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DYNAMIC SIMULATION OF EXXON'S CATALYTIC COAL-GASIFICATION PROCESS

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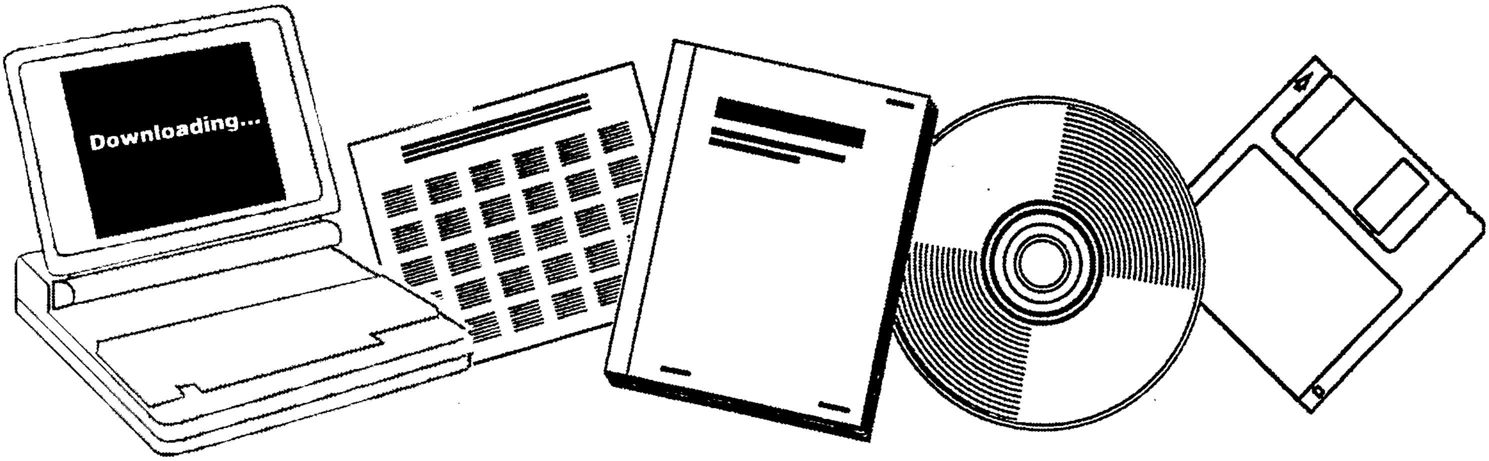

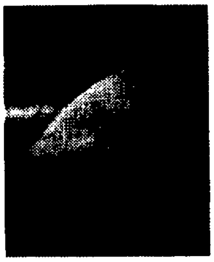

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Dynamic Simulation of Exxon's Catalytic Coal-Gasification Process

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to be presented at the 1982 AIChE Annual Meeting
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Abstract

The Exxon Catalytic Coal Gasification process is a novel method for producing methane directly from coal. Its key features from a process dynamics standpoint are use of a catalyst which causes both the highly endothermic gasification and exothermic methanation reactions to occur in the same reactor, separation of product gas in a highly heat integrated cryogenic section, and recycle of product carbon monoxide and hydrogen back into the reactor. A dynamic simulation of this process has been developed, and closed control loop responses are presented.

Exxon Research and Engineering Co. has been engaged over the last decade in the development of a unique process for the conversion of coal to methane[1,2]. The development started with the discovery that coal catalyzed with potassium salts promotes methanation of the coal gasification products. From this discovery stemmed a one reactor process concept, known as Catalytic Coal Gasification (CCG) which offers a more efficient, lower cost route to product methane from coal. This paper presents a dynamic simulation of the CCG process that was performed to aid in control scheme studies.

Process Concept and Flow Scheme

The major reactions that occur in coal gasification are shown in Figure 1. In non-catalytic gasification processes, these reactions must be carried out in separate reactors as uncatalyzed gasification rates are very slow at temperatures much below 925°C while methanation reaction equilibrium constraints strongly reduce methane production at temperatures above 800°C. In potassium catalyzed gasification, on the other hand, reasonable gasification rates and near-equilibrium yields of methane can both occur at 700°C, thus permitting direct conversion of coal to methane in a single reactor. An additional benefit of this concept is high thermal efficiency. If gasification and methanation are carried out in separate vessels, the large heat of gasification (Figure 1) must be added to one reactor while the equally large heat of methanation is removed from another at a lower temperature. Carrying out both reactions in a single vessel, on the other hand, results in a process that is approximately thermoneutral.

A flowsheet for a proposed commercial plant for Catalytic Coal Gasification (CCG) is shown in Figure 2. Coal is crushed and dried and potassium catalyst is added to the coal as a solution containing primarily KOH and K_2CO_3. The moisture from the catalyst solution is evaporated, and the prepared coal is fed to the gasifier via a lock hopper system. The coal is gasified at conditions of about 705°C and 3.5 MPa in a simple fluidized bed reactor containing no internals other than a gas distributor.

The gasifier effluent is essentially CH_4, CO, CO_2, and unconverted steam. This effluent flows through cyclones in which the coarser entrained fines are recovered for return to the reactor. After high level heat recovery from the gas, the remaining fines are removed by cyclones and a venturi scrubber (not shown on Figure 2) and acid gases are removed using commercially available technology. Product methane is separated from CO and H_2 by cryogenic distillation, and the methane is sent to sales. The CO and H_2 are recycled to the gasifier. Since the amount of CO and H_2 feed balances the amount of CO and H_2 leaving the gasifier, the net products of gasification are only methane and CO_2, along with small amounts of H_2S and NH_3.

As previously described, the overall reaction occuring in the gasifier is essentially thermally neutral, and only a small amount of heat is required to heat up the feed coal and offset heat losses. This heat is supplied by preheating the feed gases to about 815°C (1500°F) before they enter the fluid bed. A small steam/methane reformer may also be included to provide a supplemental source of synthesis gas which methanates in the gasifier and thus supplies additional heat. This approach is more economical than raising the preheat temperature much above 815°C (1500°F).

The unique features of the CCG process make prediction of the process dynamics very difficult. The mass and energy balances in the gasifier are very tightly coupled due to the large heats of gasification and methanation relative to the overall heat of reaction (Figure 1). For example, an upset to the gas composition entering the gasifier will result in an upset in the gasifier energy balance. The resulting gasifier temperature upset will affect the flow and composition of the gases leaving the gasifier, and this material balance upset will be fed back to the gasifier due to the recycle of syngas (CO and H_2) from the cryogenic distillation section. A dynamic simulation of the CCG process was therefore commissioned to determine whether the process interactions presented any controllability problems as well as to help design a control scheme for the process. While there have been previous dynamic simulation of both fixed and fluidized bed coal gasifiers[3,4,5], these simulations were all performed for noncatalytic gasification processes, and thus would not show the process dynamics implications resulting from the unique features of the CCG process.

Methodology

The simulation was developed in a modular fashion, that is, each process unit was modeled, and its dynamic differential equations integrated, in a separate subroutine. This provided for computer code that was much easier to read and debug. The simulation modules were grouped into two sections: the gasifier section and the recycle loop. The catalyst recovery system was not included in the simulation. The division into sections was prompted by the large times required for dynamic responses of the gasifier relative to the other units in the process, the gasifier being about a factor of 10 slower than any other unit. Computation efficiency thus required that the gasifier dynamic differential equations be integrated using a time step much larger than that used for the recycle loop units. As will be discussed later, the recycle loop used a variable time step that was always much smaller than the fixed gasifier time step. Coordination between these differing time steps was handled by the simulation main program which kept track of accumulated simulation time and called the gasifier and recycle loop sections whenever appropriate.

The CCG gasifier was modeled by assuming that the fluidized bed of char and catalyst solids acts as a well-stirred reactor; so that solids temperature and composition are uniform throughout the bed at any given time. The gases passing through the bed were assumed to be in plug flow and at the same temperature as the solids. The gas holdup of the bed was assumed to be negligible. These assumptions permit the gasifier to be modeled with two sets of ordinary differential equations, one set in bed height for the gas phase, and one in time for the solid phase. The resulting savings in time over modeling the bed using partial differential equations justifies these assumptions, all of which are close approximations to reality in any case.

The gasifier model structure, shown in Figure 3, parallels the modeling approach in that it is divided into solid phase and gas phase sections. At each gasifier time step the catalyst reaction section of the solids model first calculates the net generation or consumption of catalyst, char, and gas species due to a series of coal-catalyst reactions. The kinetic model is then called to integrate the differential equations associated with the gas phase up the length of the reactor, returning the flow and composition of gases leaving the gasifier, and the average density of the fluidized bed. The heat and mass balance section of the solids model then uses these results, along with information on solids feeds and catalyst reactions, to integrate the overall gasifier mass and energy balances through one time step, calculating a new pressure drop, bed height, temperature, and solids composition. The latter three parameters will be used by the kinetic model during the next time step. Controller calculations are then performed for any gasifier parameter being controlled.

The catalyst reaction section takes as input the feed catalyst and coal flow rates and compositions and calculates the amounts of solid product species formed and the amounts of gas species formed or consumed for a series of coal-catalyst reactions. The coal composition is also corrected for organic material consumed in catalyst reactions. The reactions are assumed to occur instantaneoulsy and to go to completion.

The gas phase kinetic model calculates the flow and composition of the gas leaving the gasifier as a function of inlet gas flows and composition, char solids composition, coal feed rate and composition, and bed temperature, pressure and height. The model has previously been described in detail[6,7]. This model assumes that the fluidized bed can be represented as two phases, an emulsion phase containing all of the solids and a portion of the gas, and a bubble phase containing the remainder of the gas. The fraction of gas flowing in the emulsion phase in calculated by assuming that the nominal velocity of gas in this phase equals the minimum fluidization velocity of the bed solids. Gasification and methanation reactions (Table 1) are assumed to take place in the emulsion phase only, while the gas in both phases is assumed to be in shift equilibrium at all points in the bed. Mass transfer between phases is modeled by bubbling fluidized bed mass transfer correlations whose sources are listed in Table 2.

There are two feed streams in this model. The main gas feed stream enters the emulsion phase of the bed at the bottom of the reactor, while a minor feed stream which also contains the catalyst gases is added to the bubble phase of the bed at the coal feed point, which is usually near the bottom of the bed. The coal is assumed to devolatilize at this point as well. The amounts of hydrogen, oxygen, nitrogen, and organic sulfur that become volatile are assumed to be a constant fraction of the amounts of these elements present in the feed coal after adjusting feed coal composition for catalyst reactions. The partitioning of these elements among the product gases is determined by the Gibson-Euker model[6], which calculates the yields of each product gas as a function of the coal composition and local hydrogen partial pressure. The calculated yields of carbon containing gases (CH_4, CO, CO_2) will determine the amount of carbon in the coal that is devolatilized. Devolatilization gases and coal moisture are added to the bubble phase of the bed at the coal feed point.

A series of material balances for each phase of the form

$$\frac{1}{A}\,\frac{dN_{ij}}{dz} = \frac{O_i}{RT}\,(P_{ij} - P_{ij'}) + \delta_j\,(\alpha_{iG}\,r_{jG} + \alpha_{iM}\,r_{jM})$$

where A = bed area

N_{ij} = molar flow rate of component i in phase j (bubble or emulsion)

O_i = mass tranfer coefficient between phases

P_{ij} = pressure of component i in phase j

$P_{ij'}$ = pressure of component i in other phase

δ_j = fraction of bed volume in phase j

$c_{iG,M}$ = stoichiometric coefficient for component i for gasification, methanation reactions

$r_{jG,M}$ = molar rate of gasification or methanation in phase j (= 0 if j = bubble phase)

are integrated up the length of the bed using the relations in Tables 1 and 2. Integration is performed using an explicit Runge-Kutta technique with step size adjustment. The system of differential equations are stiff, so a stability testing procedure was included in the integration routine. This procedure checks that the gas stream composition calculated at each time step has not crossed an equilibrium constraint. If it has, the step is redone with the step size halved. After each length step is integrated, the compositions of each phase are adjusted to be in water-gas shift equilibrium, and the flows through the two phases are corrected so that the velocity through the emulsion phase equals the minimum fluidization velocity. The bed pressure for the current value of the length is calculated, and the bed density integrated using the trapezoidal rule. The final average bed density is passed back to the solids balance model to be used in calculating the new bed height.

The dynamic solids mass balance calculates the bed solids inventory and composition at each time step. A separate dynamic balance is written for each organic element in the char, for coal ash, and for each inorganic potassium salt that may exist in the bed. The balance are added together to obtain a total bed inventory balance. Component material balances are based on coal and catalyst feed flows and compositions, coal-catalyst reactions, inlet gas flows and compositions, and gas product flows and compositions, the latter values being obtained from the results of the kinetic model. The simulation integrates each of the component material balances using a fixed time step Euler method, and then calculates a new normalized set of weight fractions for the char. The equation for total bed mass is then integrated, and a new bed height calculated from the bed mass and bed density. The bed height and density are then used to calculate the pressure drop across the bed.

There are two gasifier energy balances, one on the bed contents and one on the reactor vessel shell. These balances compute the enthalpies of all gas and solid streams entering or leaving the reactor, referenced to the elements at 60°F as well as heat transferred between the bed and the shell, and between the shell and ambient. The net accumulations of enthaply minus the heat loss terms are integrated using fixed time step Euler methods. New bed and shell temperatures are then calculated using the new bed solids composition.

The units in the recycle loop are all much simpler than the gasifier. In addition, they are commercially proven and as such their dynamic responses are already known. Thus, the level of modeling detail used for recycle loop modules was much less than that used for the gasifier. The fired preheater and high level heat exchangers were modeled as simple, lumped parameter systems. The low level heat recovery and acid gas removal sections were assumed to work as designed and to have first order dynamics. The supplemental steam reformer was modeled as a lumped parameter system for the flue gas and convection sections, and as a distributed parameter system on the process gas side on the radiant section. The methane recovery distillation tower was modeled using a tray-to-tray mass balance model, but with a simplified energy balance.

The cryogenic heat exchangers used to cool down the feed to the acid gas removal system were modeled as a distributed parameter system, however, due to the large temperature drop across these exchangers. The distributed parameter model used generates a series of stiff differential equations in time, which are integrated using a Runge-Kutta technique with a step size adjuster. The new time stepsize calculated at each time step is used by all other modules in the recycle loop to integrate their differential equations over the next time step. The interfacing between this variable recycle loop time step and the fixed gasifier time step is handled by the simulation main program.

The simulation runs on an IBM 3081. It currently requires considerable computing power, but improvements in its efficiency will be addressed in the future, with an eye to having it run on a VAX 11/780. Data on equipment parameters and initial conditions are input to the model via a series of data sets. The final values of all variables in these data sets are written into new data sets by the model after a simulation has ended. This permits running the model to a steady state and then saving the complete steady state, so that disturbance simulations may be run by changing only one or two numbers in the data sets. The simulation also saves values of key variables as a function of time in a format directly readable by an interactive plotting routine, allowing dynamic response plots to be generated easily and quickly.

Sample Results

The major use of the simulation to date has been to test potential control configurations for the gasifier. In one such configuration, the preheat and reformer furnaces were used to control the gasifier bed temperature, while the bed temperature was in turn used to control the bed height. As bed height setpoint will not be changed often, the configuration was tested by simulating its response to a solids flow rate upset, which consisted of a 5% increase in the flowrates of coal and catalyst fed, and char and fines withdrawn.

The responses of bed height and bed temperature are shown in Figures 4 and 5, respectively. The increase in coal to be gasified causes the bed height to climb slowly. After a pseudo-deadtime, the control scheme brings the bed temperature up, and the bed height returns to steady state. Although the dynamics are somewhat slow, the process responds stably and smoothly to the upset with a maximum bed height deviation of 0.6 m. The gasifier gas effluent composition response for this upset is shown in Figure 6. Except for a slight transient in the amount of H_2O in this stream, the gas composition does not change much during the upset.

Conclusions

A dynamic simulation has been developed for Exxon's CCG process. The simulation contains a detailed dynamic model of the gasifier and simplified models of the recycle loop units, and can be used for systems studies or control scheme tests.

Acknowledgements

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Table 1 Gas Phase Reactions Occuring in Gasifier

1) Gasification

$C + H_2O \rightleftarrows CO + H_2$

$$\text{rate} = \frac{\text{Fcat kg } (P_{H_2O} - P_{H_2O} P_{CO}/\text{Kg})}{(P_{H_2} + b_1 P_{H_2O})}$$

2) Methanation

$CO + 3H_2 \rightleftarrows CH_4 + H_2O$

$$\text{rate} = \frac{\text{Fcat km } (P_{CO} P^3_{H_2} - P_{H_2O} P_{CH_4}/\text{Km})}{(1 + b_2 P^2_{H_2})}$$

3) Shift

$H_2O + CO \rightleftarrows H_2 + CO_2$

assumed to be in equilibrium

Fcat = amount of active catalyst in bed

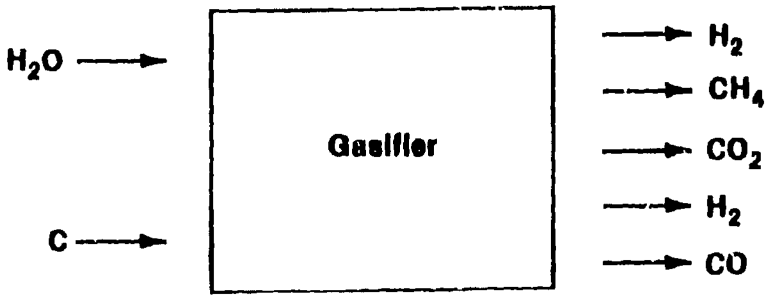
Table 2

GENERAL FLUIDIZATION RELATIONSHIPS (from Ref. 2)

- Superficial velocity at minimum fluidization, from the positive quadratic root of Ergun pressure drop relationship
- Jet height above distributor, from Mori and Wen correlation
- Bubble growth from Geldart's correlation
- Maximum stable bubble size from Coulaloglou's proprietary correlation
- Bubbling bed mass transfer coefficient, from Kunii and Levenspiel's model

Figure 1

COAL GASIFICATION CHEMISTRY



$2C + 2H_2O \longrightarrow 2H_2 + 2\,CO$ $\Delta Hr =$ 64 kcal Gasification

$CO + H_2O \longrightarrow CO_2 + H_2$ $\Delta Hr = --\ 8$ kcal Shift

$3H_2 + CO \longrightarrow CH_4 + H_2O$ $\Delta Hr = -54$ kcal Methanation

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$2H_2O + 2C \longrightarrow CH_4 + CO_2$ $\Delta Hr = 2$ kcal Overall

Figure 2

EXXON CATALYTIC COAL GASIFICATION PROCESS

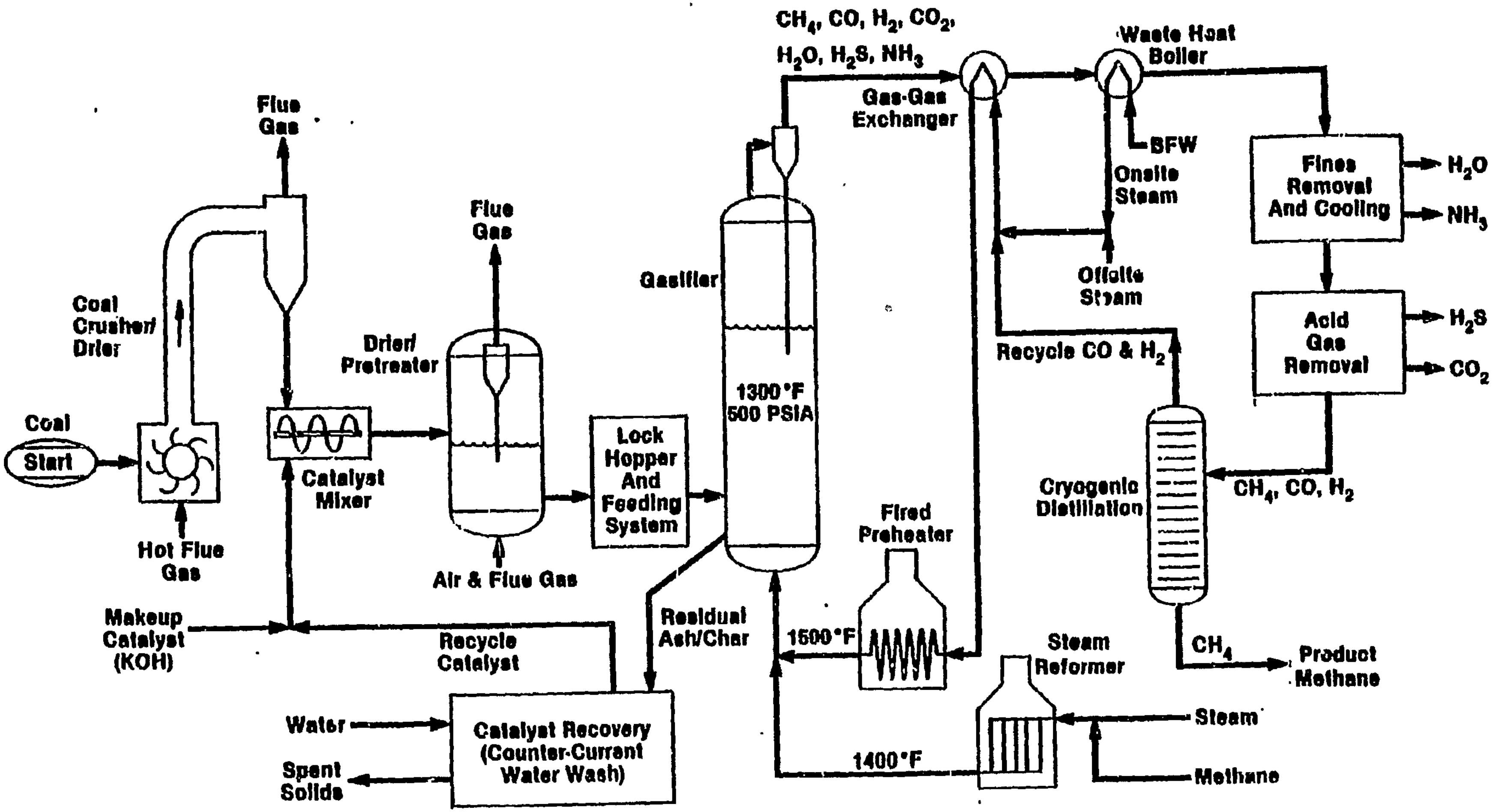

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Figure 3

STRUCTURE OF GASIFIER MODEL

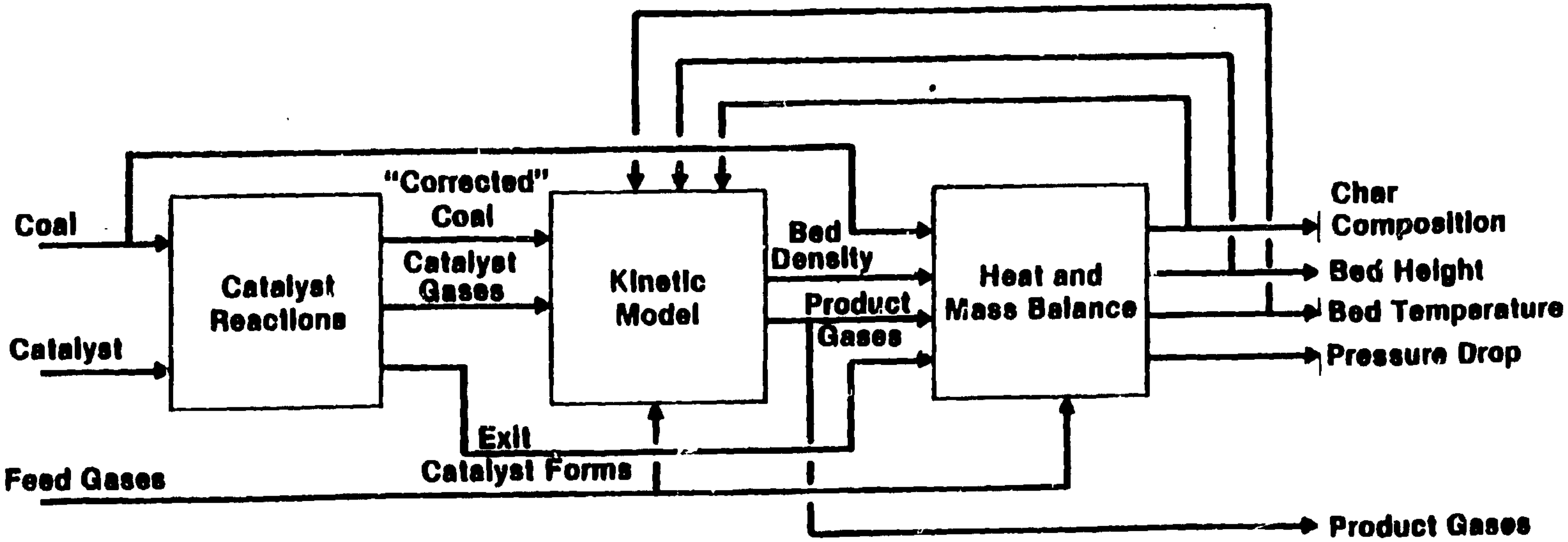

Figure 4

BED HEIGHT RESPONSE TO SOLIDS UPSET

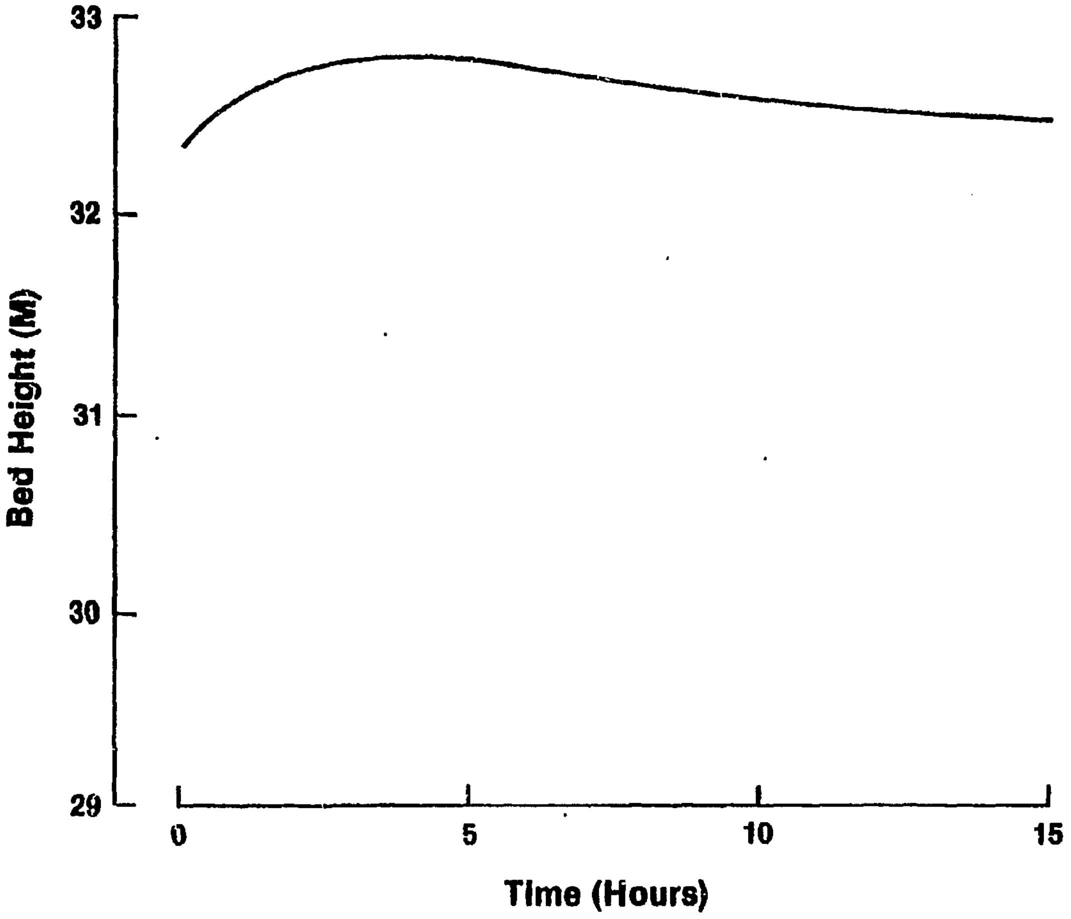

Figure 5

BED TEMPERATURE RESPONSE TO SOLIDS UPSET

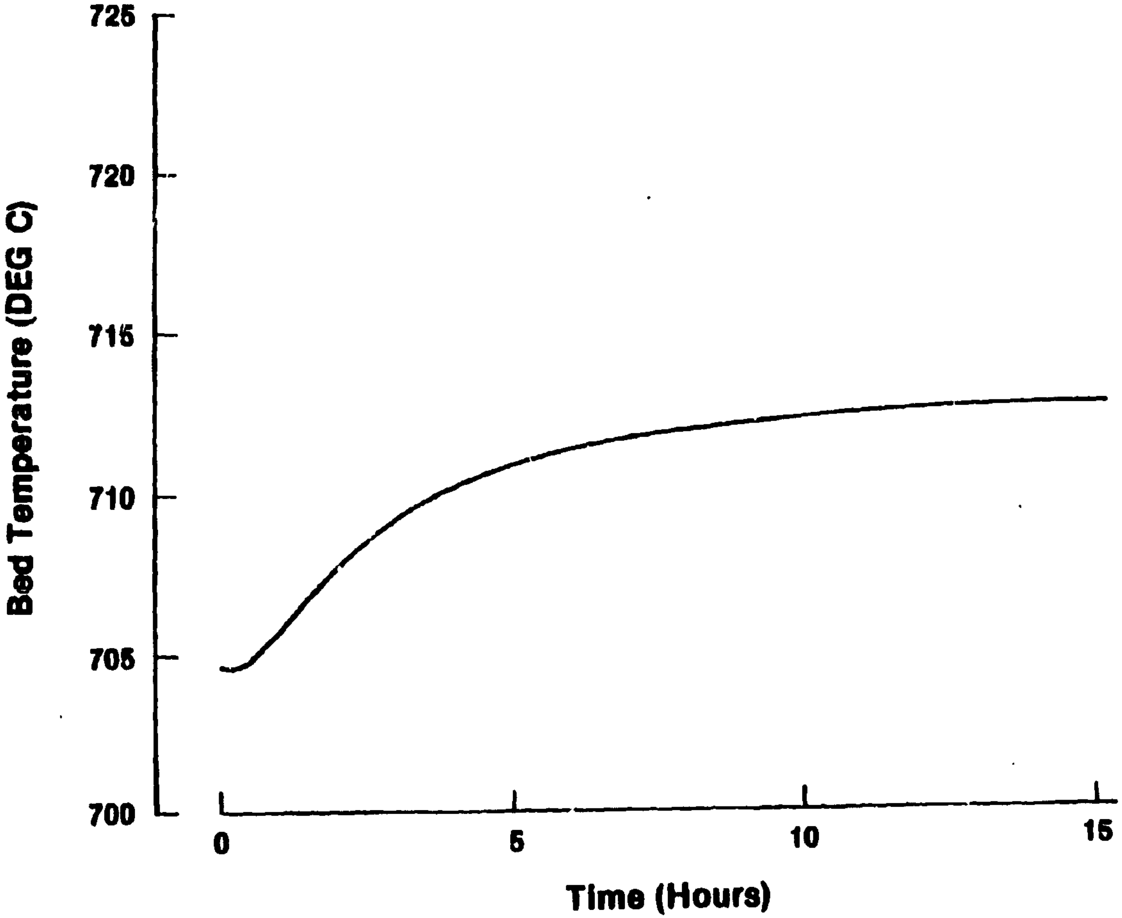

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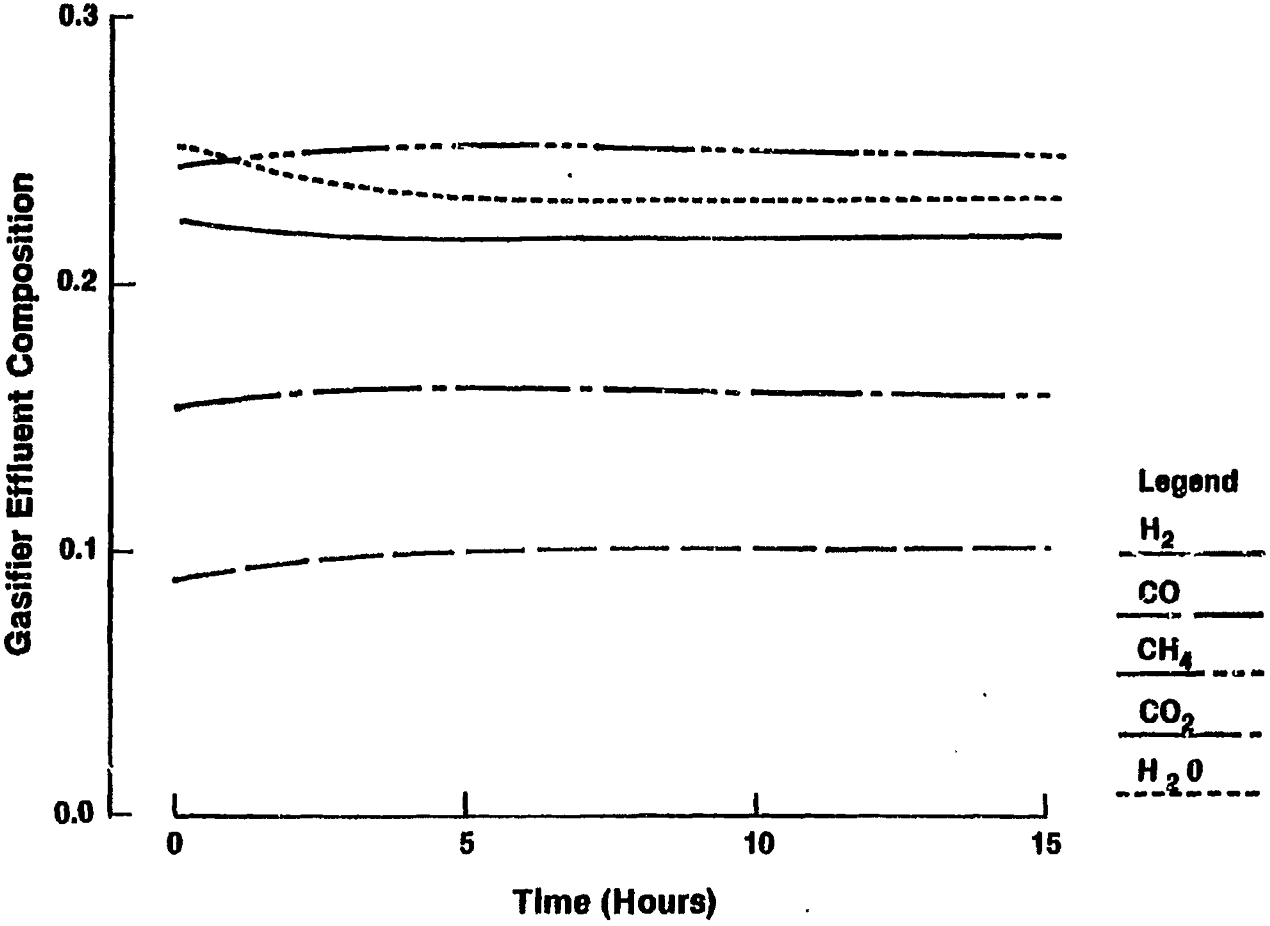
Figure 6

GASIFIER EFFLUENT COMPOSITION RESPONSE TO SOLIDS UPSET



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