might be reconstructed as:

$$k = -0.7215\ (dC/dT)/C$$

which, by definition, should be valid for any value of C as the amount of carbon remaining. Therefore, if such a reactor is sized to achieve 95% carbon (FC) conversion, the average or effective reaction rate would be the slope at C(t) = 0.05, shown as a straight line, starting at the origin, near the top of Figure 3. This would clearly apply in the case of a plug flow reactor, at its discharge (top) end, with the higher k_0 value at its bottom end. However, if a fluidized-bed reactor is assumed completely mixed, the overflow will be a mixture of particles that have been in the reactor for very different lengths of time, each representing a degree of depletion at different points along the C(t) curve. Therefore, it must be emphasized that the easily measured "reactivity" in a continuously and presumably completely mixed reactor is **not** the same parameter as that measured by the standard TGA test. So let us hereby define the "continuous reactivity" as:

$$k_c = (dC/dt)/C$$

where C is the fraction of the amount (kg or lb) of fixed carbon content in the reactor bed, determined by analysis of the bed overflow stream, leaving the system unreacted. With this assumption, the choice of units is consistent with that of the definitive equation assumed in TGA analyses, (kg/hr)/kg = 1/hr, where both weights can be expressed on a per volume basis for gasifier scaling studies. C must not be confused with simply the FC content (%) of the reactor bed, which is often higher than that of the feed stream, due to rapid loss of the carbon in volatiles.

If we plot the exponential function $C(t) = 100\ e^{-k_o t}$ for different values of k_0, or k, the advantages of increased reactivity are fairly obvious, as shown by the examples in Appendix A, many of which appear to be straight lines down to fairly low levels of residual carbon, indicating less than first-order reaction; that is, $n < 1$ in the more general equation. If we assume first-order behavior, however, and extend all C(t) curves to 90% completion, we note that the slopes of the high-k curves are eventually less than those of the low-k curves. In Figure 4, using the general equation, $C(t) = 100\ e^{-k_o t}$, the derivatives, dC/dt, are plotted against time. Note that, notwithstanding the great difference in initial rates, the ranking of reaction rates is eventually reversed. In other words, assuming first-order behavior to apply, the longer a unit charge of carbon is retained in a reaction zone to achieve near-complete conversion, the less are the advantages of an enhanced reactivity. Such long residence times, however, will generally be beyond those of any commercial significance.

As a less simplistic model of reactivity, for specific sets of reactivity data, the actual or calculated reaction rate which is also normally reported becomes more significant. See Appendix A for a more thorough discussion of calculated, as opposed to assumed, first-order reactivities.

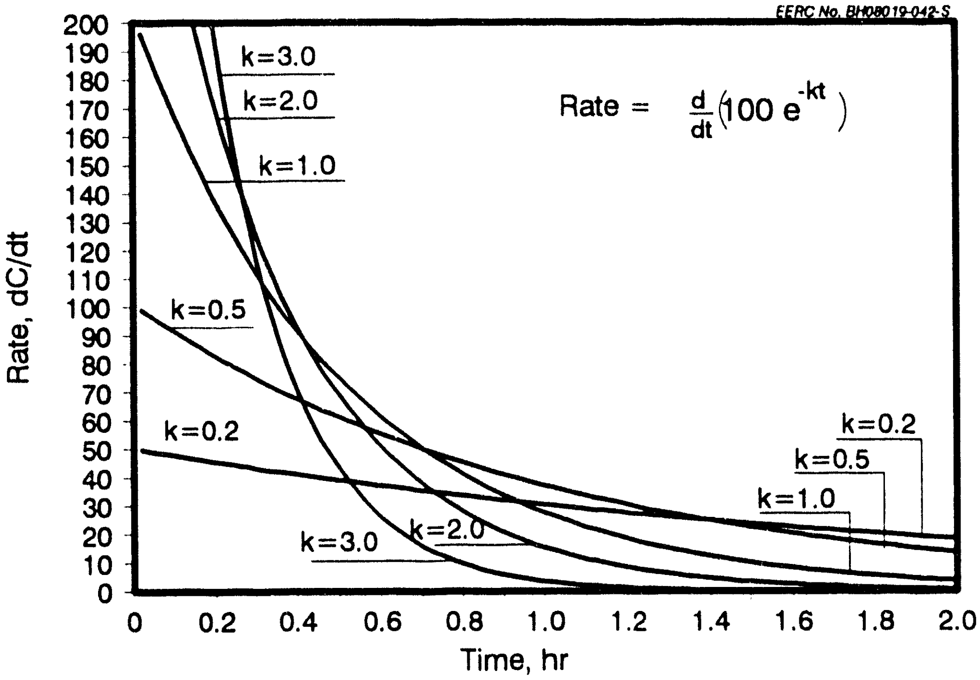

Figure 4. Reaction rates vs. time for different k values.

In a completely mixed, fluidized-bed reactor, with a low and uniform residual carbon level, there arises a question of how much difference a greatly enhanced reactivity, k, can make in throughput capacity. This question will be addressed further in a later section, in the analysis of experimental data.

There also arises the question of how and whether a k_c from a continuous reactor can be mathematically related to a k_o from TGA results. It is tempting, referring to Figure 3, to add another line, from the 100% origin to some C(x), t(x) point along the curve, where C(x) is the amount of carbon in a reactor bed at time t(x), which might be the average time in the bed of all reacting particles. Defining the slope of such a line as k_c further defines a fictitious C_o point at which C(t) = 100% at t = 0. This would be the initial weight of carbon in the reactor bed if it had been a batch reaction at an **unknown** k_o, defining a first-order function passing through C(x), t(x). This assumption now defines the following two equations:

$$C(\chi) = C_o\, e^{-k_o t}$$

$$k_c = (C_o - C(x))/t(x)$$

Unfortunately, these two equations contain three unknowns: C_o, k_o, and t(x) and, therefore, appear unsolvable. Clearly, any other-than-empirical $k_o = f(k_c)$ function would be valuable in predicting continuous process behavior from the far cheaper TGA data and warrants further investigation.

5.0 CONTINUOUS PROCESS UNIT

5.1 Apparatus and Experimental Procedure

EERC's continuous process unit is shown schematically in Figure 5. A mixture of sized coal, bed makeup, and catalyst is fed from the pressurized feed hopper through a precalibrated feed auger. The feed hopper is weighed at the beginning and end of mass balance periods. Water is fed to an electric boiler/superheater by an accurate metering pump. Nitrogen is metered in by a rotameter, backed up by weighings of the source cylinder. The system is rated for about 150 psig, although operation at this pressure was limited by the capacity of the solid feed system and minor leakage problems. All vapors are cooled and condensed in stages. Solid and liquid products are collected and weighed as often as collection pots fill up and at the end of each material balance period. Not shown in Figure 5 are several dozen thermocouples, by which temperatures throughout the system are monitored continuously. All solid feeds and product samples are available for proximate and ultimate analyses and x-ray fluorescence analyses of their ash components. A run is defined as at least a 4-hour material balance period, after steady-state operation has been achieved, which may take eight or more hours.

The combined gas flow, following condensation of nearly all water and liquid organic products, is metered through a continuous displacement gas meter of limited accuracy. A gas bag sample is taken at least once per balance period for analysis by gas chromatography (GC). A preliminary material balance is done, using standard software developed by EERC's mild gasification project. Printouts are included in Appendix B. Cumulative inaccuracies in gas flow measurements show up here as deviation from a perfect closure on the nitrogen balance. All exit gas flows, based on GC analyses, are adjusted in the same proportion until the nitrogen balance shows a 100% closure, assuming the accuracy of the nitrogen feed measurement.

The component gases are then normalized and reported on a dry, inert-free basis. This and all analyses are then fed into a graphic, "user-friendly" data reduction program composed for this project, for which an example is included as Appendix B, along with summary sheets for all seventeen runs reported here. Data for each run are then stored on disk for later, detailed analyses.

The analyses of blended feeds for these series of tests are shown in Table 2. An initial objective was to apply the KOH catalyst intimately onto the coal in a ratio of about 0.12 mols of potassium per mol of FC (fixed carbon), determined by proximate analysis. This was done by dissolving pellets of 87% KOH in minimal water, mixing with the raw coal, and then redrying. The final, as-fed blends of raw or impregnated coal were then analyzed. It is now suspected that substantial amounts of the KOH did not undergo ion exchange with the coal and were present only as a surface deposition, allowing it to separate during grinding, thus causing the wide differences in K/FC mol ratios in Table 2 and in reactor bed analyses reported later.

When the system is started up, gas, solid, and condensate products are sampled and weighed through several complete change-outs of the reactor vessel, until repeatable weights, as well as constant temperatures, pressures

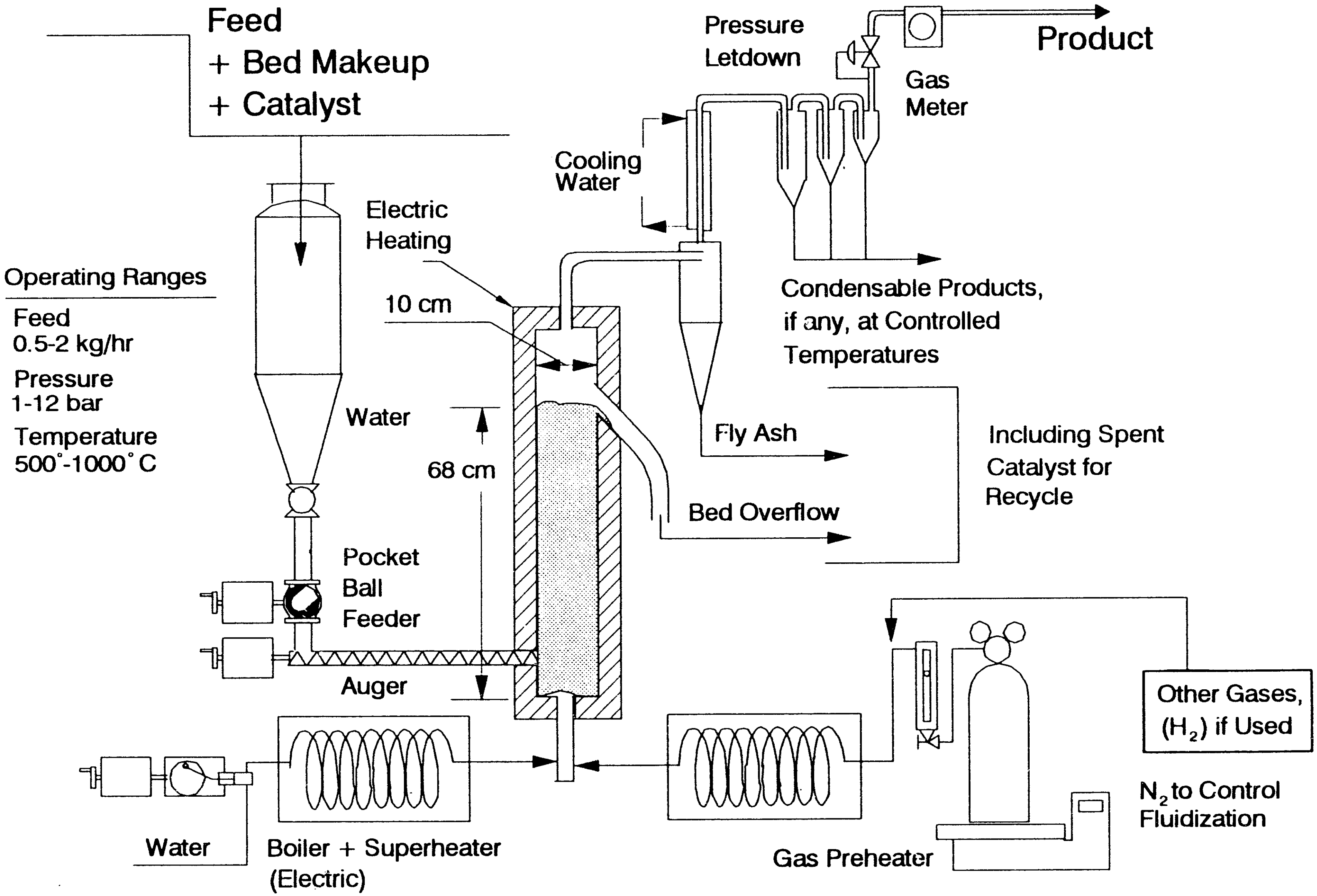

Figure 5. EERC's continuous process unit.

and flow rates, suggest that steady state is achieved. This normally requires at least eight hours. All product collection pots are then emptied, and a standard, 4-hour material balance period is started. Solid products are collected and analyzed for both the bed overflow and the cyclone, shown in Figure 5. The distribution and analysis of the two solid samples provide the primary measure of the degree of completeness of the reaction and the extent of carryover, which, in turn, indicates whether fluidization velocity was adequate or excessive. Screen analyses of the bed and cyclone solids would also indicate the degree of attrition and required bed makeup rate. In this series, however, the bed was fed at a high rate, ensuring substantial bed overflow so that a significant amount of unreacted carbon could provide some indication of the reactivity at the conditions covered.

Solid and gas samples, to be analyzed after the run, are normally taken at a time late in the 4-hour material balance period. In the first seven tests reported here, two or three sets of solid and gas samples were taken, about two hours apart, and analyzed separately to indicate the range of variation during the material balance period. This procedure was not continued through the entire series, however, in the interest of economy.

5.2 Experimental Objectives and Rationale

The intent of these experiments was to go through a minimal array of temperatures, pressures, and steam-carbon ratios for steam gasification of Wyodak coal, impregnated with potassium hydroxide, in fluidized beds of limestone and taconite. A bed makeup rate of 20% limestone or taconite is assumed. A short initial series of four runs used raw Wyodak coal and limestone, without potassium impregnation, as a basis of comparison. Earlier TGA data (2) establishes that limestone alone is a cheap, moderately effective catalyst; that taconite alone has essentially no catalytic effect; and that reactivity enhancement by KOH impregnation is substantially greater than the difference between limestone and taconite. Taconite is also of interest for its possible promotion of the methanation reaction and as a possible sulfur-capture agent in the 600°-650°C range, at which, in combination with higher pressures, methane production is favored. The temperature range selected for these tests, 600° to 700°C, is below the range known to offer good gasification rates, but was selected to best observe the effects of catalysis, in terms of both increased methane yields and the potential economy of operation at lower temperatures.

An experimental matrix consisted of tests at temperatures of 600°, 650°, and 700°C for the cases of K-impregnated coal, with a few digressions to higher pressures and steam/carbon ratios. For comparison, four tests were done with raw coal in a limestone bed, which was the basic operating condition used in earlier PDU tests (5) and which was the basis for subsequent engineering and cost study (9).

5.3 Summary of Data

Complete printouts of data for two runs are presented in Appendix B, while summaries for all runs are covered in Tables 3-A, 3-B, and 3-C for the cases of raw-coal-plus-limestone, impregnated-coal-plus-limestone, and impregnated-coal-plus-taconite, respectively. The definition of these

TABLE 2

CPU Feed Analysis

Run Nos.	Raw Coal	M-216-220	M-221-227	M-228-234
Bed Makeup	---	Limestone	Limestone	Taconite
% of Feed	---	20.0	20.0	22.5
Impregnated Catalyst*	---	None	KOH	KOH
Proximate %				
Moisture	28.60	21.30	20.70	20.70
Dry Basis				
Volatiles	45.29	48.40	46.32	39.22
Fix Carbon (FC)	47.84	35.20	28.70	28.50
Ash	6.87	16.40	24.98	32.28
Ultimate (MAF), %**				
Hydrogen	5.10	4.63	3.82	3.55
Carbon	73.49	67.94	64.00	48.51
Nitrogen	0.91	0.85	0.82	0.64
Sulfur	0.63	0.16	0.42	0.44
Oxygen	19.84	36.40	30.89	14.56
XRFA, % of Ash				
SiO_2	25.90	7.68	12.60	47.50
Al_2O_3	13.90	4.57	8.20	3.52
Fe_2O_3	7.36	3.14	4.50	28.00
CaO	24.30	73.30	12.00	4.99
MgO	8.90	4.77	4.50	2.17
Na_2O	2.07	0.35	0.90	0.37
K_2O	0.35	0.53	47.70	8.87
SO_3	15.40	5.25	8.70	4.38
Other	1.82	0.41	0.90	0.20
Mol-Equivalents/Mol FC*				
K^+	0.00	0.00	0.17	0.04
Ca^{++}	0.05	0.49	0.15	0.08
Fe^{+++}	0.01	0.02	0.05	0.44

* Based on analyses of coal-catalyst-bed mixtures, as fed.

** Variation in ultimate analysis reflects interaction of coal's carboxyl ($-COO^+$) and other organic functionalities with mobile inorganics of limestone, taconite, and/or KOH.

variables is self-evident. They are discussed and trends identified in the following section.

Table 4, subdivided into three corresponding sections, compares reliability factors suggested as predictions of the data's validity. For the first seven runs, where double sampling was done, these factors include rates of change in hydrogen content of product gas, and of fixed carbon and volatiles in both the bed overflow and cyclone solid products, all expressed as percent change during the 2-hour interval between samples. Where this variation is greater than 10%/2 hours, the data are identified as flawed by

TABLE 3-A

CPU Run Summary
Bed: Limestone
Other Catalyst: None

Run No. M-	216	217	218	220
Run Specifications				
Temperature, °C	700.0	600.0	700.0	700.0
Pressure, atm	2.4	2.4	6.1	2.4
Feed, lb/hr	1.8	1.8	1.8	1.8
lb maf/hr	1.21	1.21	1.21	1.2
Steam/Carbon Mol Ratio	2.57	2.65	2.4	1.72
Process Response Factors				
FC Consumed, %	17.88	34.97	55.23	55.13
maf Consumed, %	40.39	54.97	64.61	63.33
Prod. Gas (Dry, N_2-free)				
% H_2	56.75	46.13	62.58	58.58
% CH_4	7.70	18.75	6.54	7.96
% CO	6.01	4.48	0.65	8.16
% CO_2	29.29	30.35	26.94	24.99
% Other	0.25	0.29	0.35	0.31
Rate, scfh	22.50	8.98	21.50	21.35
Wt. Gas/maf Feed	0.82	0.35	0.66	0.72
Wt. Gas/FC Consumed	9.07	2.01	2.38	2.60
Wt. H_2/maf Feed	0.05	0.02	0.06	0.05
Wt. H_2/FC Consumed	0.61	0.10	0.21	0.19
Wt. CH_4/maf Feed	0.06	0.06	0.05	0.06
Wt. CH_4/FC Consumed	0.66	0.32	0.17	0.21
Cyclone Fines, lb/hr	1.09	0.10	0.11	0.10
% Volatiles	29.93	32.99	31.57	27.32
% FC	43.29	42.79	40.17	49.00
% Ash	26.79	24.23	28.29	23.67
maf, % of maf Feed	5.40	6.33	6.57	6.27
Bed Overflow, lb/hr	0.11	0.80	0.64	0.75
% Volatiles	34.43	27.91	31.73	30.78
% FC	27.99	44.37	35.44	30.05
% Ash	38.08	26.73	32.84	34.19
maf, % of maf Feed	65.90	47.53	35.75	37.60

TABLE 3-B

CPU Run Summary
Bed: Limestone
Other Catalyst: KOH Impregnation

Run No. M-	221	222	223	224	225	226	227
Run Specifications							
Temperature, °C	700	600	700	700	650	650	600
Pressure, atm	2.4	2.4	2.4	6.1	2.4	2.4	2.4
Feed, lb/hr	1.8	1.8	1.8	1.8	1.8	1.8	1.8
lb maf/hr	1.03	1.03	1.03	1.02	1.03	1.03	1.03
Steam/Carbon Mol Ratio	2.41	2.73	1.45	2.3	2.56	1.09	1.17
Process Response Factors							
FC Consumed, %	75.52	21.36	68.22	69.43	54.83	45.66	29.37
maf Consumed, %	65.20	33.18	62.09	64.70	62.90	62.87	54.98
Prod. Gas (Dry N_2-free)							
% H_2	63.12	59.96	56.19	63.86	60.43	60.86	56.67
% CH_4	2.72	9.00	7.45	6.25	5.67	6.01	9.55
% CO	8.68	2.07	16.56	5.33	6.54	6.36	3.68
% CO_2	25.44	28.69	19.59	24.57	56.56	25.86	29.73
% Other	0.04	0.29	0.21	0.00	0.80	0.91	0.39
Rate, scfh	32.28	10.60	24.90	27.73	18.48	18.05	12.05
Wt. Gas/maf Feed	1.25	0.43	0.98	1.02	0.74	0.71	0.51
Wt. Gas/FC Consumed	2.86	3.46	2.49	2.88	2.64	3.05	3.42
Wt. H_2/maf Feed	0.10	0.03	0.07	0.09	0.06	0.06	0.03
Wt. H_2/FC Consumed	0.24	0.26	0.18	0.25	0.20	0.24	0.24
Wt. CH_4/maf Feed	0.04	0.04	0.07	0.07	0.04	0.04	0.05
Wt. CH_4/FC Consumed	0.08	0.31	0.19	0.20	0.15	0.09	0.31
Cyclone Fines, lb/hr	0.11	0.10	0.11	0.10	0.09	0.08	0.09
% Volatiles	35.66	37.21	33.40	38.27	36.90	34.80	26.80
% FC	20.48	21.04	22.80	17.35	22.00	33.96	40.20
% Ash	43.87	41.76	43.50	44.38	41.10	41.20	33.00
maf, % of maf Feed	5.74	5.52	5.99	5.43	5.16	4.58	5.87
Bed Overflow, lb/hr	0.63	0.88	0.68	0.77	0.74	0.71	0.83
% Volatiles	36.39	33.25	33.30	36.90	32.20	27.60	26.80
% FC	19.48	50.84	24.10	18.50	29.30	37.40	40.20
% Ash	44.09	32.66	42.60	44.70	38.50	34.90	33.00
maf, % of maf Feed	34.49	71.71	37.83	41.62	44.30	44.92	54.14

TABLE 3-C

CPU Run Summary
Bed: Taconite
Other Catalyst: KOH Impregnation

Run No. M-	228	229	230	231	233	234
Run Specifications						
Temperature, °C	600	700	600	700	650	650.0
Pressure, atm	2.4	2.4	2.4	2.4	2.4	2.4
Feed, lb/hr	1.8	1.8	1.8	1.8	1.8	1.8
lb maf/hr	1.02	0.95	0.95	0.95	0.95	0.95
Steam/Carbon Mol Ratio	1.03	1.81	2.07	1.16	2.11	1.04
Process Response Factors						
FC Consumed, %	62.89	80.83	57.07	71.60	58.63	50.13
maf Consumed, %	67.92	78.62	68.25	77.90	71.12	67.33
Prod. Gas (Dry, N_2-free)						
% H_2	57.03	61.50	60.13	59.48	60.10	60.40
% CH_4	8.61	3.71	6.90	4.36	5.90	6.10
% CO	2.47	8.52	2.03	10.81	4.20	4.90
% CO_2	31.61	25.79	30.61	24.84	28.70	27.00
% Other	0.28	0.48	0.28	0.50	1.10	1.60
Rate, scfh	9.98	35.00	11.85	13.35	20.33	17.98
Wt. Gas/maf Feed	0.47	1.50	0.53	0.58	0.90	0.78
Wt. Gas/FC Consumed	1.20	2.99	1.50	1.31	2.40	2.50
Wt. H_2/maf Feed	0.03	0.12	0.04	0.04	0.07	0.06
Wt. H_2/FC Consumed	0.08	0.23	0.11	0.10	0.08	0.19
Wt. CH_4/maf feed	0.04	0.06	0.04	0.03	0.05	0.05
Wt. CH_4/FC Consumed	0.10	0.11	0.10	0.06	0.14	0.15
Cyclone Fines, lb/hr	0.20	0.22	0.19	0.16	0.18	0.17
% Volatiles	17.70	14.50	21.00	20.65	18.40	17.60
% FC	0.99	1.16	0.27	0.81	1.82	0.86
% Ash	81.30	81.40	78.80	78.54	74.76	81.52
maf, % of maf Feed	3.90	4.32	4.30	3.64	3.78	3.26
	1.12	0.75	0.88	0.66	0.79	0.87
Bed Overflow, lb/hr	17.50	19.70	17.20	16.35	16.20	15.50
% Volatiles	19.40	14.70	28.70	25.23	30.46	33.70
% FC	63.10	65.50	59.10	58.92	53.50	50.80
% Ash	51.77	27.22	42.53	28.83	38.82	44.92
maf, % of maf Feed						

TABLE 4

Data Reliability Factors

A. Bed: Limestone
Other Catalyst: None

Run No. M-	216	217	218	220
Input N_2 Accounted for	140	119	100	90
Input H_2O Accounted for	78	88	50	64
Input Ash Accounted for	140	100	102	118
Input Carbon Accounted for	106	75	69	76
Input maf Accounted for	112	109	107	107
Number of Gas Samples	2	2	1	2
H_2 Variation (1) %	2.4	7.5	---	-1.0
Cyclone Ash Samples	2	2	3	2
Volume Variation, %	-5.6	3.4	0.2	-2.6
FC Variation, %	4.6	-2.6	-2.2	1.8
Bed Overflow Samples	2	2	3	2
Volume Variation, %	8.9	0.7	1.4	1.5
FC Variation, %	-20.4	-0.6	1.7	-12.7
Flawed Data? (2)	NSS/BMB	---	---	---

B. Bed: Limestone
Other Catalyst: KOH Impregnation

Run No. M-	221	222	223	224	225	226	227
Input N_2 Accounted for	99	108	102	112	113	111	110
Input H_2O Accounted for	78	63	42	65	81	70	91
Input Ash Accounted for	95	108	98	114	94	82	89
Input Carbon Accounted for	71	91	87	95	92	92	97
Input maf Accounted for	105	110	106	112	112	112	115
Number of Gas Samples	1	2	2	2	2	2	2
H_2 Variation, %	---	0.1	-2.2	-0.6	-0.4	0.9	-0.4
Cyclone Ash Samples	2	2	2	2	2	2	1
Volume Variation, %	-0.4	1.0	3.6	8.2	-0.6	1.2	---
FC Variation, %	-5.0	-1.3	-4.2	-35.9	-95.0	-1.1	---
Bed Overflow Samples	2	2	2	1	1	1	1
Volume Variation, #	-17.1	-60.4	-1.1	---	---	---	---
FC Variation, %	15.7	-1.2	-0.1	---	---	---	---
Flawed Data? (2)	---	---	---	NSS	NSS	---	---

C. Bed: Taconite*
Other Catalyst: KOH Impregnation

Run No. M-	228	229	230	231	233	234
Input N_2 Accounted for	112	109	108	215	111	111
Input H_2O Accounted for	93	77	74	61	83	85
Input Ash Accounted for	191	149	139	113	125	128
Input Carbon Accounted for	20	67	23	67	94	96
Input maf Accounted for	124	110	115	110	114	116
Number of Gas Samples	2	2	2	2	1	1
H_2 Variation, %	1.0	-0.6	2.5	0.2	---	---
Flawed Data? (2)	BMB	---	---	BMB	---	---

* Only one set of solid samples per run in taconite series.

"NSS," for nonsteady state. In all 17 runs, material balance closures for nitrogen, water, ash, total carbon, and MAF (moisture- and ash-free) feed are indicated. An ideal material balance closure is 100%. Where deviation is greater than ± 20%, the data are identified as flawed by "BMB," for bad material balance.

In plotting data, it is normal and too easy to summarily discard any point that falls disturbingly beyond the range that defines any significant correlation. This creates "experimental artifacts," in which data are defined as valid to the extent they support the conclusions drawn from them. In this report, before observing any correlations, identifying a data point as "flawed," on the bases of Table 4, attempts to introduce a less subjective factor in assessing the validity of at least the points that can be so identified. It does not, on the other hand, assure that nonflawed points are, in fact, valid if they fail to fit correlations. These flawed data sets are identified on all following plots as "suspect" points.

Reactivity and potential scaleup data are summarized in Table 5, also divided into three sections. The reactivities are those defined above as $\mathbf{k_c}$, for continuous, completely mixed reactors. An immediate and disappointing observation from Table 5 is that reactivities are, generally, at least an order of magnitude lower than those indicated by TGA tests. As discussed at the end of the preceding section, however, it is apparent that the batch and continuous reactivities, k or k_0 and k_c, are simply not the same property, although clearly related. If one finds a need to design a hypothetical gasification plant on the basis of these data, the key process variable, also from Table 5, is the reactor capacity, $(lb/hr)/ft^3$, for the same degree of fixed carbon conversion. Finally, if one assumes that 95% conversion can be achieved by simply increasing residence time at the same rate of conversion, the "95% capacity" factor in Table 5 would define reactor size.

6.0 ANALYSIS AND DISCUSSION

6.1 Correlation of Reactivities

For the well-behaved runs summarized in Table 3-B, effective reactivities are correlated with temperature in Figure 6, with the pressures and steam/carbon ratios indicated for each point. Temperature is clearly the dominant variable, to which reactivity, k_c, is most sensitive, and shows a good correlation with the empirical function, mathematically an accelerated parabola, which closely resembles the form of plots relating TGA reactivities, k, to temperature. The constants in this equation were selected to give a visual good fit, and its mathematical form has no known theoretical significance. The single, previously defined "suspect" data point does, in fact, fall the farthest from the correlation. Variation with pressure or steam/carbon ratio, in terms of being above or below the correlation curve, is not consistent, indicating that experimental scatter is at least as great as the sensitivity of the reactivity to these variables.

Figure 7 is a plot of corresponding data from Table 3-A, for uncatalyzed coal in a limestone bed, upon which is superimposed the empirical correlation for K-catalyzed coal from Figure 6. In Figure 7, the single point for 600°C falls above the line for a more reactive, catalyzed reaction and

TABLE 5

Actual Catalyst Levels and Potassium Balance
Reactivity K = (dC/dt)C, C = Wt. FC in Reactor Bed, dC/dt = Rate of FC Conversion to Gas

A. Limestone Bed With Raw Coal (K and Fe from coal ash only)							
Run No. M-	216	217	218	220			
	700	600	700	700			
Temperature, °C	2.4	2.4	6.1	2.4			
Pressure, atm							
Reactivity, 1/hr	0.085	0.103	0.203	0.239			
Wt. KOH/Wt. FC	0.005	0.002	0.003	0.003			
FC Conversion	17.0	35.0	55.2	55.1			
% FC in Bed	24.5	44.3	35.4	30.1			
Capacity[1]	0.9	1.7	2.8	2.7			
95% Capacity	0.2	0.6	1.6	1.6			
B. Limestone Bed with K-Impregnated Coal							
Run No. M-	221	222	223	224	225	226	227
	700	600	700	700	650	650	600
Temperature, °C	2.4	2.4	2.4	6.1	2.4	2.4	2.4
Pressure, atm							
Reactivity, 1/hr	0.491	0.053	0.358	0.420	0.210	0.137	0.082
Wt. KOH/Wt FC	0.165	0.119	0.254	0.319	0.241	0.189	0.153
FC Conversion	75.5	21.4	68.2	69.4	54.8	45.7	29.4
% FC in Bed	19.4	50.8	24.1	18.5	29.3	37.4	40.2
Capacity[1]	3.7	1.0	3.3	3.0	2.3	2.0	1.3
95% Capacity[2]	2.9	0.2	2.4	2.2	1.4	0.9	0.4
C. Taconite Bed with K-Impregnated Coal							
Run No. M-	228	229	230	231	233	234	
	600	700	600	700	650	650	
Temperature, °C	2.4	2.4	2.4	2.4	2.4	2.4	
Pressure, atm							
Reactivity, 1/hr	0.408	0.692	0.25	0.357	0.242	0.187	
Wt. KOH/Wt FC	0.181	0.388	0.183	0.218	0.179	0.169	
FC Conversion	62.9	80.8	57.1	71.6	58.6	50.1	
% FC in Bed	19.4	14.7	28.7	25.2	30.5	33.7	
Capacity[1]	3.0	3.9	2.7	3.4	2.8	2.4	
95% Capacity[2]	2.0	3.3	1.6	2.6	1.7	1.3	

[1] Capacity = (lb/hr) cu. ft.

[2] Projected capacity if residence time were increased to achieve 95% FC conversion at same reaction rate.

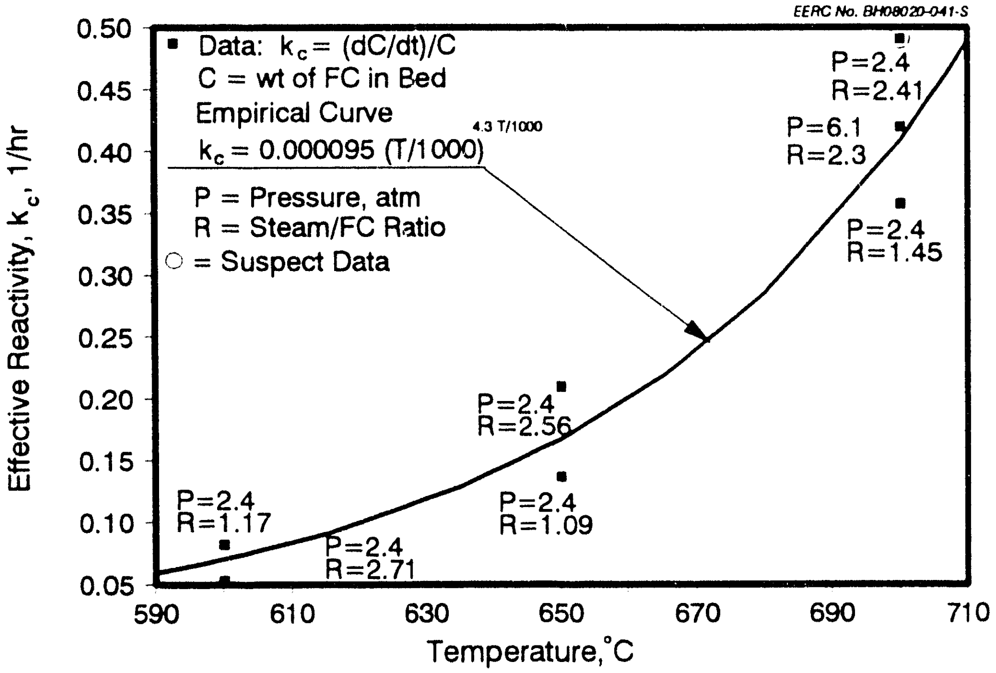

Figure 6. Effective reactivity of potassium-impregnated Wyodak Coal in a limestone bed, continuous process data.

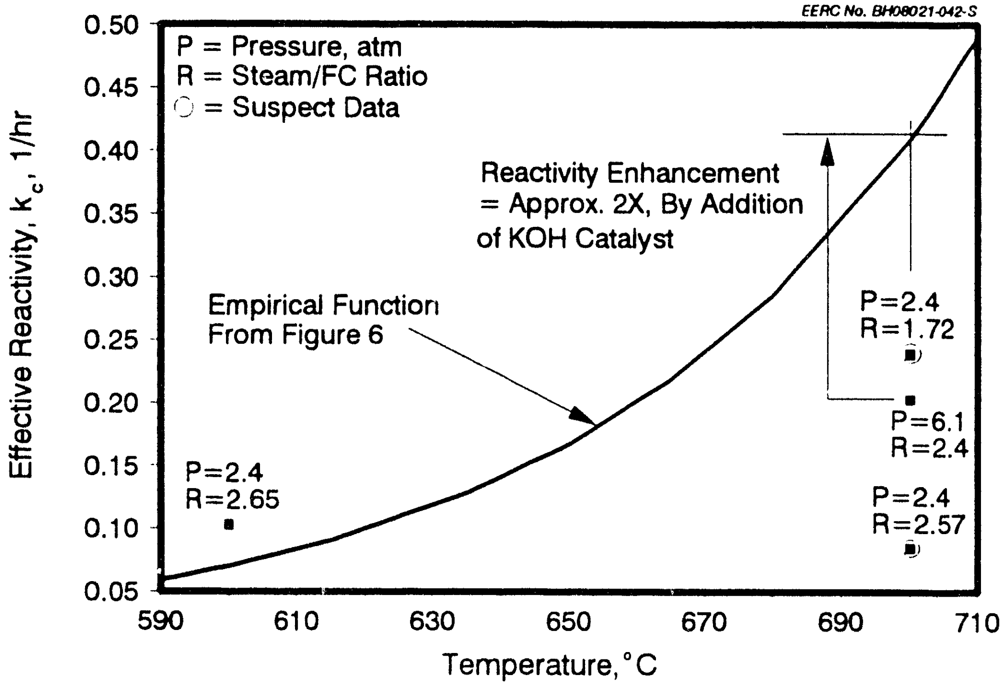

Figure 7. Effective reactivity of raw Wyodak coal in a limestone bed, continuous process data.

cannot be explained in light of accepted theory or past relevant data, even though the data set was not identified as "flawed" in Table 4. Taking the middle, nonsuspect point at 700°C as a valid average, the potassium impregnation apparently doubles reactivity, k_c. This is significantly less than the increases in k, indicated in Table 1 for TGA data, but still of substantial practical value if it could double the throughout per capital investment for a real-world gasifier.

Figure 8 is a similar comparison of the taconite bed data from Table 3-C with the empirical correlation from Figure 6. It thus compares the effects of taconite and limestone beds on K-impregnated coal. Although the experimental scatter is wider than for the limestone bed case, it is surprising that five of the six points fall well above the limestone correlation. Based on all known background experience and theory, there is no reason to believe that a valid $k_c(T)$ function would have a dip in it around some intermediate temperature. Therefore, either the 600°C or the 650°C points can be disregarded. It is of interest that the latter were the last two data sets, taken at the end of the second, week-long operating period, which suggests the possibility of some unidentified, systematic operator error, even though the data cannot be identified as "flawed."

What is very encouraging about the data of Figure 8 is that taconite, while of little catalytic value alone, appears at least as desirable as limestone as a bed material for K-catalyzed gasification. There is no explanation why it should actually be better than limestone, in terms of catalytic activity, although that might be inferred from Figure 8. No bed attrition measurements were done in these tests, although some might be inferred from the relative calcium and iron contents of the bed and cyclone

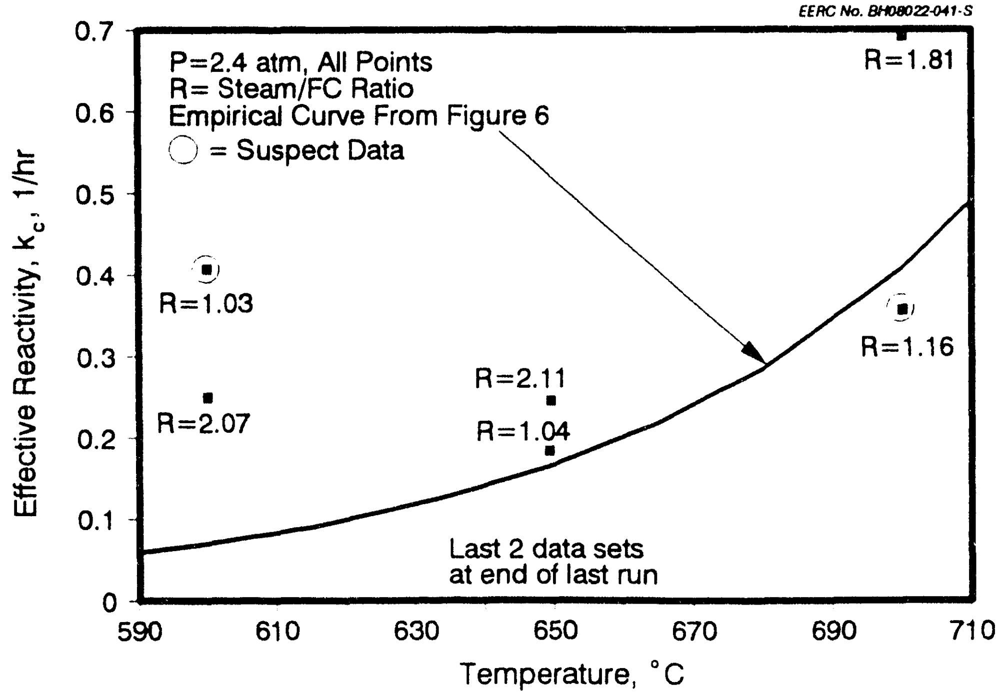

Figure 8. Effective reactivity of potassium-impregnated Wyodak coal in a taconite bed, continuous process data.

ash analyses. Since taconite is substantially harder than limestone, it will probably offer the economic advantage of lower bed makeup costs than for limestone, depending upon source proximity.

As a major but unexpected source of uncertainty in effective reactivities, Figure 9 plots the variation in actual potassium to fixed carbon (K^+/FC) from bed overflow analyses for each of the runs, compared with analyses of the blended feed. The run sequence of the three lines is that of Figures 3-A, B, and C, where the corresponding run parameters can be seen. The original target for feed preparation was the "saturation" line, which is the K/FC weight ratio corresponding to a K/FC molar ratio of 0.12, beyond which, it is believed, further addition of the catalyst results in no further increase in reactivity. This is based on TGA data for an Illinois No. 6 bituminous coal (higher rank) and for wood ("rank" = 0), suggesting that all possible active sites ($-COO^-$, $-CO^-$, and $-C^-$) are saturated with K^+ ions. The fact that the same number results for both cases may be a coincidence; although in the absence of a comparably filled-in k vs. K^+/FC profile of TGA data for Wyodak coal, a 0.12 molar saturation level was assumed here. In spite of care in blending the coal, bed material, and KOH solution, Figure 9 suggests that much of the KOH failed to ion exchange with the coal structure, resulting in loss of catalytic effectiveness. The very low ratio for the single analysis of blended feed for the taconite runs, shown in Figure 9, suggests that segregation even took place during drying, handling, and filling the pressurized feed hopper.

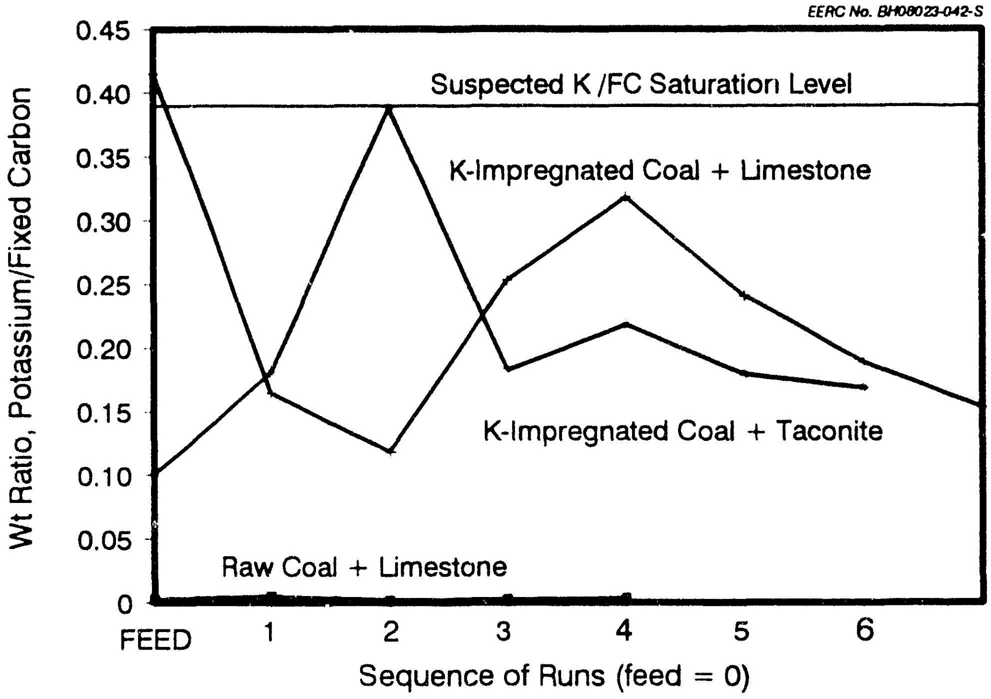

Figure 9. Actual K/FC in reactor bed.

Returning to Figure 8, it is of interest that the extremely high reactivity point at 700°C is for the second run in the taconite series, which was the only one for which the K/FC ratio was at the saturation level and over twice that for any other run. This alone could account for the single high reactivity point. It is also of interest that, through most of the taconite series, the K/FC level was actually below most of the runs in the limestone series, which makes the catalytic performance of the taconite still more impressive. The low and variable K/FC levels in the bed overflow suggest that significant amounts of the KOH are in the form of free dust and are carried out of the bed prematurely.

Material balances on potassium, as well as on calcium, sodium, and iron, showed very poor closure, which is typical of ash components due to the complexity of oxidation-reduction reactions that occur in the range of conditions in the reaction zone. In XRFA (x-ray fluorescence analyses) of dominant ash components, the nonnormalized data for both the bed overflow and cyclone samples show closures ranging from 55% to 105%, with an average in the mid-80s, with the higher numbers, >100%, occurring mostly in the taconite runs. Standard procedure in these analyses is to normalize raw data, so that percentages of oxides of elements of interest (Al, Si, Fe, Ca, Mg, Na, K, P, Ti, and S) add up to 100%.

Notwithstanding the uncertainty in potassium analyses, an attempt to track the potassium through the process and close a material balance led to an unexplained but clearly significant observation, summarized in Table 6. Analyses of the content of cyclone ash and bed overflow samples, in Tables 3-A, B, and C, and original XRFA data on each, as shown in the examples of Appendix B, all indicate no significant difference in the two streams' composition. Table 6 indicates quite consistent weight distributions of potassium between the two products, the cyclone cut being of finer particle size and carried over with the product gas. As an attempted material balance for potassium, the sum of these product amounts is expressed as a percentage

TABLE 6

Potassium Balances

Bed Material	Limestone	Limestone	Taconite
Catalyst	None[1]	KOH	KOH
Number of Data Sets	3[2]	7	6
% of Ash K_2O in Bed[3]	88.1	86.6	89.3
% of Input K_2O Accounted for[4]	69.3	34.2	119.8
% Variation in Above Averages, ±	6	8	13

[1] Only potassium present is small amount (See Figure 9) found in coal's ash, initially combined in unknown mineral species.

[2] One of "suspect" data points (Run M-217) was extremely inconsistent and excluded from average. It is the only data point not included in Table 6.

[3] Based on XRFA analyses to determine the weights of K_2O in bed overflow and in cyclone ash, with total = 100%

[4] Based on input weight of K_2O in feed coal-bed-catalyst ash component, per Table 2, by XRFA.

of the total input potassium, also expressed/assumed as K_2O, as indicated by XRFA analyses. The poor closure is generally attributed to the potassium, as the coal is consumed, reacting with the remaining limestone or taconite, forming mineral species far more complex than the initial KOH. While the extreme variation, from a theoretical 100%, of percentages of presumed K_2O in the feed cannot be explained within the scope of this project, they are strikingly different and extremely consistent within each bed-catalyst category, as indicated by the bottom row of Table 6. Thus the variation in potassium balance closure suggests that potassium, in a high-temperature reducing environment, enters into complex and quite different inorganic reactions with the limestone and taconite.

As to coal feed preparation, all the potassium was impregnated onto the coal from solution before the coal was mixed with limestone or taconite, so that variation in potassium actually present in the reactor bed, as tracked in Figure 9, was earlier assumed to be a result of errors or randomness in impregnation procedure. It has also been assumed that the standard XRFA is consistent and accurate in identifying the key inorganic elements, expressed as equivalent weights of oxides. In the light of Table 6, there now appears some doubt as to whether XRFA identifies all of the potassium present. This, if possible, in turn suggests the possibility that during the taconite runs some significant amount of potassium, undetected by XRFA, may have, in fact, been present, contributing to the high reactivity. The wide but consistent difference in K-balance closures between limestone and potassium could also imply that much of the potassium in the limestone bed may be tied up in some XRFA-invisible form, such as amorphous compounds. Another possibility is that some elemental potassium, produced in the reducing atmosphere, may simply vaporize, to be condensed with the water, which was not analyzed in these tests.

Early in the past year of this project, tentative plans were made to consider the use of a potassium-impregnated taconite bed material on the 40-lb/hr PDU scale, based on preliminary TGA tests. This would have required an auxiliary, high-temperature process to prepare the sintered potassium-taconite catalyst material. These plans were canceled, however, as the project scope became limited by time and funds available. It was also decided that, in the interest of process economics, bed materials would be limited to cheap, disposable materials, such as the limestone and (site-specific) taconite. It would now appear that long-term development should not rule out synthetic, recoverable bed-catalyst materials. While near-complete recovery of potassium is clearly essential to economic viability (2), studies on external bed regeneration or recovery must be justified by estimates of their process costs as a trade-off against replacement costs. The only leaching studies at the EERC to date (2) have dealt with the extraction of potassium from mixtures of gasifier coal ash and wood ash. The possibility of stable potassium-iron compounds, intentional or inherent, may complicate the recovery problem. It is worth noting that a successful pressurized, fluidized-bed gasification program, by the Institute of Gas Technology (10) has used durable ceramic spheres as a bed material, essentially eliminating bed replacement costs. This suggests that such spheres could be made of some methane-catalyzing, taconite-derived substrate that might hold saturation levels of potassium in some catalytically useful form.

The above discussion and Table 6 clearly raise more questions than they answer. However, the following conclusions and recommendations can be supported:

1. The chemical form and probably the mobility of potassium in the reactor bed is dependent upon its interactions with the bed material, which, though still unknown, are very different for limestone, taconite, and coal ash.
2. Standard analytic means of tracking the potassium through this process are now suspect, requiring review or new procedures development.
3. EERC has extensive experience in sophisticated studies of mineral transformations during combustion. Any future work in catalytic gasification should include application of some of these more rigorous methods of tracking potassium or other catalysts through the process.
4. As longer-term research, more sophisticated, synthetic bed materials, such as potassium-impregnated, iron-ceramic spheres, should be investigated, at least by bench-scale tests.

Returning to the above discussion of the possibility of labile or free floating potassium, probably as K_2O or KOH, in the reactor bed, there is a more sinister possibility of it causing agglomeration and some loss of fluidization, since the melting point of anhydrous KOH is only 360°C. While there was no firm evidence of bed plugging during the runs reported here, even minor, intermittent agglomeration could result in incomplete fluidization and channeling, which in turn would introduce random variation in the residence time and thus the reaction rates. In a slightly earlier, parallel project (3), similar tests were done using wood in place of coal, catalyzed by massive admixture of recycled ash. Even in the best of cases, wood is difficult to fluidize. With the ash addition, the bed frequently became plugged, exhibiting massive clinkers when shut down. It should be kept in mind, at this point, that if a fluidized-bed reactor has any possible reason for plugging or channeling, the probability of it happening increases sharply with decreasing bed diameter.

These wood gasification tests made a major contribution to this project, leading to the decision to make these final coal tests with impregnated (homogeneous) catalyst impregnation, rather than simply cofeeding dry (heterogeneous) KOH catalyst. This is also consistent with earlier experience in the EERC 40-lb/hr PDU (4), in which sodium-bearing trona and nahcolite catalysts were cofed with Wyodak coal, resulting in bed plugging by quite large agglomerates.

One of the "loose ends" of this project is the knowledge that, according to TGA data, sodium is as good a catalyst as potassium and would be far cheaper. However, no continuous tests have been done with homogeneous sodium catalyst, impregnated from solution, as was done in these tests with potassium, to determine whether the agglomeration problem can thus be avoided. Similarly, the EERC has done no continuous PDU tests with heterogeneous (cofed) potassium-bearing catalysts, for comparison with the earlier trona and nahcolite tests. Qualitative observation of material remaining after TGA tests indicates that the tendency of bituminous coals to agglomerate was apparently significantly reduced by adhesion of K_2CO_3 presumably reduced to K_2O. The definitive work by Exxon (8) at least reports no agglomeration problem using K_2CO_3, while personnel at IGT (10), gasifying wood and coal in a pressurized fluidized bed similar in concept to the EERC PDU, report verbally that some agglomeration was observed using potassium salts, consistent with EERC's experience with wood (4).

An interesting correlation of reactivity data is shown in Figure 10. Here the effective reactivity, k_c, defined as lb/hr of fixed carbon consumed per lb of fixed carbon in the bed, is plotted against the percentage of fixed carbon in the bed. A significant uncertainty in computing k_c is estimating the FC weight in the bed, which is a function of particle density and void fraction, neither of which can be observed directly under reaction conditions. In Figure 10, for design purposes, k_c, determined from a plot such as Figures 6, 7, or 8, is actually the independent variable, while the %FC will reach some equilibrium defined by the empirical correlation shown in Figure 10. It is of interest that, at this point, temperature, pressure, steam/carbon ratio, and catalyst selection are essentially out of the way as design variables. For this reason, no legend is given to identify the three kinds of symbols, corresponding to the data sets of Tables 3-A, B, and C.

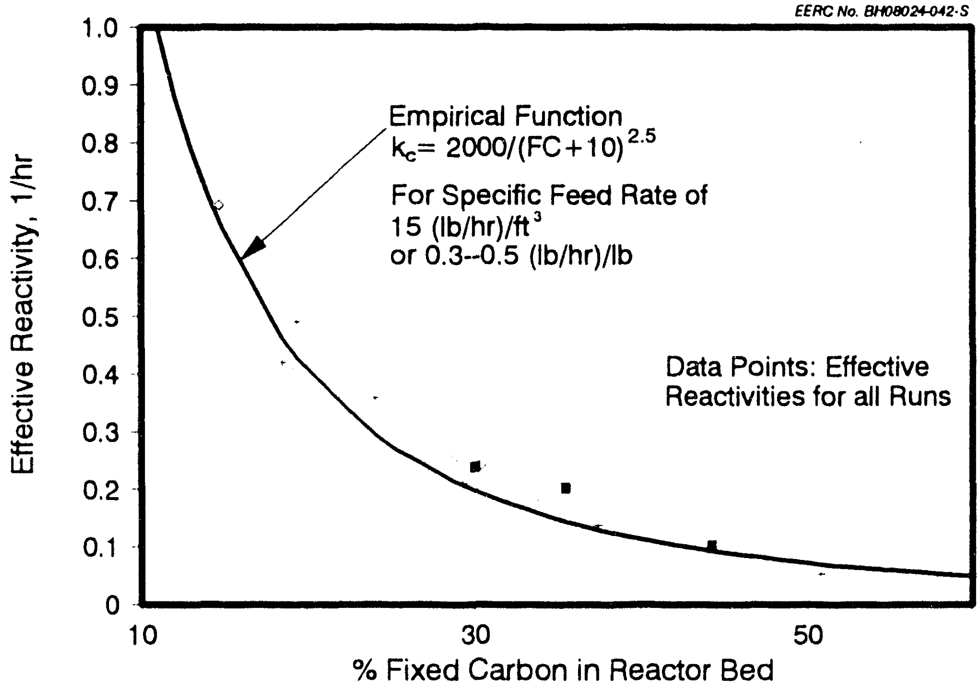

Figure 10. Effective reactivity vs. % fixed carbon in reactor bed, composite for all runs.

Finally, instead of the reactivity, the more directly applicable design parameter, specific capacity, SC, defined as lb/hr of FC consumed per reactor volume, is also plotted against %FC in Figure 11. The reactivity correlation from Figure 10 is added for comparison. This simple, straight line function, SC = f(%FC) says, in effect, that when changing any operating conditions, feed, or catalyst to enhance reactivity or specific capacity, the equilibrium %FC in the fuel bed will reach an equilibrium given by the line of Figure 11. It must be emphasized that Specific Capacity is a feed-catalyst-bed-condition material property. Changing the feed rate or the bed volume, limited by the overflow level, will require computing a new SC, which is simply the rate of FC consumption by a new reactor volume. This was done in Table 5 for an assumption of 95% complete FC consumption, resulting in far lower SC values. Also of interest in Figure 11 is that SC and k_c are obviously related, but not in linear proportion.

6.2 Supporting TGA Data

The theoretical discussion of Section 4 is based on an assumption that the fixed carbon fraction of a coal has a certain reactivity that is constant even as it is depleted to very low levels. This presumes that the reactivity of even a low, but constant, level of fixed carbon in a fluidized-bed gasifier has the same TGA-determined reactivity that it did when fed, even though the rate of reaction, -dC/dt, is greatly reduced. This raises a question of whether a coal's reactivity actually reflects a composite of various different chemical structures, such as the different macerals, that may individually

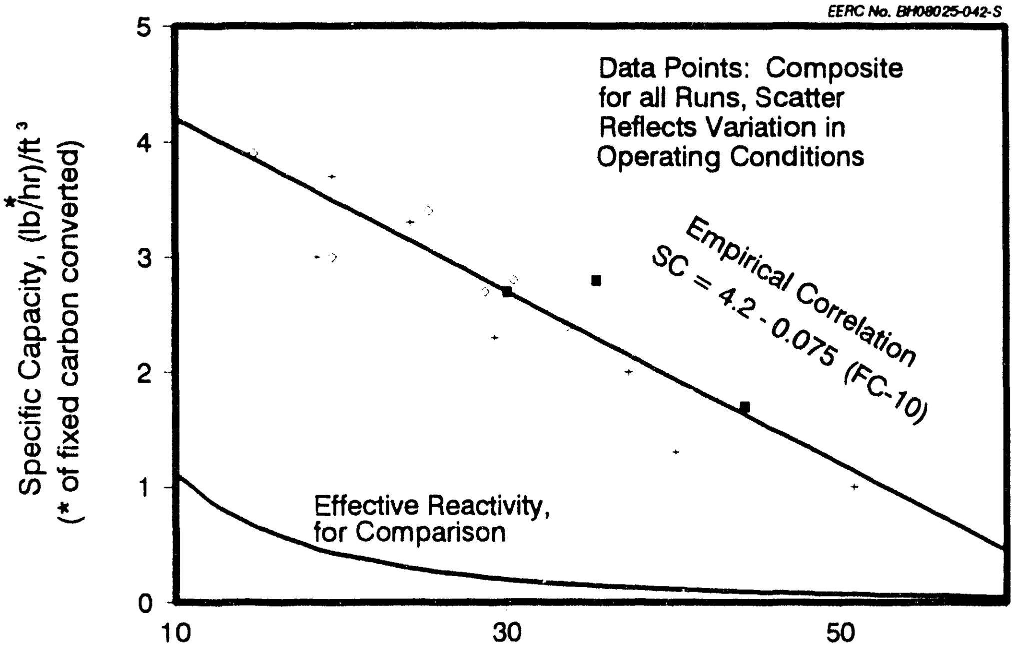

Figure 11. Fixed carbon conversion (specific capacity) vs. fixed carbon content of reactor bed.

have different reactivities. To support the assumption that reactivity is in fact a constant and uniform property, retained samples of the blended feed for two of the runs reported here were submitted for TGA analyses, along with samples of the bed overflow material. These results are presented in Table 7. Comparing the TGA reactivities of feed with overflow product, for both feed mixtures, confirms that reactivity is, in fact, constant with time and with fixed carbon consumption.

The two runs checked by the TGA analyses of Table 7, though at different temperatures, were selected because both are non-"suspect" data points and are extremely close to the same empirical correlation line of Figures 6 and 8. (These are also the data sets presented in their entirety as Appendix B.) Also of interest is the reduction of reaction order in these samples. The taconite samples (feed and product) were noticeably less than first-order, while the more heavily catalyzed limestone samples appeared to be actually closer to zero order. In a zero-order reaction, the rate, $-dC/dt$, is essentially constant and independent of the amount of fixed carbon remaining. That is, the reaction will be faster at low levels of remaining fixed carbon. This is certainly desirable to reduce reactor size for a required throughput.

Table 7

Comparison of TGA Reactivities on Blended Feed and Residual Bed Material

Run Number	M-224	M-233
Bed Material	Limestone	Taconite
Catalyst and Coal	KOH-Impregnated Wyodak	KOH-Impregnated Wyodak
Temperature	700°C	650°C
% FC Consumed	69.43	58.63
% FC in Reactor Bed	24.1	30.46
CPU Reactivity, k_c, 1/hr	0.42	0.24
TGA Reactivity,[1] k, 1/hr		
Feed Material	3.97	3.31
Bed Overflow	3.79	3.34
Ratio, k/k_c		
Feed Material	9.45	13.79
Bed Overflow	9.02	13.91
TGA Reactivity,[2] k, 1/hr		
Reaction Order [2]	0	1-
Feed Material	2.93	2.45
Bed Overflow	2.35	2.89
Ratio, k/k_c		
Feed Material	6.98	10.20
Bed Overflow	5.52	12.04

[1] Assumed first-order reaction, per standard simplifying assumption. See Appendix A for definition and significance of reaction order.

[2] Calculated reaction order, also per normal TGA procedure.

Since no consistent rule to predict reaction order has been identified, the normal first-order assumption, which is the basis of all assumptions discussed above, provides a conservative estimate of reaction rates. To the extent that relative reactivities are used to compare or predict gasifier behavior, real-world reaction rates are more likely to be greater, than less, than predicted.

Figure 12 shows a correlation between the specific capacities, (lbFC/hr)/ft^3, and CPU-determined reactivities, 1/hr, for all of the K-impregnated coal runs. Superimposed on these data are two points correlating the TGA data on residual, in 1/hr, correlated with two corresponding values of k_c, in 1/hr. These two points do not have the same units as shown on the vertical axis of Figure 12, but are numerically consistent with the other points and, insofar as two points can define an empirical function, appear to vary in the same proportion.

6.3 Gas Yields and Compositions

Plots of the product gas composition and yield data of Figures 3-A, B, and C were generally disappointing. Variation with pressure, steam-carbon ratio, and bed or catalyst selection was less than the experimental scatter, which is attributed mainly to the uncertainty in gas flow measurements discussed earlier. When all data are averaged for each temperature point, the results show the variation with temperature shown in Figure 13, which is consistent with theory and expectations. Only with temperature was the variation greater enough (than the experimental scatter) to enable correlations with any statistical validity.

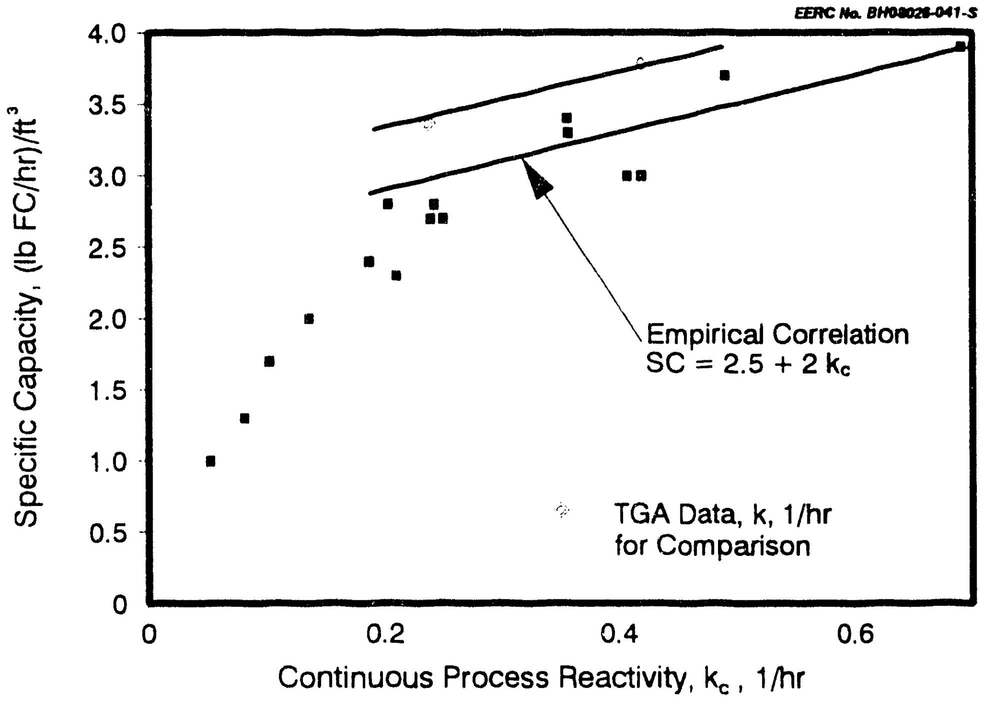

Figure 12. Comparison of reaction rate measurements.

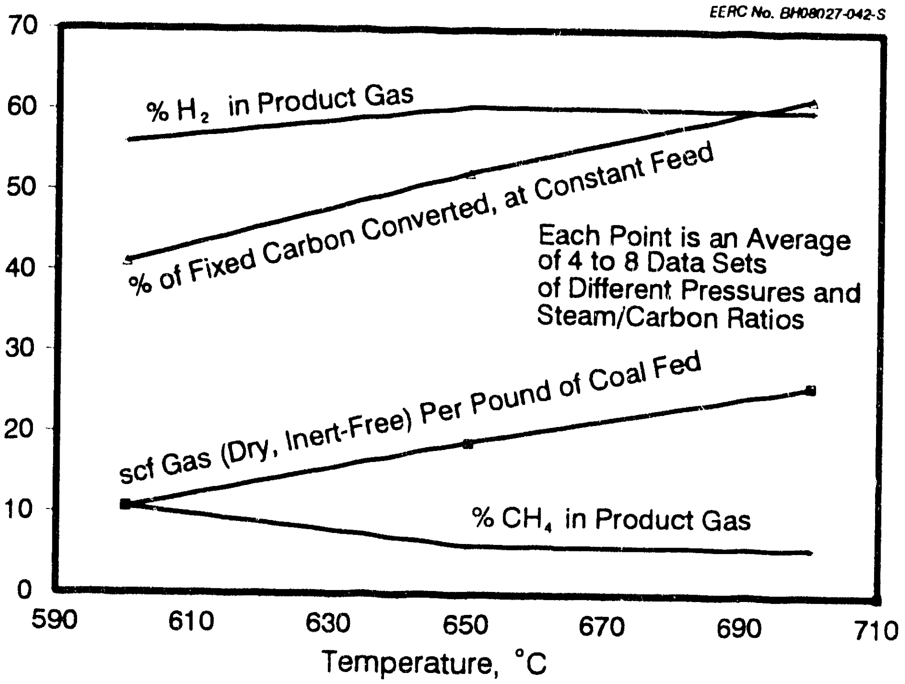

Figure 13. Average gas yield summary.

Plots to show whether the use of a taconite bed increased methane content of the product gas or methane yield per MAF or FC consumed showed no correlation. It is probable that longer tests at the same sets of conditions, such as 24 to 36 hours, with multiple material balance periods with multiple gas and solid samples taken during each period, would have yielded statistically valid data, such as the temperature correlations of Figure 13. This approach, though expensive, is under consideration for future tests in a parallel project using Illinois No. 6 bituminous coal.

It must be emphasized that for this report single data points were rejected as "flawed" or "suspect" only for reasons other than simply not falling close to a desired correlation curve. For a data base of too few points for valid statistical correlation, at any one set of conditions, arbitrary rejection of points would reduce correlations to creative experimental artifacts. (This is very analogous to an attorney's freedom to reject jurors "for cause" who appear unlikely to render a desired verdict.) The only exception in this case was Run M-217, with limestone bed and no KOH, at 600°C, which showed a methane yield simply far too high to be believable. This run also shows an unbelievably high yield, considering the lack of KOH catalyst, in Figure 7 and is excluded from the 600°C averages of Figure 13.

7.0 INTEGRATED BENCH-SCALE GASIFIER SHAKEDOWN DATA AND POTENTIAL

A newly developed research tool at EERC is the integrated bench-scale gasifier (IBG), in which a sample of 200 to 300 g of coal is injected into a preheated fluidized bed. After a selected reaction time, the entire bed is dumped and quenched, while all gas, condensible, and solid products are saved for analysis. This differs from the TGA in that the particle heatup rate in the IBG is essentially instantaneous, as when coal is fed into a fluidized-bed gasifier, so that devolatilization and the steam-char reactions start concurrently. This unit was initially conceived to enable production of samples of char and condensable liquid products big enough for analysis, far more cheaply than possible using the CPU. Unlike the TGA apparatus, the pressure rating of the IBG is 150 psig. The unit is also provided with a hot sampling probe immediately over the bed and optical windows to enable on-line studies of the hot gases by mass spectroscopy, atomic absorption/emission spectroscopy and FTIR (Fourier transform infrared) analysis.

During the brief test period, using a constant stream of preheated steam and nitrogen for fluidization, the carbon monoxide level in the product gas is measured continuously. Since the amount of CO, or any other product gas, is a fair measure of the rate of reaction, this easily observed variable becomes a reaction rate measurement, directly equivalent to the rate of weight change in TGA tests. For a recently completed shakedown test, a CO(t) plot is presented in Figure 14, along with analyses of it performed by a data reduction program. Also shown on the plot are the periods of opening and closing the feed and discharge valves, arranged as shown in the system sketch of Figure 15, and the point at which a gas sample is taken for analysis. Feed gas streams may include any mixture of gas, simulating different process concepts, and multiple product gas samples may be taken.

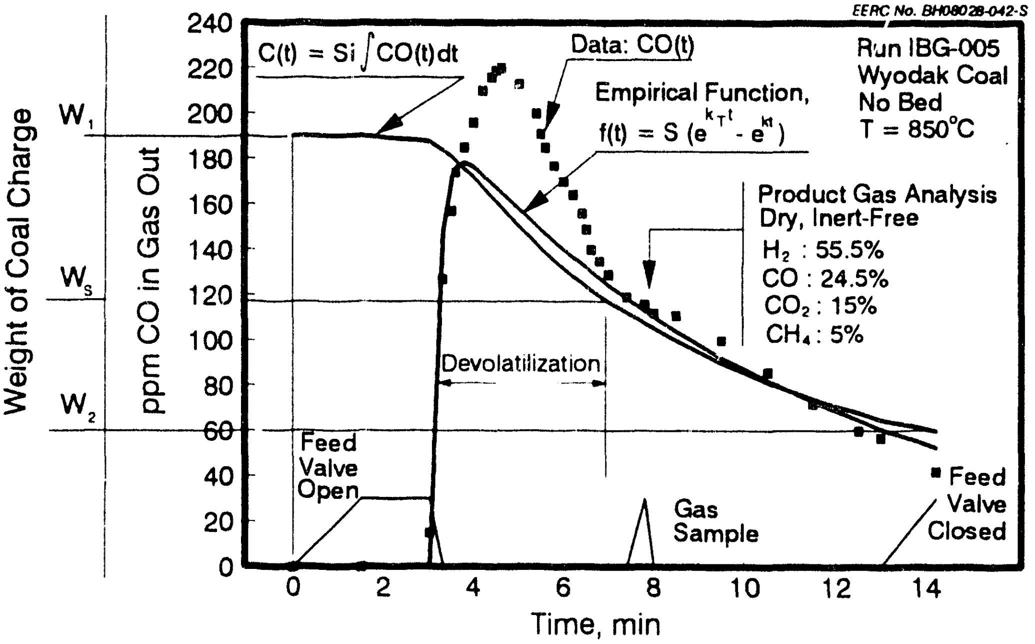

Figure 14. Typical IBG data sample.

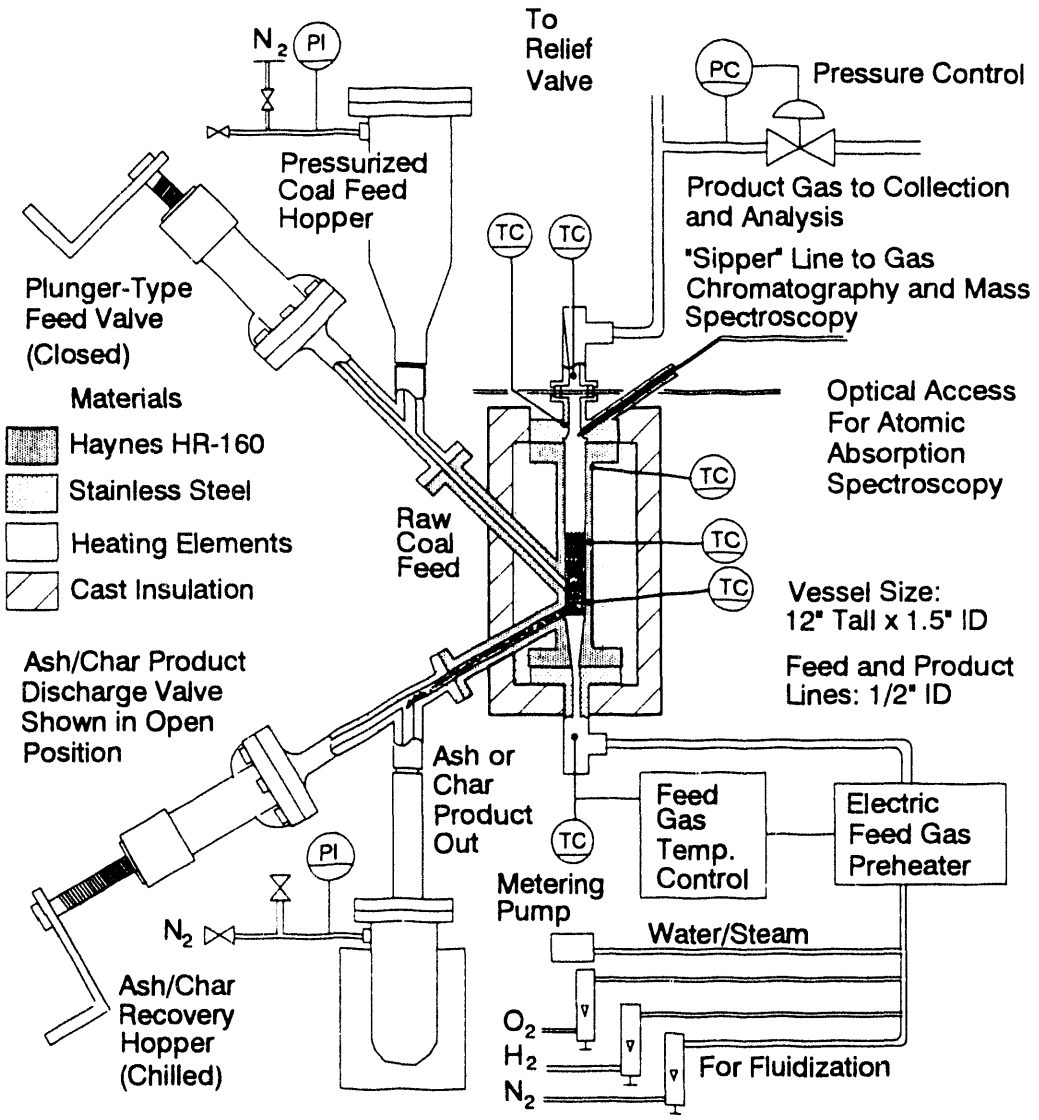

Figure 15. The EERC integrated bench-scale gasifier (IBG) schematic.

The most significant data treatment is the numerical integration shown in Figure 14, which defines a function proportional to the momentary weight of the decreasing amount of fixed carbon in the charge. With initial and final sample weights, and intermediate weights prorated according to the curve, reactivities can be calculated for direct confirmation of TGA data.

Another mathematical treatment of the data is the double exponential empirical function shown on Figure 14, in which reactivity, k, a much faster warmup rate constant, k_T, related to the heat-transfer behavior in the bed, and an overall scale factor, S, are juggled by trial and error to achieve a visual best fit to the portion of the curve representing the rate of the gasification reaction, as shown. Further sophistication could add automatic, iterative calculations to generate a least squares best fit for these functions. Since taking the derivative or integral of an exponential changes only the scale factor, the k in the empirical function is expected to show a good correlation with the corresponding reactivity computed from the weights and the empirical integral function. The initial hump, rising beyond the two computed functions, is believed to represent an additional CO release during devolatilization or pyrolysis. The empirical function can also be juggled to show a fair correlation with the devolatilization hump, which is of relatively little interest, but not with both sections of the curve. Gas samples taken around the devolatilization peak may indicate differences between pyrolysis gases and gasification products.

As of this writing, the IBG system is scheduled for near-future use as the major process projection tool in two related projects, both dealing with production of hydrogen and methane from bituminous coal for fuel cell applications. Another potential application for this unit is in the development of more advanced bed-catalyst combinations, such as a potassium-iron-ceramic bed material suggested in Section 6.1 above.

8.0 COMPARISON WITH 40-LB/HR PILOT-SCALE DATA

A preliminary report of the last series of runs was included in the previous semiannual project report (2). The objectives of this run series were to confirm operability and to generate baseline data for Wyodak coal with limestone alone, in preparation for later runs with impregnated KOH catalyst and limestone or taconite beds. Following the massive reconfiguration of the combined gasifier system during 1990, for hydrogen production, mild gasification, and pressurized fluid-bed combustion, this run series was intended to establish continuity with a series of Wyodak-limestone runs (4) completed in 1988. Unfortunately, the PDU was not in as operable a condition as expected, requiring four shakedown runs to identify problems and make somewhat costly modifications as needed, mainly with respect to instrumentation, hot-gas cleanup, gas quenching/scrubbing, and increased pressure ratings of associated piping. By the completion of the last run series of 1991, reported here, the project budget was partially depleted ahead of schedule, and a decision was made to complete testing in the much smaller-scale CPU system. A major goal of the system modifications was achieved, in that the PDU system was left in as-designed, operable condition, available for future gasification tests. Due to decisions beyond the scope of this project, however, the gasifier itself was subsequently dismantled, to make room for a planned transport reactor or fast circulating bed gasifier.

For comparison with the above CPU data, the essential data from these three PDU runs are summarized in Table 8-A and 8-B. The nominal 40-lb/hr PDU is a complete process simulation in that the required heat is supplied internally, by combustion of part of the coal feed. As expected, gas compositions are somewhat higher in CO_2 and correspondingly lower in other components, but represent a credible gas composition to assume for a commercial-scale design.

As configured for these runs, the gasifier had no bed overflow, so that bed level was determined by the feed and reaction rates and was observed as a temperature profile, indicated by in-bed thermocouples. The unit was provided with a vertical, top-entry bed sampling probe that became plugged and proved unworkable, so that bed samples were available only at the end of the third run, when the vessel was opened for cleaning, yielding the end-of-run bed analysis of Tables 8-A and 8-B. An element of uncertainty is created by how instantly the entire bed is effectively quenched at shutdown. The effective intervals between sequentially turning off coal feed, oxygen, and steam and turning on a quench stream of nitrogen are limited by computer-operator response times and the thermal inertia of the system. Consequently, the carbon content of the single bed sample is probably somewhat lower than was typical during operation.

Throughout this report, reactivities and specific capacities have been computed as (dC/dt)/C, defining C as fixed carbon (FC), as determined by a standard proximate analysis, to be consistent with definitions established by TGA tests. In the earlier phase of this project, reactivities were based on total carbon, as determined by a standard ultimate analysis, as was also done by Exxon (8) in what is considered the definitive early work on potassium-catalyzed coal gasification. For this report, however, the FC-based definition was used because it is the reaction of steam with char, as measured by TGA, that determines overall reaction rates. Much of the total carbon is

Table 8-A

Data Summary for 40-lb/hr PDU Tests

Objectives 1. Confirm operability 2. Baseline data

Feed	Wyodak Subbituminous
Fluidized Bed	Limestone: 35 lb
Catalyst	None (Intrinsic)
Run Duration	44 hours
Each Material Balance	2 hours
Btu/lb	
As received 8,945	
Dry 11,060	

	Feed	Bed[1]
Feed Proximate Analysis, wt%		
Moisture	19.10	
Volatiles	37.30	
Fixed Carbon (FC)	38.50	
Ash	5.10	
Ultimate Analysis, wt%		
Hydrogen	6.1	0.60
Carbon	52.88	5.40
Nitrogen	0.65	0.10
Sulfur	0.51	0.20
Oxygen	34.73	0.00
Ash	5.11	93.70

[1] At end of Run -3, indicating 90%+ carbon depletion.

Table 8-B

Data Summary for 40-lb/hr PDU Tests

Run No. H_2-91-5	-1	-2	-3
Temperature, °C	754	702	652
°F	1390	1296	1205
Pressure, atm	1.1	1.2	1.2
Coal Feed, lb/hr	25.5	17.0	17.0
Oxygen, lb/hr	16.0	12.7	10.2
Steam, lb/hr	27.2	26.9	27.7
Steam/FC, Mol/Mol	1.8	2.7	2.8
Product Gas,* lb/hr	29.1	31.9	29.3
scfh	498	53[illegible]	495
Analysis, Mol% H_2	42.0	42.5	44.7
(Dry, N_2-free), CO	16.5	12.0	9.1
CO_2	37.4	41.6	43.0
CH_4	3.0	2.8	2.6
H_2S	0.1	0.1	0.1
C^+	1.0	0.9	0.5
Cyclone Fines, lb/hr	2.63	3.80	4.10
Hydrogen %	1.08	1.68	1.90
Carbon %	54.20	69.31	70.00
Nitrogen %	0.70	0.98	0.86
Sulfur %	0.96	0.33	0.42
Oxygen %	1.08	7.10	7.04
Ash %	41.96	20.60	19.78
Gas/MAF Fed, scf/lb	25.79	41.33	38.43
Gas/FC Fed, scf/lb	50.77	81.38	75.67
Gas/C Fed, scf/lb	36.96	59.25	55.09
Gas/C Converted, scf/lb	41.33	83.80	80.93
H_2/C Converted, scf/lb	8.12	5.48	5.75
CH_4/C Converted, scf/lb	1.26	2.38	2.12
Carbon Converted, scf/lb	89.4	70.7	68.1
Min.[1] specific capacity			
(lb FC/hr)/ft^3	8.88	4.68	4.51
(lb c/hr)/ft^3	14.19	9.46	9.46

[1] Assuming maximum bed depth of 4 ft (at ID = 6.5")

included in volatile components, which break down to form product gas by other reactions which are substantially faster, as described in Appendix A. In short, the overall gas production rate is determined by that portion of the carbon that reacts relatively slowly with steam.

The bed was not drained between runs. Due to an operational oversight, the residual bed material at shutdown was not weighed. Consequently, no calculation of reactivity based on weight of carbon, fixed or total, in the bed was possible. From a design point of view, specific capacity is more directly useful. As another oversight, no proximate analyses were ordered for the end-of-run bed sample. It can be reconstructed from the ultimate analysis, however. Going back to the CPU product char analyses for all the runs of Tables 3-A and 3-B, it was found that the ratio of FC(prox.)/C(Ult.) is a remarkably constant 0.7, with a random variation of less than 10%. Therefore, the amount of total carbon leaving the PDU in cyclone ash was multiplied by 0.7 and subtracted from the fixed carbon to determine an approximate carbon consumption rate. With the fluidized-bed depth of four feet, observed in the form of a temperature profile, the effective capacities, in (lb FC/hr)/ft^3 at the bottom of Tables 8-A and 8-B, were determined. Also reported for comparison is the specific capacity in terms of total carbon per hour per bed volume.

For comparison with CPU results, for the limestone and limestone+KOH cases, effective reactivities are plotted in Figure 16. The lines added to Figure 16 are again an accelerated parabola correlation, similar to that defined in Figure 6, at two different 580°C intercepts. Although the number of points is few and the experimental scatter great, it appears that the PDU specific capacity (SC) for Wyodak coal with limestone, at about 70% carbon conversion, is roughly 2.5 times that derived from the CPU data, at 55% carbon conversion. _If_ the CPU SC figures were increased by 70/55, reflecting a longer residence time for more complete reaction, this disparity would be reduced, but far from eliminated. _If_ the volumetric reaction rate is assumed proportional to pressure, and the PDU SC increased by 2.4/1.2, reflecting the operating pressures in atmospheres from Table 3-A and Table 8, this disparity will be increased further.

In conclusion, the PDU tests were successful in demonstrating operability of the recently modified system and indicate performance generally comparable to that reported in the earlier phase of this project. Unfortunately, broader EERC priorities required dismantling the reactor vessel to make room for the expected transport reactor, thus precluding the possibility of proposing any near-term follow-on efforts in this area. Because the PDU is a more complete process simulation, its specific capacity data inspire greater confidence than the CPU results, in spite of operational difficulties in the brief run series reported here. The use of CPU data is thus recommended as a lower-cost basis for preliminary process design because it is clearly conservative with respect to reactor capacities. Overall conclusions are summarized in Section 1.

9.0 PROJECT EVALUATION AND RECOMMENDED FUTURE EFFORTS

9.1 Evaluationn

In regard to the project goals, restated in Section 3.1, The data reported here and in previous reports establish that potassium-impregnated coal shows a substantially higher reactivity in a fluidized bed of limestone or taconite, while limestone alone is established at least as a fair catalyst, with the advantage of being disposable. "Loose ends" worthy of interest include the unexplained, but apparently beneficial, interaction between KOH and taconite, plus the possibility that sodium may be a cheaper alternative to

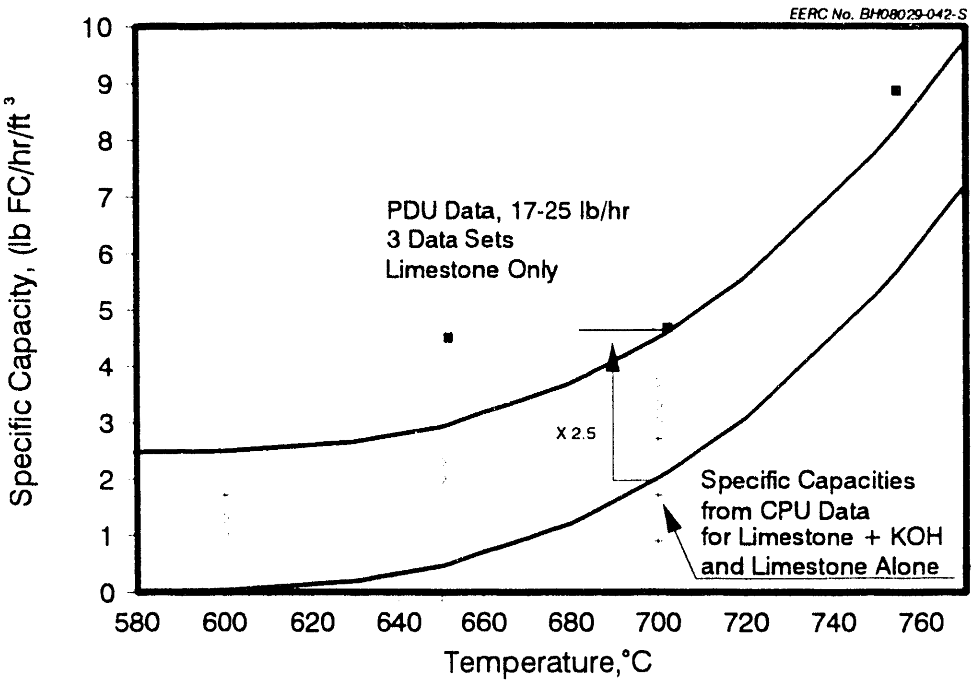

Figure 16. Specific capacity, PDU data.

potassium, depending on how it is applied to the coal during gasification, that is, homogeneously (impregnated) or heterogeneously. In general, identification of chemically desirable or optimal catalysts has not resolved the mechanical distribution or bed management aspects of applying them to the coal during reaction.

The project as a whole has proven to be a bit overscoped, with too many digressions and ramifications for the budget in the final two years of effort. The objective of extending catalyst optimization to the production of liquid and char products never moved much beyond the planning stage, since they were not directly related to hydrogen production, nor to the more pressing need to develop continuous catalytic gasification data. The design and construction of the IBG were originally intended for this application, however.

Some theoretical effort was expended on kinetic modeling and yield prediction, but never proceeded beyond a simple equilibrium model. This study, requiring no laboratory efforts, is still "on hold" and will be pursued under subsequent Cooperative Agreement efforts. This will include obtaining the best nonproprietary computer modeling software and adding provisions for including the effects of catalysis.

The possibility of in-bed sulfur capture was one of the motivations in selection of taconite as a bed material. However, because of the low sulfur content of the Wyodak coal, selected under EERC's mission to concentrate on low-rank coals, sulfur levels in ash and gas were too low to yield significant conclusions, within the range of experimental scatter. At present, the EERC has firm commitments, starting in the imminent projects for the new fiscal year, to continue efforts to control the effects of sulfur and other undesirable trace elements, using both the IBG and CPU hardware.

9.2 Possible Follow-On Efforts

Starting on the smallest physical and economic scales, several of the pending questions or "loose ends" described above appear worthy of further effort. Primarily, the question of how potassium, and possibly sodium, should best be impregnated upon the feed coal and what kinds of complexes they may form on limestone or taconite bed material during reaction can be explored on a small scale. The IBG unit may prove quite valuable as a screening tool for this type of study.

It is expected, however, that further CPU runs would be needed, primarily to achieve long-term equilibrium with regard to mineral transformation reactions. This would best be accomplished by relatively long CPU runs, perhaps of a whole week, at each of a very few sets of conditions, with multiple replication of material balances and sample analyses. This would also provide statistical confirmation of the relative rating of the three bed + catalyst systems studied here. Such runs should be at the highest pressures possible to explore the probable enhancement of methane production, as a desired component in gas feeds to advanced fuel cells. It is of interest here that the EERC is presently committed to remodeling the CPU system, over the next two years, to operate at substantially higher pressures.

As originally stated, all the original objectives of this project had to do solely with the chemistry of catalytic gasification for hydrogen and methane production. As a valid generality, most of the loose ends discussed herein deal with mechanical aspects of continuous processes, such as bed distribution and agglomeration, all of which are exacerbated in minimum-scale continuous testing. There is thus a need for larger scale, at least 100-lb/hr, process demonstration tests to identify and solve these mechanical design problems. The PDU operations described here, and in earlier project reports (4), were too brief and attempted to cover too broad an experimental matrix to truly qualify as a process demonstration.

EERC has on hand all of the components of a 30,000 scfh, slagging, fixed-bed gasifier system that achieved successful operation in 1982 (11, 12). The vessel, which is certified for about 550 psig and equipped with a generous profusion of large nozzles, was last used with a 29-inch inside diameter, with 6 inches of refractory lining. This vessel could easily be reassembled and modified for an impressive variety of different fluidized-bed designs. Based on the last inside diameter, such a PDU would offer roughly twenty times the capacity of the PDU runs reported above, or 500 lb/hr of Wyodak coal feed, at 750°C, producing nearly 10,000 scfh of gas, at near atmospheric pressure, or much higher rates at higher pressures. In its 1979-1983 project period (11, 12), it was operated at pressures up to 300 psig. Most of the components are still present and recoverable. The major new component needed would be a screw feed system, in turn fed from lock hoppers, to convert it into a bottom fed, fluidized-bed system. The size of such a unit would provide a very realistic, integrated demonstration project, which could include a next-generation, state-of-the-art hot-gas cleanup system and an advanced molten carbonate fuel cell by Energy Research Corporation, or possibly multiple fuel cells by different manufacturers. It would also allow considerable latitude in the design and redesign of internals to optimize bed behavior. Such a demonstration system, to be justified, would have to be financed for semicontinuous operation for several years, with its own operating staff and no priorities or agendas overlapping those of other EERC projects.

The reassembly and shakedown operation of such a system can be accomplished at substantially reduced cost by the use of existing hardware, although construction and shakedown operation costs will still be on the order of several million. In view of the reconfirmed certainty, described above and in various parallel works (7-9), that enhanced reaction rates by potassium plus limestone and probably taconite is desirable, a demonstration project would be the logical next step to commercialization.

Finally, in view of the cost of the recommended expanded-scale efforts, a careful review of all "available" fluid-bed gasification technology should consider that current state of the art is now defined to point where a demonstration project is justified. In short, the question is whether further pilot-scale efforts to merely determine that fluidized-bed gasification works are justified, unless some truly novel mechanical design needs a proof-of-concept demonstration. PDU-scale, or smaller, studies of process chemistry are clouded by mechanical design issues, as indicated in this report, that may not be clearly resolved on this scale, may not be relevant in a commercial-scale system, or may require quite different design solutions on a larger scale.

The recommended demonstration plant would be a complete gasifier system, based on the most convincing available reactor designs, integrated with a utility plant, which could provide coal preparation, process steam, cooling water, ash disposal, and other off-site and auxiliary functions at the utility's internal, variable cost, thus greatly reducing the capital and operating costs required for a completely autonomous pilot project. The product gas, following cleanup steps, could be consumed by on-site, or near-site, fuel cells, as an integrated demonstration. Or, as a minimal effort, the hot, uncleaned product gas could be fed to the utility's boilers at a cost per Btu equal to the raw coal, thereby recouping at least part of the subsidized cost of the demonstration project. If the selected demonstration site should have a cyclone-type boiler, the gasifier's product could be used in the reburn mode, introduced downstream of the very hot cyclone burner, to reduce NO_x formation (13, 14). Normally, natural gas is used for this purpose, thus setting a substantially higher value on the gasifier's product.

With such a demonstration plant once in continuous operation, using raw coal in a limestone bed as the simplest and cheapest process option, it would provide a site at which other process options could be tested at relatively little additional cost. For example, substituting taconite for limestone for a few weeks of operation would entail little more than some differential transportation cost. Potassium-impregnation of a week's supply of coal would require some additional feed preparation equipment that would be substantially cheaper than building a separate gasifier PDU.

The scale of such a demonstration project, while limited by the funding level available, should also be influenced by the possibility of its being economically self-sufficient in operating costs. To project such scale-dependent costs, it is essential to determine whether such a major step toward commercialization should be undertaken, rather than to build a bigger PDU. Clearly, the demonstration program will serve a wider range of technical and political objectives than further exploration of process chemistry by PDU efforts. Economic bases for such a determination can probably be established by one or two man-years of feasibility study, focused on selected utility plant sites.

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FORM EIA-459E
(10/80)

U.S. DEPARTMENT OF ENERGY

FEDERAL ASSISTANCE MANAGEMENT SUMMARY REPORT

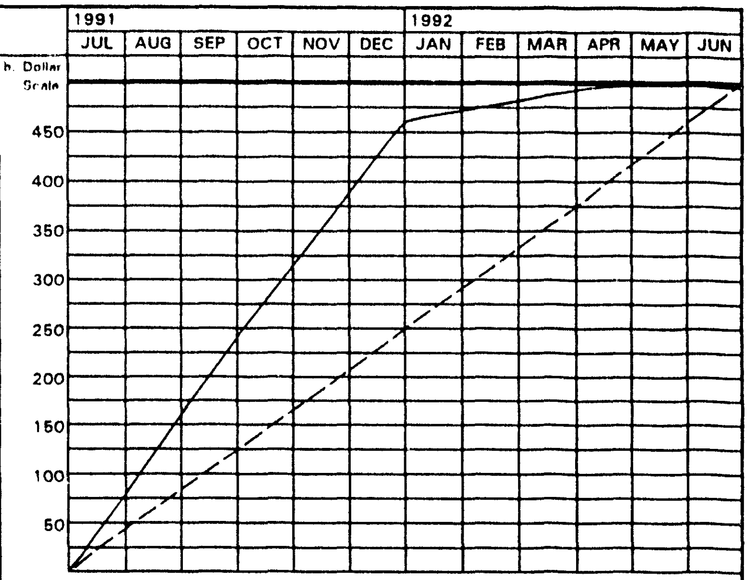
FORM APPROVED
OMB NO. 1900 0127
Page 1 of 2

1. Program/Project Identification No. DE-FC21-86MC10637	2. Program/Project Title Production of Hydrogen and By-Products from Coal (6.1)	3. Reporting Period 4-1-92 through 6-30-92
4. Name and Address Energy and Environmental Research Center University of North Dakota Box 8213, University Station, Grand Forks, ND 58202 (701) 777-5000		5. Program/Project Start Date 4-1-86 6. Completion Date 9-30-92

7. FY 91/92

8. Months or Quarters: Quarters

9. Cost Status a. Dollars Expressed in Thousands b. Dollar Scale



10. Cost Chart

Fund Source		Quarter 1st	2nd	3rd	4th	Cum. to Date	Tot. Plan
DOE	P	125	125	125	128	503	503
	A	248	217	32	3	500	
	P						
	A						
	P						
	A						
	P						
	A						
Total P		125	125	125	128	503	503
Total A		248	217	32	3	500	
Variance		(123)	(92)	93	125	3	

P = Planned A = Actual

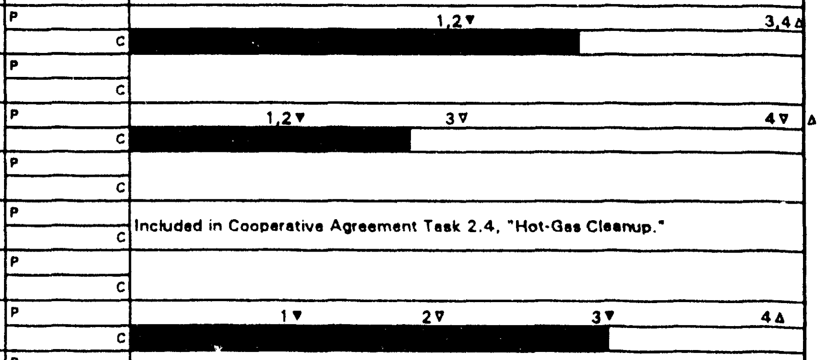
Total Planned Costs for Program/Project

$503

c. Cumulative Accrued Costs

	JUL	AUG	SEP	OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN
Planned			125			250			375			503
Actual			248			465			497			500
Variance			(123)			(215)			(122)			3

11. Major Milestone Status — Units Planned / Units Complete



A. Gasification Kinetics	P	1,2▼ 3,4▲
	C	
B. Production of Carbon, Liquid, and Gas By-Products	P	1,2▼ 3▽ 4▽ ▲
	C	
C. Gas Conditioning and System Integration	P	Included in Cooperative Agreement Task 2.4, "Hot-Gas Cleanup."
	C	
D. Pilot-Scale Hydrogen Production	P	1▼ 2▽ 3▼ 4▲
	C	
E. Final Report	P	▲
	C	

12. Remarks

Due to the EERC fiscal year end, the June books do not close until July 25, 1992. Costs posted through July 8 have been included.

13. Signature of Recipient and Date: July 29, '92

14. Signature of DOE Reviewing Representative and Date

FORM EIA-459E
(10/80)

U.S. DEPARTMENT OF ENERGY

FEDERAL ASSISTANCE MANAGEMENT SUMMARY REPORT

FORM APPROVED
OMB NO. 1900 01.
Page 2 of 2

1. Program/Project Identification No.: DE-FC21-86MC10837
2. Program/Project Title: Production of Hydrogen and By-Product from Coal (6.1)
3. Reporting Period: 4-1-92 through 6-30-92
4. Name and Address:
Energy and Environmental Research Center
University of North Dakota
Box 8213, University Station
Grand Forks, ND 58202 (701) 777-5000
5. Program/Project Start Date: 4-1-86
6. Completion Date: 9-30-92

Milestone ID. No.	Description	Planned Completion Date	Actual Completion Date	Comments
Task A	Gasification Kinetics:			
a.1	Evaluation of catalysts for gas production (Topical Report)	12-31-91		
a.2	Char surface properties measurement and control (bench-scale and IBG)	12-31-91		
a.3	Evaluation of catalysts for liquid production (IBG scale)	6-30-92		
a.4	Topical report on catalytic effects in char and liquid production	6-30-92		
Task B	Production of Carbon, Liquid, and Gas By-Products:			
b.1	Construction and shakedown of IBG system	9-30-91	1-24-92	
b.2	Vortex venturi cold testing and evaluation	9-30-91	1-24-92	
b.3	Activated carbon lab-scale production and testing (IBG-scale)	12-31-91		
b.4	Subpilot-scale activated carbon production (1-4 lb/hr continuous)	6-30-92		
b.5	Liquid product lab-scale production and testing (IBG-scale)	6-30-92		
Task C	Gas Conditioning and System Integration (evaluation of pilot-scale work conducted under Hot-Gas Cleanup task, relative to hydrogen production application).			
Task D	Pilot-Scale Hydrogen Production:			
d.1	Evaluation of catalyst behavior during extended operation	12-31-91	12-31-91	
d.2	Vortex venturi hot (in-process) testing and evaluation, pending encouraging results of Task b.2.	3-31-92		
d.3	Catalyst evaluation topical report	6-30-92		
Task E	Final Report	8-31-92		

APPENDIX A

THE DEFINITION AND MEASUREMENT OF CHAR REACTIVITY IN COAL AND WOOD GASIFICATION PROCESSES

by

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January 1992

GASIFICATION REACTIVITY DEFINED

The objective of gasification of coal or biomass is to convert the solid feed to the maximum possible amount of organic gases and/or condensible vapors, at the maximum possible rate, consuming the minimum heat from partial combustion of feed to supply the heat of reaction. This transition from solid carbon to a highly variable mixture of gases during gasification is the result of a complex interplay of many different chemical reactions. The overall rate is dominated by the well-known steam-char reactions:

$$C + H_2O \rightarrow H_2 + CO$$

and

$$C + 2H_2O \rightarrow 2H_2 + CO_2$$

There are of course many concurrent reactions that happen, at various rates determined by distribution of intermediates in reacting system, by temperature and pressure, by the presence of catalysts and by the structure of the carbonaceous feed. The most significant of these are described below.

Volatilization and thermolysis (cracking) of hydrocarbons and heteroatom-containing hydrocarbons which can be represented by:

$$C_aH_{b(s\ or\ l)} \dashrightarrow C_aH_{b(g)}$$

$$C_cH_d(O,\ N\ or\ S)_{e(s\ or\ l)} \dashrightarrow C_cH_d(O,\ N\ or\ S)_{e(g)}$$

$$C_mH_n \dashrightarrow C_xH_y + C_vH_w$$

$$C_hH_i(O,\ N\ or\ S)_j \dashrightarrow C_kH_l(O,\ N\ or\ S)_s + C_tH_u$$

These reactions proceed quite rapidly and may account for H_2 and CH_4, but are dependent only on temperature, pressure, and the chemical nature of the feed, being influenced only slightly by the gaseous product concentration and

shifting: $CO + H_2O \rightarrow H_2 + CO_2$

methanation: $CO + 3H_2 \rightarrow CH_4 + H_2O$

whose rates are limited by the rate of CO and H_2 produced by the steam-char reaction, and

combustion: $C +)_2 \rightarrow C)_2$

which is essentially instanteous, compared with the above reactions, and is controlled only by the amount of oxygen available in the reaction system.

finally: $C(s) + 2H_2 \rightarrow CH_4$

which is a fairly slow reaction producing a significant amount of methane in an H_2-rich environment, where its rate will be determined by H_2 availability.

Thus the rate of the steam-char reactions is the dominant factor that controls and limits the overall rate of carbon consumption. Reactivity is defined as the property of any char that is defined by its rate of reaction with steam. By definition, char is any carbonaceous material that has been thermally stripped of any volatilites as well as moisture by the above cracking reaction.

Reactivity is that basic property of a coal or wood char that determines whether gasification can proceed rapidly enough at a prescribed set of conditions of temperature and pressure to justify further process research. It provides information regarding the required temperatures and residence time in a gasifier vessel, which in turn serve as basis for design of the vessel of desired throughput capacity and ultimately determine the capital investment in that vessel.

Laboratory-scale measurement of reactivity is done by thermogravimetric Analysis (TGA) in a device shown schematically in Figure A-1. As temperature is increased to the desired gasification temperature with the sample chamber swept by inert argon to remove volatiles, the sample weight decreases as shown in Figure A-2, until the weight loss curve, dW/dt levels out, indicating that all volatiles have been removed. The remaining, thermally stable char which generally includes over 50 wt% carbon, is then reacted with superheated steam. The char carbon is consumed by the steam-char reaction at a decreasing rate defined by the following differential equation:

$$- dC/dt = kC^n \qquad \text{[Eq. 1]}$$

The differential term, dC/dt is the rate of carbon disappearance, C is the amount of carbon present per reacting volume at any instant, k is the rate constant or "reactivity," and n is the order of the reaction. The rate constant, k, is the accepted measure of reaction rate and roughly predicts whether the reaction can be practically carried out in a gasifier of reasonable size using a given feed at a temperature found to produce a desired gas mix. The rate constant is also the measure of relative effectiveness of different catalysts, either inherent, as lignite ash, or added, as mineral to the gasifier feed. That k varies over an extremely wide range for different coals, at the same temperature, is shown by Figure A-3.

A complicating factor is reaction order, n, determined from the slope of a plot of log dC/dt vs. log C and is an indication of the manner in which the rate of the reaction varies with the concentration of active carbon.

The solution to this equation, for the simple first order case where n = 1, is as follows:

$$C(t) = C_0 e^{-kt} \qquad \text{[Eq. 2]}$$

This equation describes the steam-char reaction alone. However, both isothermal rate and equilibrium are affected by at least a dozen or so other reactions between the C, H_2O, CO, CO_2, CH_4, O_2, N_2 (as a diluent), other light organics, and volatile tars (especially in the case of bituminous coals). Their net result on the reactions (1) above, is as follows:

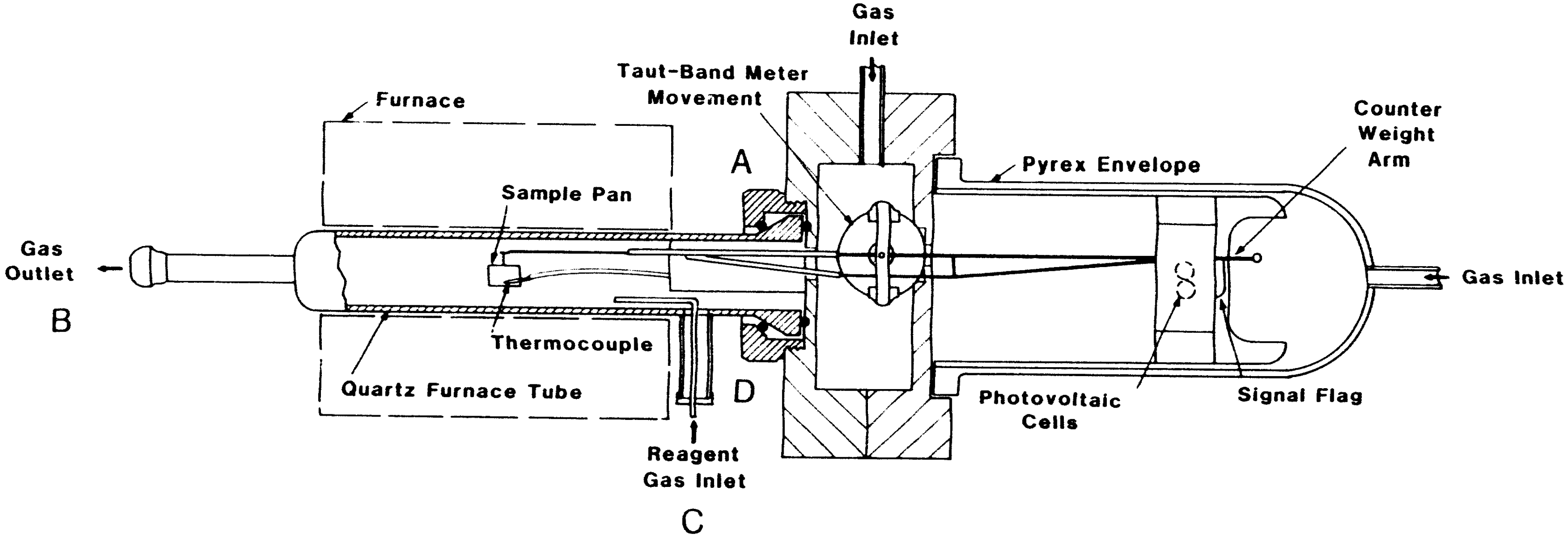

Figure A-1. Thermogravimetric analyzer.

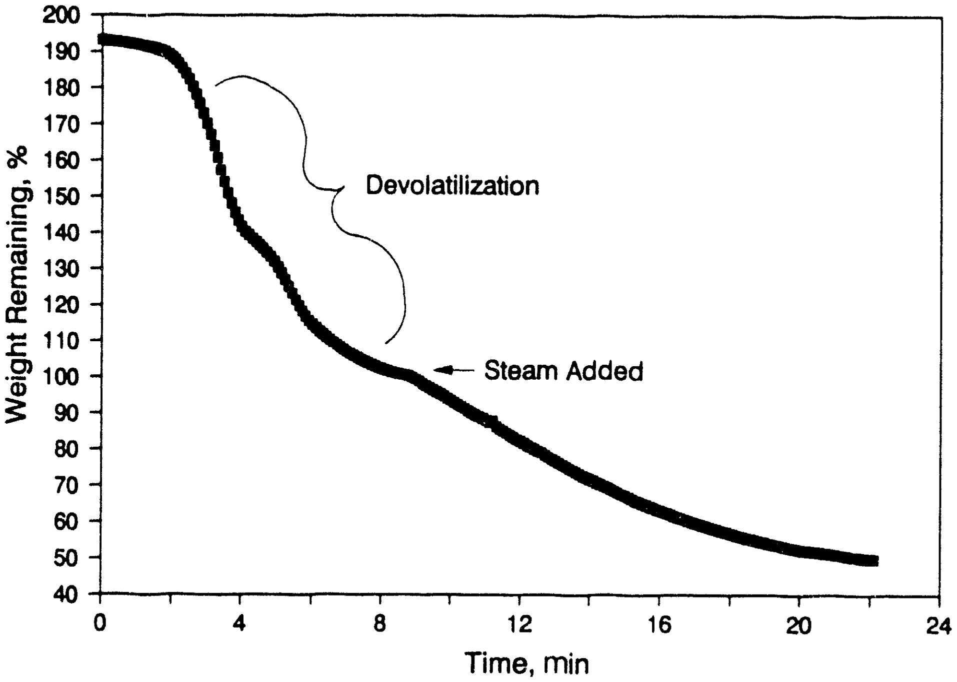

Figure A-2. Thermogravimetric analysis--typical data.

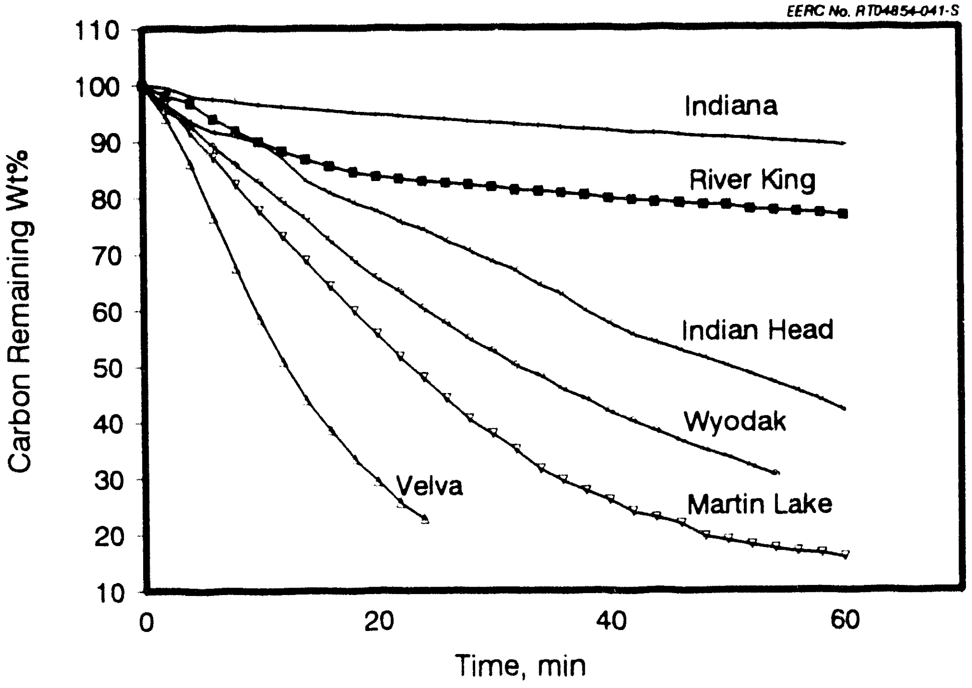

Figure A-3. Wt% carbon conversion versus time for two bituminous, one subbituminous, and three lignite coal chars at 750°C.

$$C(t) = C_o/(C_o kt + 1) \qquad \text{for } n = 2 \qquad [\text{Eq. } 3]$$

$$C(t) = C_o - (kt/2)C_o^{1/2} + k^2t^2/4 \qquad \text{for } n = 1/2 \qquad [\text{Eq. } 4]$$

$$C(t) = C_o - kt \qquad \text{for } n = 0 \qquad [\text{Eq. } 5]$$

There are rare documented cases of chemical reactions of ternary or higher order. Zeroth order is not uncommon, especially in surface reactions where there is a high degree of surface adsorption involved. In the gasification reaction, carried out in excess steam to suppress any rate control due to deficiency of water, formation of an intermediate activated complex may or may not be dependent on the carbon. If only selected carbons reach the activated state in the presence of adsorbed water, the order with respect to concentration of active carbon will have a nonzero value. If, however, the reaction occurs without dependence on active carbon since the concentration of activation sites may be taken as constant, the order of the reaction is zero with respect to carbon.

The above equations give reasonable approximations of k, although a much broader array of n values exist and can be determined. For a single set of C(t) data, determination of k presents the problem of a single equation in two unknowns. Substituting n obtained from the plot described above enables k to be determined. However, on reducing TGA data, values of n = 0.5, 1 or 2 selected on the basis of agreement with experimental n generally give satisfactory matches between experimental data and theoretical curves making it unnecessary to use the precise value of n. In gasification of complex materials such as wood, coal, solid waste, etc., experience has shown that fine resolution (e.g., n = .9 or n = 1.7) is unnecessary since it implies greater than the experimental accuracy.

The thermogravimetric analyses (TGA) of the steam gasification reactions were carried out on a commercial 100 mg capacity DuPont 951 TGA module, shown in Figure A-1, interfaced to a DuPont 1090 thermoanalyzer data station. Selected experiments were repeated on a 10-gram capacity TGA built at EERC. The smaller scale kinetics experiments involved 30 to 50 milligrams (dependent on fineness of grind and wood density) of ground wood loaded on a sample pan under argon flowing at 160 cc/min. The temperature was raised to a predetermined target temperature of 700, 750 or 800°C at ~100°C/min. During this temperature increase, the sample was devolatilized, producing a char, and when the temperature reached the target, excess steam flow was introduced through a side arm into the sample chamber. The argon carrier flow was reduced to ~ 60 cc/min for the duration of the experiment. When the char weight reached < 50% of its original value, the experiment was terminated. Total gas effluent was collected in a gas bag for analysis by gas chromatography (GC). Weight, time, and temperature were automatically recorded at 2, 3, or 6 second intervals by the data station on a floppy disk for later processing. An example of data collected during one of the tests is shown in Figure A-2.

Another essential property of a reactive char is the energy of activation. Reaction rate is dependent on the number of atoms or molecules in the activated state. In gasification reactivity studies the activation of carbon controls the rate since the other reactant, steam, is in large excess and presumably contains an excess of activated steam molecules. Because the number of active sites is a function of temperature, increasing the temperature increases the number of active carbons which in turn increases reaction rate. The char carbon reactivity in the absence of reaction control by mass transfer increases with increasing temperature allowing calculation of energy of activation according to the theory of Arrhenius:

$$d(\ln k)/dT = E/RT^2 \quad \text{or} \quad k = A\,e^{-E/RT} \qquad \text{[Eq. 6]}$$

where k is the reactivity, A is the preexponential (frequency) factor, E is the energy of activation, T is absolute temperature (°K) and R is the universal gas constant. The physical interpretation of the preexponential factor, A, which is also referred to as a frequency factor is not without some rigor. The solution as given by W.C. McC. Lewis (1) suggests that A is equal to the frequency of collisions between molecules for reactions of order > 1 in which case the application of the term frequency is intuitively obvious. For example, for a reaction between two molecules:

$$v = ze^{-E/RT} \quad \text{in molecules cc}^{-1}\ \text{sec}^{-1} \qquad \text{[Eq. 7]}$$

where z is the number of collisions per second in 1 cc of gas and is given by kinetic theory as

$$z = n_A n_B \sigma^2_{AB}[8\pi KT((m_A + m_B)/m_A m_B)]^{1/2} \qquad \text{[Eq. 8]}$$

n's are the concentrations, σ_{AB} is the average molecular diameter, m_A and m_B are molecular masses, and K is the Boltzmann constant. Since

$$v = kn_A n_B \qquad \text{[Eq. 9]}$$

and

$$k = \sigma^2_{AB}[8\pi KT((m_A + m_B)/m_A m_B)]^{1/2}\ e^{-E/RT} \qquad \text{[Eq. 10]}$$

then

$$k = Ze^{-E/RT} \qquad \text{[Eq. 11]}$$

where Z is the collision number and for Arrhenius theory Z = A.

Energy of activation is calculated from the slope of a plot of ln k vs 1/T where the reaction is carried out at a minimum of three temperatures and where the rate of conversion is assumed to be described by Equation 2. The E's measured in these experiments are apparent energies and, since they are dependent on heating rate (among other factors), are understood to be apparent procedural activation energies. The preexponential factor, A, is the intercept of the curve. The curve is linear when the reaction is under chemical control and non-linear Arrhenius plots may indicate a change in reaction mechanism or mass transfer control of the reaction.

The TGA method has become a routine procedure at EERC for rapid and inexpensive screening of large numbers of coals or woods, with and without catalysts over ranges of temperatures for rough approximation of their performance as gasifier feedstock. An on-going area of fundamental research is the determination of why different coals have widely different values of reactivity, k. All work at EERC supports the contention that the major factor in determining k is the concentration of active sites on the carbonaceous matrix, at which various catalytic cations (K^+, Na^+ or Ca^{++}, for example) are or can be attached. Figure A-3 shows the effect of variations in intrinsic catalysis for different coals, depending not only on the amount of catalytic elements present as ash, but on the extent to which they are organically bonded to active sites, as opposed to being in the form of stable mineral grains. Coals with a generous surplus of active sites are amenable to greatly enhanced reactivity by saturating the sites with mobile catalytic cations, either during the gasification reaction, as in the case of the TGA data of Figure A-4, or by prior chemical impregnation. The entire array of potentially practical combinations of coals, catalysts and gasification conditions approaches infinity. The value of TGA analysis is as a simple, minimal cost, screening step, to select candidate combinations for more detailed and costly testing, as indicated in Figure A-5.

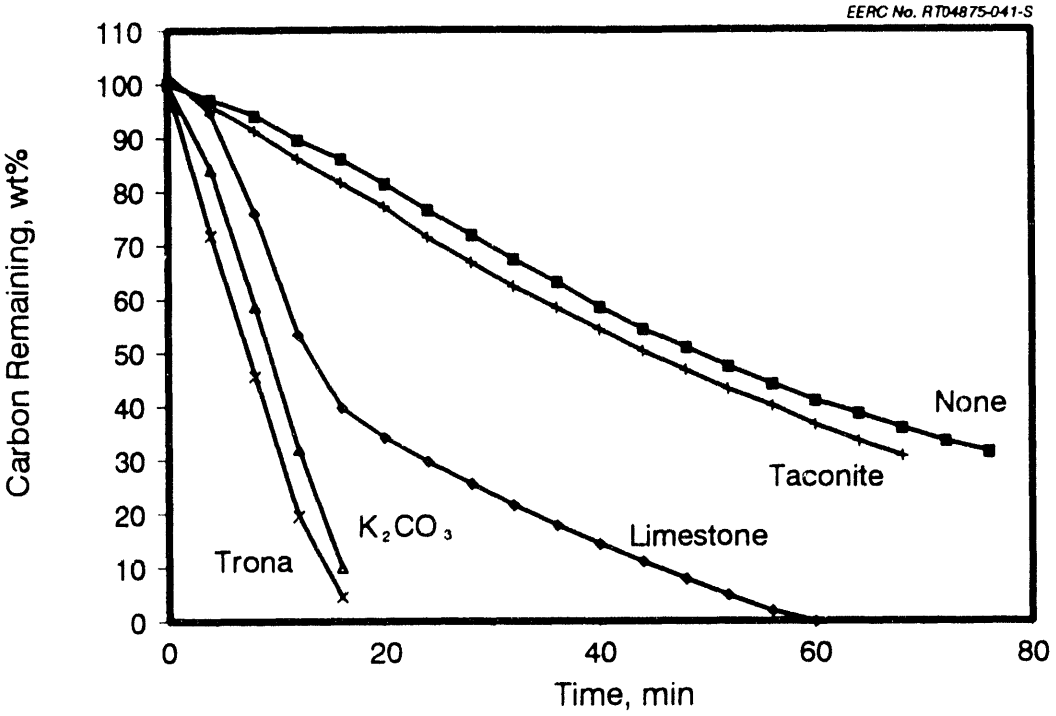

Figure A-4. Effects of different catalysts on reactivity of Velva lignite.

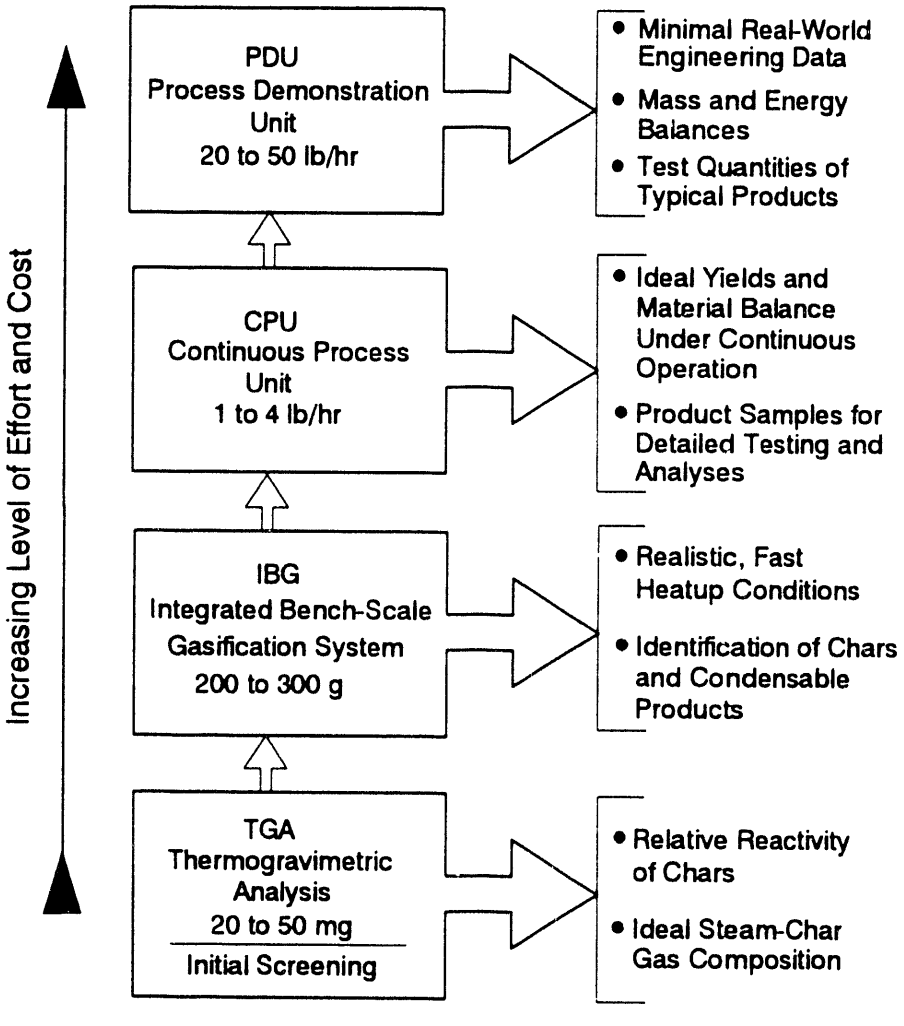

Figure A-5. EERCs program sequence for evaluation of coal-catalyst-process candidates.

APPENDIX B

TWO EXAMPLES OF COMPLETE PRINTOUTS FOR ANALYSIS OF DATA FROM EERCS CONTINUOUS PROCESS UNIT (CPU), OPERATING IN THE GASIFICATION MODE

Examples presented: Run M-224 (KOH-impregnated Wyodak coal in limestone bed) and Run M-233 (KOH-impregnated coal in taconite bed)

The first sheet in each set is a condensation of raw, on-line data generated by CPU operators. These data, plus laboratory analyses of all gas, solid, and (if desired) liquid products are inputs to Lotus file CPUDATA.WKI, which generates the minimum of five subsequent sheets.

1/9/92

Run # M233
i-Wyodak/Taconite
Temp. 650 C
Pressure 34.7 psia

% H2O	28.4
% Ar	0.0
% N2	71.6
% NO	0.0
% CO2	0.0

	Gms In	Gms Out	Yields	N Yields	SCF
MAF (Coal/char)	1723.6	730.5	42.4	32.7	
H2O in coal/Char	734.7	5.8	-42.3	-42.3	
H2O in H2O/Cond.	3384.0	3429.9	2.7	18.5	
Ash	821.7	1019.7	11.5	0.3	
Sulfur	69.4	69.4	0.0	0.0	
Ash(sulfur free)	752.3	950.3	11.5	0.3	
Cond. Total		29.06	1.69	1.82	
ibp-165		0.00	0.00	0.00	
<C10		0.00	0.00	0.00	
BXT		0.00	0.00	0.00	
165-220		0.00	0.00	0.00	
C10-C12		0.00	0.00	0.00	
Phenols		0.00	0.00	0.00	
Cresols		0.00	0.00	0.00	
Naphthal.		0.00	0.00	0.00	
220-375		0.00	0.00	0.00	
C13-C22		0.00	0.00	0.00	
C2-Phenol		0.00	0.00	0.00	
Phytene		0.00	0.00	0.00	
375-550		0.00	0.00	0.00	
C23-C30		0.00	0.00	0.00	
550-1000		0.00	0.00	0.00	
Aliphatics		0.00	0.00	0.00	
Phenolics		0.00	0.00	0.00	
BP>1000		0.00	0.00	0.00	
Char Fines		0.00	0.00	0.00	
Residue		0.00	0.00	0.00	
Gas Total	13245.2	16410.7	183.7	89.0	81.3
H2		124.7	7.2	6.5	48.5
CO2		1302.3	75.6	68.0	23.0
C3H8		0.0	0.0	0.0	0.0
C3H6		0.0	0.0	0.0	0.0
i-C4		0.0	0.0	0.0	0.0
COS		0.0	0.0	0.0	0.0
n-C4		0.0	0.0	0.0	0.0
H2S		0.0	0.0	0.0	0.0
1-Bu		0.0	0.0	0.0	0.0
t-2-Bu		0.0	0.0	0.0	0.0
i-C5		0.0	0.0	0.0	0.0
c-2-Bu		0.0	0.0	0.0	0.0
n-C5		0.0	0.0	0.0	0.0
C2H4		17.6	1.0	0.9	0.5
C2H6		18.9	1.1	1.0	0.5
O2	0.0	0.0	0.0	0.0	0.0
N2	13245.2	14723.0	85.7	0.9	0.5
CH4		100.8	5.8	5.3	4.9
CO		123.4	7.2	6.4	3.4
NH3		0.0	0.0	0.0	0.0
Total	19909.2	21625.7	199.6	100.0	

Mat. Balance 108.6

% loss to char1	0
% loss to char2	21
% loss to liq	-16
% loss to gas	95

EERC CONTINUOUS PROCESS UNIT - RAW DATA SUMMARY. PAGE 0
THIS PAGE: ALL DATA FROM MILDGAS PERSONNEL.
Spreadsheet last edited/revised: March 3, '92 RUN NO.: M-233
DATA SOURCE/USE CODE: DATE: 12-12-91
R = RAW LABORATORY DATA SHEETS AND NOTEBOOK. Entered: 3-28-92
M = MILDGAS MAT'L BAL NORMALIZATION SPREADSHEET.
A = ANALYSIS OF SAMPLE (PROX/ULT/XRFA/--), RPRTD P.1 OR 2.
I = CALCTD. INPUTS TO FOLLOWING PAGES. NR = NOT REPORTED.

	DATA ITEM	UNITS	REPORTED	CONVTD.	
M	Coal		Wyodak		
R	Max. Particle Size.	inch.	0.25	6.35 mm	
M	Bed Material		Taconite		
R	Max. Particle Size.	inch.	0.05	1.17 mm	
R	Co-fed Catalyst		KOH		
M	Duration of run.	Hrs.	4.00		
M	Temperature	degC	650	1202 F	
M	Pressure	PSIA	34.70	2.4 Atm	
M	Coal Feed, MAF.	gms	1723.6		
I		Lb/Hr.		0.948	
M	Moisture in Coal.	gms	734.7		22.4 %
M	Ash in Coal.	gms	821.7		25.1 %
I		Lb/Hr		0.452	
I	Coal Feed, Raw/As Recvd.	gms	3280.0		
I		Lb/Hr		1.804	
M	Sulfur.	gms	69.4		
M	Product Gas (Dry, N2-free).	SCF	81.3		98.2 %
I		SCFH		20	
M	H2	SCF	48.5		59.7 %
M	CO	SCF	3.4		4.2 %
M	CO2	SCF	23.0		28.3 %
M	CH4	SCF	4.9		6.0 %
M	H2S	SCF	0.0		0.0 %
R	Bed Overflow Ash	gm	1434.0		
I		Lb/Hr		0.789	
R	Fly Ash from Cyclone.	gm	322.0		
I		Lb/Hr		0.177	
R	Condensate	gm	3459.0		
I	(Assume density of water)	Lb/Hr		1.902	
M	Water In, as Steam.	gm	3384.0		
I		Lb/Hr		1.861	
M	Nitrogen In.	gm	13245.0		
I		Lb/Hr		7.285	
M	Total Water Out.	gm	3435.7		
I	Difference. *	% Input			-16.6 %
M	Nitrogen Out.	gm	14723.0		
I	Difference. *	% Input			11.2 %

Reflects leakage &/or inacuracy of water and gas flow measurement, before normalization of product gas flow.

```
    EERC CONTINUOUS PROCESS UNIT - RUN SUMMARY CALCULATIONS.    PAGE 1
    RUN NO.: M-233    DATE:        12-12-91   DURATION:         4 HRS.
           >>>>>>>>>>>  INPUT DATA BLOCK  <<<<<<<<<<<<<<<

 /----------------------\           /-------------------------------------\
 ¦ FEED SPECIFICATION ¦             ¦ FEED RATE (WHOLE):      1.80 LB/HR   ¦
 ¦ WYODAK          75.7 % ¦         ¦ FEED RATE (MAF):        0.95 LB/HR   ¦
 ¦ (H2O:           28.6 %)¦         ¦                       6469.0 BTU/HR  ¦
 ¦ (Ash:            4.9 %)¦         ¦ BED TEMP.:            1202.0 deg F   ¦
 ¦ (VM, MAF:       48.6 %)¦         ¦                        650.0 deg C   ¦
 ¦ (FC, MAF:       51.4 %)¦         ¦ PRESSURE:               20.0 PSIG    ¦
 ¦ (BTU/LB:      6824.0 ) ¦         ¦ STEAM/FC (MOLS):         2.1         ¦
 ¦ CATALYST:        4.4 % ¦         \-------------------------------------/
 ¦ NEW BED:        20.0 % ¦         /-------------------------------------\
 ¦ BED: TACONITE          ¦         ¦ PRODCT* GAS/VAPOR:     20.33 SCFH    ¦
 ¦------------------------¦         ¦                   =     0.85 LB/HR   ¦
 ¦ COMBINED PROX., DRY ¦Calctd./ ¦  (* Dry N2-free)                        ¦
 ¦ (Prox./XRFA)        ¦Predctd. ¦   YIELD:      47.26 % OF FEED.          ¦
 ¦ V.M.:         39.22 % ¦  34.30 ¦  YIELD:      89.94 % OF MAF.           ¦
 ¦ F.C.:         28.50 % ¦  36.20 ¦                                        ¦
 ¦ ASH:          32.20 % ¦  29.50 ¦ N2:                    7.28 LB/HR      ¦
 ¦ Total:        99.92 % ¦(Pre-run ¦                      100.60 SCFH      ¦
 ¦ COMBINED ASH **       ¦ Target) ¦ Steam:                39.98 SCFH      ¦
 ¦     47.50 % SiO2      ¦  45.18 ¦ Combined Flow:        201.35 ACFH      ¦
 ¦      3.52 % Al2O3     ¦   3.21 ¦ Fluidizing Vel.:        1.14 Ft/sec    ¦
 ¦     28.00 % Fe2O3     ¦  26.83 ¦----------------------------------------¦
 ¦      4.99 % CaO       ¦   4.53 ¦              (1)Mol%  (2)Mol%  Wt. %   ¦
 ¦      2.17 % MgO       ¦   1.74 ¦ H2            60.10    59.66    7.41   ¦
 ¦      0.37 % Na2O      ¦   0.38 ¦ CO             4.20     4.18    7.25   ¦
 ¦      8.87 % K2O       ¦  15.13 ¦ CO2           28.70    28.29   77.85   ¦
 ¦      4.38 % SO3       ¦   2.65 ¦ CH4            5.90     6.03    5.82   ¦
 ¦      0.20 % Other     ¦   0.35 ¦ H2S            0.00     0.00    0.00   ¦
 ¦-----------------------¦        ¦ C2/C2+         0.90             1.66   ¦
 ¦ ULTIMATE, MAF         ¦        ¦             ----------       -------- ¦
 ¦ C             71.63 % ¦        ¦ Total         99.80            100.00  ¦
 ¦ H              5.25 % ¦        ¦          (1) Lab    (2) From           ¦
 ¦ S              0.64 % ¦        ¦          analysis.   Page 0            ¦
 ¦ O+N+Other        22 % ¦        ¦ AVG.FUEL VALUE, BTU/LB:        6265    ¦
 \-----------------------/        ¦                 = BTU/SCF:      276    ¦
   GAS INPUTS                     ¦                   BTU/HR:      5342    ¦
    STEAM:       1.86 LB/HR       \---------------------------------------/
                 0.10 MOLS/HR       LIQUID (ORGANIC) PRODUCTS
    N2:          7.28 LB/HR       /---------------------------------------\
 ---------------------------------¦ CONDENSATE:             1.90 LB/HR     ¦
   GAS YIELD SUMMARY              ¦ % ORGANICS:             4.67 %         ¦
                           Lb/Lb  ¦ % SOLIDS:                 nr %         ¦
   WT. GAS/MAF FEED:       0.899  ¦ ORGANICS:               0.09 LB/HR     ¦
   WT. GAS/FC CONSUMED:    2.471  ¦    % OF MAF FEED:       9.37 %         ¦
   WT. H2/MAF FEED:        0.067  ¦                                        ¦
   WT. H2/FC CONSUMED:     0.183  \---------------------------------------/
   WT. CH4/MAF FEED:       0.052    % FC CONSUMED:                 58.63 %
   WT. CH4/FC CONSUMED:    0.144    GAS BTU/FEED BTU:                 83 %
```

```
 EERC CONTINUOUS PROCESS UNIT - RUN SUMMARY CALCULATIONS.   PAGE 2
 RUN NO.: M-233
   >>>>>>>>>>>  SOLIDS ANALYSIS INPUT DATA <<<<<<<<<<<<<<
/--------------------\       / ----------------------------------\
| FLY ASH FROM CYCLONE|      |             ASH                   |
|    0.18 LB/HR (DRY)|   /===>   52.50 % SiO2                    |
|    9.82 % OF FEED  |   ||  |    1.48 % Al2O3                   |
|    0.04 LB/HR (MAF)|   ||  |   38.80 % Fe2O3                   |
| V.M.:       18.40 %|   ||  |    2.55 % CaO                     |
| F.C.:        1.82 %|   ||  |    0.47 % MgO                     |
| ASH:        79.78 % =====/ |    0.26 % Na2O                    |
|                    |       |    3.40 % K2O                     |
|    3.78 % MAF FEED |       |    0.54 % SO3                     |
|--------------------|       |    0.00 % Other                   |
| ULTIMATE (MAF)     |       \-----------------------------------/
| C           85.88 %|       /-----------------------------------\
| H            2.05 %|   /===>             ASH                   |
| N+O         11.20 %|   ||  |   47.50 % SiO2                    |
| S            0.79 %|   ||  |    3.15 % Al2O3                   |
|                    |   ||  |   31.10 % Fe2O3                   |
\--------------------/   ||  |    3.27 % CaO                     |
/--------------------\   ||  |    1.53 % MgO                     |
| BED OVERFLOW       |   ||  |    0.36 % Na2O                    |
|    0.79 LB/HR      |   ||  |   10.20 % K2O                     |
|   43.72 % OF FEED  |   ||  |    2.74 % SO3                     |
|    0.37 LB/HR (MAF)|   ||  |    0.15 % Other                   |
| V.M.:       16.20 %|   ||  \-----------------------------------/
| F.C.:       30.46 %|   ||   FIXED CARBON (from Prox. Anal.)
| ASH:        53.52 % =====/  MAF FEED                0.95 LB/HR
|                    |        MF FEED:                1.40 LB/HR
|                    |        MAF OUT:                0.40 Lb/Hr
|   38.82 % MAF FEED |        MAF Consumed:          71.12 %
|--------------------|        FC IN * :               0.59 LB/HR
| ULTIMATE (MAF)     |        FC OUT.
| C           94.85 %|         Cyclone:               0.00 LB/HR
| H            0.93 %|         Bed Overflow:          0.24 LB/HR
| N+O          3.31 %|         Total:                 0.24 LB/HR
| S            0.80 %|        FC CONSUMED ** :        0.34 LB/HR
|                    |            % of Feed:         58.63 %
\--------------------/ K BAL.     LB/HR-FT^3:         2.81
 ASH BALANCE (LB/HR). (LB/HR)   * FC IN:              0.05 MOLS/HR
 TOTAL IN:    0.45     0.0401   ** = dC/dt for Reactivity.
 ASH OUT.
 CYCLONE:     0.14     0.0048   K in Feed:            0.00 MOLS/HR
 OVERFLOW:    0.42     0.0431   K/FC Mol. Ratio:      0.02
 TOTAL:       0.56     0.0479 Total Carbon (from Ult. Anal.)
            ---------           C in:                 0.68 LB/HR
 ACCNT'D.:  124.66 %   119.39 % C out. Cyclone:       0.15 LB/HR
                                       Overflow:      0.35 LB/HR
 Volatile matter balance               Total:         0.50 LB/HR
 on next page.                TOTAL C CONSUMED:       0.18 LB/HR
                                       % of Feed:    26.20 %
```

```
EERC CONTINUOUS PROCESS UNIT - RUN SUMMARY CALCULATIONS.     PAGE 3
RUN NO.: M-233

                                VOLATILE MATTER
                                VM in:                  0.49 LB/HR
                                VM out.  Cyclone:       0.03 LB/HR
                                         Overflow:      0.06 LB/HR
                                         Total:         0.09 LB/HR
                                TOTAL VM CONSUMED:      0.40 LB/HR
                                         % OF fEED:       81 %

====================================================================
                                Wt. Fraction Calculation
Avg. Mol. Wt.:           16.22                 Mol %            Wt. %
Density, Lb/SCF:        0.0419  H2               60     1.20    7.41
BTU/Lb.                         CO                4     1.18    7.25
 Calculated here =        6589  CO2              29    12.63   77.85
 From Lab. Anal. =        6265  CH4               6     0.94    5.82
BTU/SCF=                   276  H2S               0     0.00    0.00
Production, SCFH =       20.33  C2/C2+ *          1     0.27    1.66
            Lb/Hr =       0.85          ---------- -------  -------
                                Total           100    16.22  100.00
                                * All C2/C2+ assumed C2H6, if < 1%.
Wt. % C in Gas =         30.04 %
WT. C OUT AS GAS =        0.26 Lb/Hr
TOTAL C IN FEED =         0.68 Lb/Hr  -- Based on C in Ult. Anal.
C--> Gas Convrsn.=       37.71 %  -- incl. both FC and VM sources.
FC consumed =             0.34 Lb/Hr,

CARBON BALANCE.
C OUT, CYCLONE:          0.031 Lb/Hr
C OUT, OVERFLOW:         0.349 Lb/Hr
C ACCOUNTED FOR:         93.6 %
=====================================================================
                                              ;  BED DIMENSIONS
REPORTED PROBABLE WEIGHT OF BED MATERIAL.     ;  Dia. =         3 "
                         LOW       HIGH       ;  Ht. =         30 "
                                              ;  A, Ft^2:    0.05
                 2000.00 g  2256.00 g         ;  Ft^3 =      0.12
                    4.41 Lb    4.97 Lb        ;  Liters =    1.39
                                              ;_________________
FIXED CARBON IN BED:    1.34 Lb    1.51 Lb       = C, Lb

-dC/dt (Lb/Hr) = kC, ASSUMING 1st ORDER (n = 1), =      0.34 Lb/Hr

REACTIVITY, k = (dC/dt)/C =                    LOW:    0.257 1/Hr
                                              HIGH:    0.228 1/Hr
                                              AVG.:    0.242 1/Hr
```

```
/------------------------------------------------------------------------\
!         EERC CONTINUOUS PROCESS UNIT.               RUN NO. M-233      !
!         RUN SUMMARY SHEET                          DATE:     11-19-91  !
! RUN SPECIFICATIONS.                                                    !
!    Coal Feed:         Wyodak                Top Size=    6.35 mm       !
!    Bed Material:      Taconite              Top Size=    1.17 mm       !
!    Bed Make-up Rate:        20 % of Feed.                              !
!    Co-fed Catalyst:   KOH                                              !
!                              4 % of Feed.   K/FC=        0.02 Mol/Mol  !
!                                                                        !
!    TEMPERATURE:            650 degC         H2O/FC:      2.11 Mol/Mol  !
!                           1202 degF                                    !
!    PRESSURE:              34.7 PSIA         DURATION      4.0 Hours    !
!                            2.4 Atm          SHUT-DOWN    Planned.      !
! COAL FEED.                                                             !
!    Moisture (Raw):       28.60 %      Feed, Raw          1.80 Lb/Hr    !
!    Ash (Raw):             4.90 %      Feed, MAF          0.95 Lb/Hr    !
!    Volatiles, MAF:       48.60 %      MAF Convrtd.:     71.12 %        !
!    FC, MAF:              51.40 %      FC Convrtd.:      58.63 %   (1)  !
!                                                                        !
! PRODUCT GAS (Normalized Mol. %).                                       !
!   H2         60.10 %                                                   !
!   CO          4.20 %          Gas Yield Summary:        Lb/Lb          !
!   CO2        28.70 %          Wt. Gas/MAF Feed:          0.90          !
!   CH4         5.90 %          Wt. Gas/FC Consumed:       2.47          !
!   H2S         0.00 %          Wt. H2/MAF Feed:           0.07          !
!   C2/C2+      0.90 %          Wt. H2/FC Consumed:        0.18          !
!           ---------%          Wt. CH4/MAF Feed:          0.05          !
!   Total      99.80 %          Wt. CH4/FC Consumed:       0.14          !
!                                                                        !
!  BTU/SCF:       276                                                    !
!                                                                        !
! EFFECTIVE REACTIVITY:                           0.242 1/Hr             !
! Volumetric Throughput Capacity =                 2.81 Lb/Hr-Ft^3       !
! (1) If bed expanded     0.123 to    0.199 Ft^3, to achieve 95% FC      !
!      conversion, vol. capacity would =           1.73 Lb/Hr-Ft^3       !
!                                                                        !
! ACCURACY/VALIDITY.                                                     !
!   Input N2 accounted for:                       111.2 %  (2)           !
!   Input water accounted for:                     83.4 %                !
!   Input Ash accounted for:                      124.7 %                !
!   Input Carbon accounted for:                    93.6 %                !
!                                                                        !
! (2) As-measured raw gas flow adjusted to make this closure = 100%      !
!     to establish "normalized" product gas flow.                        !
\------------------------------------------------------------------------/
```

2/5/92

Run # M224
i-Wyodak/Limest
Temp. 700
Pressure 89.7

% H2O 11.6
% Ar 0.0
% N2 88.4
% NO 0.0
% CO2 0.0

	Gms In	Gms Out	Yields	N Yields
MAF (Coal/char)	1867.9	875.0	46.8	41.3
H2O in coal/Char	790.5	2.0	-42.2	-42.2
H2O in H2O/Cond.	3276.2	2639.6	-34.1	-11.9
Ash	621.6	705.0	4.5	0.0
Sulfur	67.8	67.8	0.0	0.0
Ash(sulfur free)	553.8	637.1	4.5	0.0
Cond. Total		22.40	1.20	1.39
ibp-165		0.00	0.00	0.00
<C10		0.00	0.00	0.00
BXT		0.00	0.00	0.00
165-220		0.00	0.00	0.00
C10-C12		0.00	0.00	0.00
Phenols		0.00	0.00	0.00
Cresols		0.00	0.00	0.00
Naphthal.		0.00	0.00	0.00
220-375		0.00	0.00	0.00
C13-C22		0.00	0.00	0.00
C2-Phenol		0.00	0.00	0.00
Phytene		0.00	0.00	0.00
375-550		0.00	0.00	0.00
C23-C30		0.00	0.00	0.00
550-1000		0.00	0.00	0.00
Aliphatics		0.00	0.00	0.00
Phenolics		0.00	0.00	0.00
BP>1000		0.00	0.00	0.00
Char Fines		0.00	0.00	0.00
Residue		0.00	0.00	0.00

	Gms In	Gms Out	Yields	N Yields	SCF
Gas Total	38956.0	45902.8	371.9	101.5	110.9
H2		181.2	9.7	8.6	69.6
CO2		1504.2	80.5	71.7	26.3
C3H8		0.0	0.0	0.0	0.0
C3H6		0.0	0.0	0.0	0.0
i-C4		0.0	0.0	0.0	0.0
COS		0.0	0.0	0.0	0.0
n-C4		0.0	0.0	0.0	0.0
H2S		0.0	0.0	0.0	0.0
1-Bu		0.0	0.0	0.0	0.0
t-2-Bu		0.0	0.0	0.0	0.0
i-C5		0.0	0.0	0.0	0.0
c-2-Bu		0.0	0.0	0.0	0.0
n-C5		0.0	0.0	0.0	0.0
C2H4		0.0	0.0	0.0	0.0
C2H6		0.0	0.0	0.0	0.0
O2	0.0	0.0	0.0	0.0	0.0
N2	38956.0	43793.5	259.0	1.0	0.6
CH4		136.7	7.3	6.5	6.6
CO		287.2	15.4	13.7	7.9
NH3		0.0	0.0	0.0	0.0
Total	45512.2	50146.8	348.1	90.1	
Mat. Balance		110.2			

% loss to char1	0
% loss to char2	4
% loss to liq	-9
% loss to gas	109

EERC CONTINUOUS PROCESS UNIT - RAW DATA SUMMARY. PAGE 0
THIS PAGE: ALL DATA FROM MILDGAS PERSONNEL.
Spreadsheet last edited/revised: March 3, '92 RUN NO.: M-224
DATA SOURCE/USE CODE: DATE: 12-9-91
R = RAW LABORATORY DATA SHEETS AND NOTEBOOK. Entered: 3-9-92
M = MILDGAS MAT'L BAL NORMALIZATION SPREADSHEET.
A = ANALYSIS OF SAMPLE (PROX/ULT/XRFA/--), RPRTD P.1 OR 2.
I = CALCTD. INPUTS TO FOLLOWING PAGES. NR = NOT REPORTED.

	DATA ITEM	UNITS	REPORTED	CONVTD.	
M	Coal		Wyodak Subbt.		
R	Max. Particle Size.	inch.	0.25	6.35 mm	
M	Bed Material		Limestone		
R	Max. Particle Size.	inch.	0.07	1.65 mm	
R	Impregnated Catalyst		KOH		
R	Duration of run.	Hrs.	4.00		
M	Temperature	degC	700	1292 F	
M	Pressure	PSIA	90	6.1 Atm	
M	Coal Feed, MAF.	gms	1862.9		
I		Lb/Hr.		1.025	
M	Moisture in Coal.	gms	790.5		24.1 %
M	Ash in Coal.	gms	621.6		19.0 %
I		Lb/Hr		0.342	
I	Coal Feed, Raw/As Recvd.	gms	3275.0		
I		Lb/Hr		1.801	
M	Sulfur.	gms	67.8		
M	Product Gas (Dry, N2-free).	SCF	110.9		99.5 %
I		SCFH		28	^^^^^^^^^
M	H2	SCF	69.6		62.8 %
M	CO	SCF	7.9		7.1 %
M	CO2	SCF	26.3		23.7 %
M	CH4	SCF	6.6		6.0 %
M	H2S	SCF	0.0		0.0 %
R	Bed Overflow Ash	gm	745		
I		Lb/Hr		0.229	
R	Fly Ash from Cyclone.	gm	416.0		
I		Lb/Hr		0.229	
R	Condensate	gm	2662.0		
I	(Assume density of water)	Lb/Hr		1.464	
M	Water In, as Steam.	gm	3276.2		
I		Lb/Hr		1.802	
M	Nitrogen In.	gm	38956.0		
I		Lb/Hr		21.426	
M	Total Water Out.	gm	2641.6		
I	Difference. *	% Input			-35.0 %
M	Nitrogen Out.	gm	43793.5		
I	Difference. *	% Input			12.4 %

* Reflects leakage &/or inaccuracy of water and gas flow measurement, before normalization of product gas flow.

```
   EERC CONTINUOUS PROCESS UNIT - RUN SUMMARY CALCULATIONS.   PAGE 1
   RUN NO.: M-224    DATE:        12-9-91    DURATION:       4 HRS.
            >>>>>>>>>>>>  INPUT DATA BLOCK  <<<<<<<<<<<<<<<<

 /---------------------\            /------------------------------------\
 ! FEED SPECIFICATION  !            ! FEED RATE (WHOLE):     1.80 LB/HR   !
 ! WYODAK        75.7 % !           ! FEED RATE (MAF):       1.02 LB/HR   !
 ! (H2O:         28.6 %)!           !                      8398.6 BTU/HR  !
 ! (Ash:          4.9 %)!           ! BED TEMP.:           1292.0 deg F   !
 ! (VM, MAF:     48.6 %)!           !                       700.0 deg C   !
 ! (FC, MAF:     51.4 %)!           ! PRESSURE:              75.0 PSIG    !
 ! (BTU/LB:    8197.0 ) !           ! STEAM/FC (MOLS):        2.3         !
 ! CATALYST:      4.3 % !           \------------------------------------/
 ! NEW BED:      20.0 % !           /------------------------------------\
 ! BED: LIMESTONE       !           ! PRODCT* GAS/VAPOR:    27.73 SCFH    !
 ! ---------------------!           !                   =    1.05 LB/HR   !
 ! COMBINED PROX., DRY  !Calctd./   ! (* Dry N2-free)                     !
 ! (Prox./XRFA)         !Predctd.   !   YIELD:     58.04 % OF FEED.       !
 ! V.M.:        46.32 % !   34.30   !   YIELD:    102.04 % OF MAF.        !
 ! F.C.:        28.70 % !   36.20   !                                     !
 ! ASH:         24.98 % !   29.50   ! N2:                   21.43 LB/HR   !
 ! Total:      100.00 % !(Pre-run   !                      295.88 SCFH    !
 ! COMBINED ASH         ! Target)   ! Steam:                38.71 SCFH    !
 !    12.60 % SiO2      !    6.26   ! Combined Flow:       195.43 ACFH    !
 !     8.20 % Al2O3     !    2.51   ! Fluidizing Vel.:       1.11 Ft/sec  !
 !     4.50 % Fe2O3     !    1.88   !-------------------------------------!
 !    12.00 % CaO       !   68.64   !             (1)Mol%  (2)Mol%  Wt. % !
 !     4.50 % MgO       !    2.19   ! H2           63.86    62.76   8.76 !
 !     0.90 % Na2O      !    0.39   ! CO            5.33     7.12  10.24 !
 !    47.70 % K2O       !   14.98   ! CO2          24.57    23.72  74.15 !
 !     8.70 % SO3       !    2.73   ! CH4           6.25     5.95   6.86 !
 !     0.90 % Other     !    0.42   ! H2S           0.00     0.00   0.00 !
 ! ---------------------!           ! C2/C2+        0.00            0.00 !
 ! ULTIMATE, MAF        !           !            ---------       -------!
 ! C            64.00 % !           ! Total       100.01          100.00 !
 ! H             3.82 % !           !            (1) Lab.   (2) From     !
 ! S             0.45 % !           !            Analysis   Page 0       !
 ! O+N+Other    31.71 % !           ! AVG.FUEL VALUE, BTU/LB:       6265 !
 \---------------------/            !                = BTU/SCF:      280 !
   GAS INPUTS                       !                  BTU/HR:      6550 !
    STEAM:        1.80 LB/HR        \------------------------------------/
                  0.10 MOLS/HR        LIQUID (ORGANIC) PRODUCTS
    N2:          21.43 LB/HR        /------------------------------------\
   -------------------------------  ! CONDENSATE:            1.46 LB/HR   !
   GAS YIELD SUMMARY                ! % ORGANICS:            4.28 %       !
                            Lb/Lb   ! % SOLIDS:                NR %       !
   WT. GAS/MAF FEED:        1.020   ! ORGANICS:              0.06 LB/HR   !
   WT. GAS/FC CONSUMED:     2.882   !    % OF MAF FEED:      6.12 %       !
   WT. H2/MAF FEED:         0.089   !                                     !
   WT. H2/FC CONSUMED:      0.252   \------------------------------------/
   WT. CH4/MAF FEED:        0.070     % FC CONSUMED:                69.43 %
   WT. CH4/FC CONSUMED:     0.198     GAS BTU/FEED BTU: %           77.99 %
```

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 EERC CONTINUOUS PROCESS UNIT - RUN SUMMARY CALCULATIONS.   PAGE 2
 RUN NO.: M-224        >>>>>  SOLIDS ANALYSIS INPUT DATA <<<<<<
/---------------------\      /------------------------------------\
! FLY ASH FROM CYCLONE!    /====>          ASH                     !
!     0.10 LB/HR (DRY)!   !!    !    7.56 % SiO2                   !
!     5.55 % OF FEED  !   !!    !    3.36 % Al2O3                  !
!     0.06 LB/HR (MAF)!   !!    !    2.44 % Fe2O3                  !
! V.M.:        38.27 % !   !!    !   61.50 % CaO                   !
! F.C.:        17.35 % !   !!    !    3.17 % MgO                   !
! ASH:         44.38 % =====/    !    0.39 % Na2O                  !
!                     !         !   19.40 % K2O                   !
!     5.43 % MAF FEED !         !    1.92 % SO3                   !
! --------------------!         !    0.26 % Other                 !
! ULTIMATE (MAF)      !         \-------------- ------------------/
! C            62.85 % !         /------------------------------------!
! H             1.14 % !   /====>          ASH                     !
! N+O          36.01 % !   !!    !    7.46 % SiO2                   !
! S             0.00 % !   !!    !    2.88 % Al2O3                  !
!                     !   !!    !    2.20 % Fe2O3                  !
\---------------------/   !!    !   69.20 % CaO                   !
/---------------------\   !!    !    2.45 % MgO                   !
! BED OVERFLOW        !   !!    !    0.33 % Na2O                  !
!     0.77 LB/HR      !   !!    !   13.20 % K2O                   !
!    42.75 % OF FEED  !   !!    !    2.04 % SO3                   !
!     0.43 LB/HR (MAF)!   !!    >    0.24 % Other                 !
! V.M.:        36.89 % !   !!    \------------------------------------/
! F.C.:        18.49 % !   !!     FIXED CARBON (from Prox. Anal.)
! ASH:         44.65 % =====/     MAF FEED                 1.02 LB/HR
!                     !          MF FEED:                 1.37 LB/HR
!                     !          MAF OUT:                 0.48 Lb/Hr
!    41.62 % MAF FEED !          MAF Consumed:           64.70 %
! --------------------!          FC IN * :                0.52 LB/HR
! ULTIMATE (MAF)      !          FC OUT.
! C            65.11 % !           Cyclone:               0.02 LB/HR
! H             0.63 % !           Bed Overflow:          0.14 LB/HR
! N+O          34.26 % !           Total:                 0.16 LB/HR
! S             0.00 % !          FC CONSUMED ** :         0.36 LB/HR
!                     !              % of Feed:          69.43 %
\---------------------/ K BAL.       LB/HR-FT^3:          2.96
 ASH BALANCE (LB/HR).  (LB/HR)     * FC IN:               0.04 MOLS/HR
 TOTAL IN:     0.34     0.1631     ** = dC/dt for Reactivity.
 ASH OUT.
 CYCLONE:      0.04     0.0086     K in Feed:             0.00 MOLS/HR
 OVERFLOW:     0.34     0.0454 %   K/FC Mol. Ratio:       0.10
 TOTAL:        0.39     0.0540    TOTAL CARBON (from Ult. Anal.)
            ---------               C in:                 0.66 LB/HR
 ACCNT'D.:  113.54 %     33.11 %    C out. Cyclone:       0.04 LB/HR
                                           Overflow:      0.50 LB/HR
 Volatile matter balance                   Total:         0.54 LB/HR
 on next page.                    TOTAL C CONSUMED:        0.12 LB/HR
                                      % of Feed:         18.12 %
```

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EERC CONTINUOUS PROCESS UNIT - RUN SUMMARY CALCULATIONS.   PAGE 3
RUN NO.: M-224

                                VOLATILE MATTER
                                VM in:                   0.53 LB/HR
                                VM out.  Cyclone:        0.02 LB/HR
                                         Overflow:       0.28 LB/HR
                                         Total:          0.31 LB/HR
                                TOTAL VM CONSUMED:       0.22 LB/HR
                                    % of Feed:             42 %
=================================================================
GAS CALCULATIONS.
                                Wt. Fraction Calculation
Avg. Mol. Wt.:          14.58                Mol %            Wt. %
Density, Lb/SCF:       0.0377   H2              64     1.28    8.76
BTU/Lb.                         CO               5     1.49   10.24
 Calculated here =       7433   CO2             25    10.81   74.15
 From Lab. Anal. =       6265   CH4              6     1.00    6.86
BTU/SCF=                  280   H2S              0     0.00    0.00
Production, SCFH =      27.73   C2/C2+ *         0     0.00    0.00
            Lb/Hr =      1.05            --------- ------- -------
                                Total          100    14.58  100.00
                                * All C2/C2+ assumed C2H6, if < 1%
Wt. % C in Gas =        29.75 %
WT. C OUT AS GAS =       0.31 Lb/Hr
TOTAL C IN FEED =        0.66 Lb/Hr  -- Based on C in Ult. Anal.
C--> Gas Convrsn.=      47.43 %  -- incl. both FC and VM sources.
FC consumed =            0.12 Lb/Hr
Wt. VM Consumed =        0.22 Lb/Hr

CARBON BALANCE.
C OUT, CYCLONE:         0.035 Lb/Hr
C OUT, OVERFLOW:        0.278 Lb/Hr
C ACCOUNTED FOR:         95.1 %
=================================================================
                                             ! BED DIMENSIONS
REPORTED PROBABLE WEIGHT OF BED MATERIAL.    ! Dia. =         3
                         LOW       HIGH      ! Ht. =         30
                                             ! A, Ft^2:    0.05
                     2000.00 g  2256.00 g    ! Ft^3 =      0.12
                        4.41 Lb    4.97 Lb   ! Liters =    1.39
FIXED CARBON IN BED:    0.82 Lb    0.92 Lb   !_________________

-dC/dt (Lb/Hr) = kC, ASSUMING 1st ORDER (n = 1), =   0.36 Lb/Hr
REACTIVITY, k = (dC/dt)/C =                LOW:     0.445 1/Hr
("C" = FC)                                HIGH:     0.394 1/Hr
                                          AVG.:     0.420 1/Hr
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/-----------------------------------------------------------------------\
!          EERC CONTINUOUS PROCESS UNIT.               RUN NO. M-224    !
!          RUN SUMMARY SHEET                           DATE:     11-19-91!
! RUN SPECIFICATIONS.                                                   !
!    Coal Feed:          Wyodak Subbt.        Top Size=     6.35 mm     !
!    Bed Material:       Limestone            Top Size=     1.65 mm     !
!    Bed Make-up Rate:         20 % of Feed.                            !
!    Co-fed Catalyst:    KOH                                            !
!                               4 % of Feed.   K/FC=        0.10 Mol/Mol !
!                                                                       !
!    TEMPERATURE:                 700 degC        H20/FC:      2.30 Mol/Mol !
!                                1292 degF                              !
!    PRESSURE:                   89.7 PSIA        DURATION      4.0 Hours !
!                                 6.1 Atm         SHUT-DOWN    Planned.  !
! COAL FEED.                                                            !
!    Moisture (Raw):            28.60 %      Feed, Raw          1.80 Lb/Hr !
!    Ash (Raw):                  4.90 %      Feed, MAF          1.02 Lb/Hr !
!    Volatiles, MAF:            48.60 %      MAF Convrtd.:     64.70 %     !
!    FC, MAF:                   51.40 %      FC Convrtd.:      69.43 %   (1) !
!                                                                       !
! PRODUCT GAS (Normalized Mol. %).                                      !
!   H2          63.86 %                                                 !
!   CO           5.33 %            Gas Yield Summary:      Lb/Lb        !
!   CO2         24.57 %            Wt. Gas/MAF Feed:        1.02        !
!   CH4          6.25 %            Wt. Gas/FC Consumed:     2.88        !
!   H2S          0.00 %            Wt. H2/MAF Feed:         0.09        !
!   C2/C2+       0.00 %            Wt. H2/FC Consumed:      0.25        !
!             ----------%          Wt. CH4/MAF Feed:        0.07        !
!   Total      100.01 %            Wt. CH4/FC Consumed:     0.20        !
!                                                                       !
!  BTU/SCF:       280                                                   !
!                                                                       !
! EFFECTIVE REACTIVITY:                              0.420 1/Hr         !
! Volumetric Throughput Capacity =                    2.96 Lb/Hr-Ft^3   !
! (1) If bed expanded      0.123 to    0.168 Ft^3, to achieve 95% FC    !
!     conversion, vol. capacity would =               2.16 Lb/Hr-Ft^3   !
!                                                                       !
! ACCURACY/VALIDITY.                                                    !
!   Input N2 accounted for:                          112.4 %  (2)       !
!   Input water accounted for:                        65.0 %            !
!   Input Ash accounted for:                         113.5 %            !
!   Input Carbon accounted for:                       95.1 %            !
!                                                                       !
! (2) As-measured raw gas flow adjusted to make this closure = 100%     !
!     to establish "normalized" product gas flow.                       !
\-----------------------------------------------------------------------/
```