

## HYDROGEN PROCESSING OF COAL AND THE KINETICS OF DESULFURIZATION

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### INTRODUCTION

The desulfurization of coal by hydrogen in the interests of abatement of air pollution, is a process with a potential for 90% sulfur removal or better, depending on the details of reactor design to cut down resorption back-reactions, and on other factors such as hydrogen concentration and reactor residence or contact time. The pollutant problem of course, is that of  $\text{SO}_2$  and  $\text{SO}_3$  formation during combustion of the coal - which is the dominant current use of coal - and there are in general two approaches to abatement. First, removal of the sulfur oxides from the combustion gases after formation. Second, the prevention of their formation by prior desulfurization of the coal. The first approach has the general drawback that even high S percentages in coal become very small percentages after dilution in air converted to combustion products. This means handling large volumes of gas containing small quantities of pollutant. Even on a weight basis the dilution is substantial: a given weight of S (say 0.05 lb) in one lb. of coal becomes about the same weight in about 12 lbs. of combustion products. Direct removal of the S from the coal by hydrogenation to form  $\text{H}_2\text{S}$ , therefore, has the appeal of handling substantially smaller quantities of material, either by weight or volume, together with the advantage that the component concentrations are also proportionately higher, thus improving chances of achieving a given target for efficiency of removal.

Desulfurization by hydrogen, however, is not a straightforward process since the  $\text{H}_2\text{S}$  formed in the first instance is very rapidly resorbed on carbon. Since the resorption is accentuated by higher temperatures and longer residence times, this generally means that net efficiencies of removal fall with increasing temperature and larger quantities of coal being processed. In considering reactor designs, which is the practical target of these desulfurization investigations, this chemical behavior means that an efficient reactor should operate at not too high a temperature, and that either the sweep gas should be at a very high velocity or else that a preferential absorber should be available in close proximity to the coal during hydrogenation. As a further consideration it is also evident that a suitable reactor design would either be a batch unit (such as a fluid bed), or a continuous counterflow, so that the terminal discharge of the almost cleaned coal should be in contact with a high hydrogen and low  $\text{H}_2\text{S}$  concentration.

The physical size of and retention time in any reactor are then determined by the desulfurization kinetics both in the presence and the absence of any preferential absorber. In a previous paper (1) we have already described most of

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what we now know of the chemistry and kinetics of the hydrodesulfurization of coal, obtained by adaptation of the Juntgen (2) "non-isothermal" method of experiment and analysis. This paper is concerned with discussing these and additional results of such experiments on S removal from coal, and H<sub>2</sub>S capture by coal char, carbon, and CaO (as a possible preferential absorber) particularly as these relate to reactor design. This includes a brief outline of a possible reactor complex and a Sankey (Energy Flow) Diagram for such a system.

### NON-ISOTHERMAL KINETICS

The non-isothermal method of Juntgen was extended theoretically and applied experimentally to the hydrodesulfurization of ten bituminous coals ranging from 1 to 5% (3). This powerful method overcomes the difficulties of partial achievement of equilibrium conditions of temperature, by treating temperature as a controlled variable. Essentially continuous measurements of reaction products in a flow system provide experimental functions whose theoretical interpretation identify sets of chemical reactions which are responsible for desulfurization. The kinetics of desulfurization of all ten coals are accounted for satisfactorily by five chemical reaction systems. This method gives activation energies and frequency factors for each chemical reaction.

We may summarize these chemical reactions and the rate data of coal desulfurization in hydrogen atmospheres by listing the measured kinetic parameters for the five major reactions and the two back reactions, as shown in Table I. Non-isothermal studies were also made of the removal of all H<sub>2</sub>S by calcined dolomites and limestones and some regeneration kinetics of the resulting calcium sulfide as shown in Table II.

TABLE I

#### CHEMICAL REACTIONS AND RATE DATA OF COAL DESULFURIZATION IN HYDROGEN ATMOSPHERES

No.	Reaction	E <sup>kcal</sup> /mole	k <sub>0</sub>
1	(Org-S) <sub>I</sub> + H <sub>2</sub> → H <sub>2</sub> S	34.5	3.1 × 10 <sup>10</sup> (atm H <sub>2</sub> ) <sup>-1</sup> min <sup>-1</sup>
2	(Org-S) <sub>II</sub> + H <sub>2</sub> → H <sub>2</sub> S	41.5	2.8 × 10 <sup>11</sup> " "
3	FeS <sub>2</sub> + H <sub>2</sub> → H <sub>2</sub> S + FeS	47	2.8 × 10 <sup>12</sup> " "
4	FeS + H <sub>2</sub> → Fe + H <sub>2</sub> S	55	2.1 × 10 <sup>13</sup> " "
5	(C-S) + H <sub>2</sub> → H <sub>2</sub> S	52	~ 2 × 10 <sup>13</sup> " "
6	Fe + H <sub>2</sub> S → H <sub>2</sub> + FeS	18	6.5 × 10 <sup>6</sup> (atm H <sub>2</sub> S) <sup>-1</sup> min <sup>-1</sup>
7	Coke + H <sub>2</sub> S → (C-S) + H <sub>2</sub>	32	2.3 × 10 <sup>8</sup> " "

TABLE II

8	CaO + H <sub>2</sub> S → CaS + H <sub>2</sub> O	38	4.7 × 10 <sup>13</sup> (atm H <sub>2</sub> S) <sup>-1</sup> min <sup>-1</sup>
9	CaS + H <sub>2</sub> O → CaO + H <sub>2</sub> S	55	1.0 × 10 <sup>14</sup> (atm H <sub>2</sub> O) <sup>-1</sup> min <sup>-1</sup>
10	CaCO <sub>3</sub> → CaO + CO <sub>2</sub>	58	3.0 × 10 <sup>12</sup> min <sup>-1</sup>
11	CaO + CO <sub>2</sub> → CaCO <sub>3</sub>	17	5.0 × 10 <sup>4</sup> (atm CO <sub>2</sub> ) <sup>-1</sup> min <sup>-1</sup>

The significance of these results to conditions of sulfur control can be seen by expressing them as rate constants versus temperature over the range of engineering interest. The rate constants for these reactions are shown from 400°C to 1000°C in Figure 1. There emerges a desulfurization band which encompasses the desulfurization reactions which account for the hydrodesulfurization of the ten bituminous coals studied.

## REACTOR SELECTION FOR HYDRODESULFURIZATION

The requirement that back reaction of H<sub>2</sub>S with carbon is to be suppressed by a combination of fast removal of product (H<sub>2</sub>S), preferential absorber, and/or maintenance of high H<sub>2</sub> and low H<sub>2</sub>S concentrations at termination of the reaction means that suitable reactors seem to be restricted to the fluid bed or some counterflow unit. In this paper we suggest that a continuous counterflow reactor is a better choice. There are, however, some simple general considerations on relative sizing that are pertinent and will be discussed first.

### Relative Sizing of Reactors

Suppose any reactor has a true or effective capacity of C lb/hr. of material being treated. If the reactor volume is V cu. ft., the reaction time required is t (hours), and the average materials density is  $\bar{\rho}$  (lb/cu. ft.) then these factors are related by

$$C = \bar{\rho}V/t \quad (1)$$

The specific capacity can then be defined as

$$C_v = (C/V) = \bar{\rho}/t \quad (2)$$

These two simple equations can now be used to provide estimates of the relative size of any pretreatment reactor for coal subsequently being burned in a boiler. If subscripts zero refer to the boiler, we first have the condition that the pretreatment and boiler capacities must be equal: so

$$C = \bar{\rho}V/t = \bar{\rho}_0 V_0/t_0 \quad (3)$$

or 
$$V/V_0 = (\bar{\rho}_0/t_0) / (\bar{\rho}/t) = C_v^0/C_v \quad (4)$$

Consequently, if we want a pretreatment reactor say 10% of the boiler volume, the corresponding specific capacity must be ten times greater. Considering next that

$$C_v/C_v^0 = (\bar{\rho}/\bar{\rho}_0) (t_0/t) \quad (5)$$

then, for the same reaction times, the materials density must be ten times greater in the pretreatment reactor. In a boiler, C<sub>v</sub><sup>0</sup> averages 2 lb/hr. cu. ft., t<sub>0</sub> is about 2 sec., and  $\bar{\rho}_0$  is, therefore, about 0.02 oz/cu. ft. The pretreatment reactor density would then be about 0.2 oz/cu. ft. which corresponds to a fairly dense cloud. From our non-isothermal experiments (1, 3), it is clear that the reaction times are more likely to lie in the range from 20 to 200 sec., so that the pretreatment reactor densities must lie between 2 and 20 oz/cu. ft. (or g/litre). Since this latter figure is still below what is found in fluidized beds, such density loadings are possible, but these estimates also

illustrate the magnitude of the problem in terms of the solid loadings required. The fluid bed, however, has the disadvantage that it is a batch, not a continuous, process. On the other hand a continuous process that will provide the necessary particle loadings and still allow the potential for rapid exchange of gases with a preferential absorber would only seem to be provided by the cascade reactor (described below), unless the preferential absorber is mixed with coal which then creates problems of separation.

### The Cascade Reactor

The cascade reactor is a vertical tube containing inclined shelves or plates to break the fall of particles cascading down from the top of the tube, against a rising current of reactive gas. It is based on the Cascade Heat Exchanger (4), which is a device intended to promote efficient heating of a gas by a solid (or vice versa) by counterflow, with advantage being taken of the relatively high heat exchange coefficient and large surface area of fine particles. One could, in principle, also obtain such exchange simply by pouring the particles into the top of a tube, but the nominal effectiveness of such a system is almost completely nullified by two factors. If the upward gas flow is slow, the particle shower can quite well create its own path by what is known as a "Chute-en-Masse" effect whereby the particles descend at very much higher velocities than in free fall of a single particle through a viscous fluid. Gas "contained" in the cloud is dragged with it, and incoming gas is likely to be short circuited through a more or less particle free region. Alternatively, if the gas velocity is quite high, the fastest velocities are at the center of the channel, which can pick up fines and carry them out of the system, while the velocity gradients throw the larger particles to the walls where they will fall at their greatest speed. If the particle concentration is also high at the walls the Chute-en-Masse effect may accelerate the rate of fall still further.

The purpose of the cascade plates can be described as a device for breaking the fall of the dust so that the retention time, and, therefore, the time available for heat exchange, is increased. The plates, therefore, prevent the dust plummeting down the center of the tube or the wall region.

The use of the cascade heat exchanger as a reactor is not known to have been proposed before. As a reactor it utilizes the counterflow operation of the cascade heat exchanger, with the possible gains to be achieved from breaking the fall of the dust to increase the retention time, but using the device for promoting reaction between a gas and a finely divided solid. The proposed reactor is intended to treat raw coal of appropriate fineness, with the objective of removing sulfur, delivering sulfur-free char and pyrolysis gas as primary output products, with  $H_2S$  as a potential source of sulfur as a by product (or co-product).

The basis of the method is low-temperature ( $700^\circ C$ ) hydrogenation, using a recycled fraction of the pyrolysis gas, during which: (1) a sulfur-containing pyrolysis gas is evolved for cleaning in a later or parallel stage; and (2) the coke formed is also rendered sulfur-free by direct heterogenous reaction between hydrogen and the sulfur in the coke, generating  $H_2S$ .

To estimate the mean velocity of the particle stream through the reactor designated as  $v_m$ , will be crucial in all subsequent analyses of all purposes the reactor may be used for.

In such a system the chute-en-masse effect is likely to override all other factors, such as viscous drag through the gas. In fact, the viscous drag can be responsible for entrainment of gas in the same direction as the dust flow. This can be thought of as an ejector action helping to stimulate a cyclic flow. In the limit, therefore, the particles are most probably close to free fall under gravity without significant retarding forces.

The simplest condition, therefore, is for the particle stream to fall vertically from the tip of one plate to the tip of the next. It is assumed to accelerate at  $g$  from zero velocity to a maximum which is again reduced to zero on impact. In fact, of course, there will be a horizontal component after impact, but this will be considered later. Suppose, therefore, a cascade element has a depth  $d$ , so the free-fall-distance apart of the plate tips is  $(d/2)$ : then

$$(d/2) = (1/2) g t_{\text{imp}}^2 \quad (6)$$

where  $t_{\text{imp}}$  is the time to impact; or

$$t_{\text{imp}} = d/g \quad (7)$$

The mean velocity  $v_m$  is, therefore

$$v_m = (d/2) / t_{\text{imp}} \quad (8)$$

$$= (1/2) g d \quad (9)$$

The velocity varies only slowly with the cascade depth ( $d$ ). If  $d=1\text{ft.}$  (plate spacing 6 in.)  $v_m = 2.8 \text{ ft./sec.}$  If  $d=6 \text{ in.}$ ,  $v_m=2 \text{ ft./sec.}$  If  $d=1.5 \text{ in.}$ ,  $v_m = 1 \text{ ft./sec.}$  This last is very narrow; the plate spacing is only 0.75 in. This would be adequate for many laboratory scale studies but handling 100 tons/hr. would be difficult.

It should, however, be emphasized that the calculations given above assume close to the worst conditions, and are, therefore, rather pessimistic. Average velocities of 1/2 to 1 ft/sec for plate spacings of 4 to 6 in. may be realistic with proper design. A 30 to 60 sec. retention time should, therefore, be possible with a unit 30 ft. high.

#### Cascade Reactor: Simple Analysis

The reactions involved in the cascade desulfurizer include the coal pyrolysis (initially assumed to be independent of the hydrogenation reactions).

For initial analysis purposes this can be treated as first order reaction using operational velocity constants. The rate of reaction can, therefore, be obtained directly as a function of time independent of the material location in the reactor. The location of the material in the reactor is then obtainable from the throughput velocity. This is valid for a plug flow system.

Assume that the rate of loss of pyrolysable material is proportional to the pyrolysable fraction. Let the pyrolysable fraction at any time  $t$  be  $V$  lb/lb of solid, then

$$dV/dt = -kV \quad (10)$$

where  $k$ , the velocity constant, may be the real velocity constant at a specified temperature, particle size, etc.; or it may be an "operational" velocity constant representing an effective or average constant that is valid to a specified margin of accuracy for a number of competing or consecutive reactions, possibly including changes in particle size and temperature. The variation of  $V$  with time (at constant temperature) is

$$V = V_0 \exp(-kt) \quad (11)$$

where  $V_0$  is the maximum pyrolysable fraction. The relation to distance is then given by

$$z = v_m t \quad (12)$$

where  $z$  is the distance travelled through the reactor in a given time  $t$ , if  $v_m$  is constant, where  $v_m$  is the mean velocity. Equation (11) becomes

$$V = V_0 \exp[-(k/v_m)z] = V_0 e^{-kz} \quad (13)$$

showing that the slower the material travels through (small  $v_m$ ), the larger the "distance constant, ( $k'$ )" and the more complete the reaction. This is quite obvious but equation (13) makes the point explicitly. This re-emphasises that anything that can be done by way of reactor design to reduce  $v_m$  can provide more effective control of the completeness of reaction.

Consider now the throughput at two different planes. Take  $z=0$  and  $z=z$ . At  $z=0$ , if the specific mass rate of input, lb. per hour per sq. ft. of reactor cross-section is  $M_0$ , then the rate of input of pyrolysable solids is  $(V_0 M)$ ; and the rate of input of non pyrolysable solids is  $(1-V_0)M$ . Similarly, at  $z = z$ , the mass rate of flow of non pyrolysable solids is  $(1-V)M$ . At steady state this quantity must be constant right through the reactor so

$$(1-V_0) M_0 = (1-V)M \quad (14)$$

$$\text{or } (M/M_0) = (1-V_0) / (1-V) = (1-V_0) / (1-V_0 e^{-kz}) \quad (15)$$

These equations can be rearranged in the form of a reactor efficiency.

Suppose  $M_c$  is the mass flow rate in an infinitely long reactor when pyrolysis is complete (i.e. the mass flow rate at any point of non-pyrolysable solids) then

$$M_c = M_0 (1-V_0) \quad (16)$$

Now suppose that for a finite length reactor the reaction is not complete, but the mass flow rate is  $M_{\text{exit}}$ . So

$$M_{\text{exit}} = M_o (1 - V_o) / (1 - V_{\text{exit}}) = M_c / (1 - V_{\text{exit}}) \quad (17)$$

Now defining reactor efficiency,  $n$ , as

$$n = \frac{V_o - V}{V_o} = 1 - V/V_o = 1 - e^{-kt} \quad (18)$$

In terms of the mass flow rates this can be written

$$n = (1 - M_c/M_o) / (1 - M_{\text{exit}}/M_o) \quad (19)$$

Since only mass flow ratios are involved the efficiency is independent of mass flow except to the extent that this might possibly affect the mean velocity through the reactor.

### Reactor Efficiency Compatibilities

The information developed by the above analysis can now be combined with the kinetic data set out in Tables I and II and Figure 1 to estimate possible reactor efficiencies. The values obtained are essentially order of magnitude estimates but this is sufficient for our immediate purpose in demonstrating the reasonableness, or otherwise, of using the Cascade Reactor for at least some of the reactions involved in the desulfurization process. Primarily we are interested in estimating reactor temperatures at which reasonable reactor efficiency can be achieved; and to establish these (as estimates) let us assume 99% efficiency in each reaction. In Equation (18) we, therefore, have

$$\exp(-kt) \approx 10^{-2} \quad (20)$$

as the criterion for such efficiency. Since  $\exp(-kt)$  can be written as  $10^{-kt/2.3}$ , and since the reactor retention time is estimated (above) to be 1/2 to 1 min., the values of the velocity constant,  $k$ , to meet the criterion of Equation (20) is that:

$$k \approx 5 \text{ to } 10 \text{ or greater (min)}^{-1} \quad (21)$$

Referring now to Figure 1 we find listed values of rate constants with dimensions  $(\text{atm. min})^{-1}$  since all the reactions are all first order with respect to a reactive gas ( $\text{H}_2$ ,  $\text{H}_2\text{S}$  etc.). If the reactive gas concentrations are in large excess and in the region of 0.1 atm. then multiplying all the values of the rate constants given by  $10^{-1}$  changes them in effect to pseudo first order constants for comparison with the criteria of Equations (20) and (21). For the values of  $k$  to lie between 5 and 10 the true rate constants must lie between 50 and 100. From Figure 1, this corresponds to temperatures in the desulfurization band of roughly 600 to 700°C. If the reactive gas concentrations are 0.01 atm., the rate constants then required (for 99% reaction efficiency) are raised to the range (roughly) of 700 to 900°C. With reactive gas concentrations of 0.001 atm. the required temperatures would be in the range 900 to 1200°C.

Summarizing, therefore, what we have estimated here: we have used the

cascade reactor retention times (estimated by the free fall assumptions) in combination with the reactor analysis for a first order reaction, to estimate the temperature ranges required for the reactor to be operated at, if reaction efficiency is to be 99%. To do this, the second order rate constants given in Figure 1 have been treated as pseudo first order constants by multiplying by 0.1, 0.01, and 0.001 atm. to represent average concentrations of the reactive gas involved; and for the desulfurization reactions the temperature range is found to be 700 to 800°C for an average reactive gas concentration of 0.01 atm.

This, it must be emphasized, is no more than a rough estimate to determine whether the cascade reactor may be a possible rational choice in any complete desulfurization scheme; and from the estimates obtained here it would seem that it probably is.

### A REACTOR COMPLEX FOR HYDROGEN PROCESSING OF COAL

Although the prime purpose of this paper is to initiate analysis of suitable generalized reactors for desulfurization, by hydrogenation, of coal in terms of the kinetic behavior of known mechanisms (with particular attention, of course, to the cascade reactor), a brief look at a possible complete scheme for continuous hydrogen processing is not out of place. This brings into focus the inter-relationships that have to be developed quantitatively between component parts of any such scheme, particularly as this influences choice of any given type of reactor.

#### Schematic for Continuous Processing

As already mentioned above, one of the principal problems in desulfurization by hydrogenation is the speed of the back reaction as  $H_2S$  is resorbed on carbon (reaction 7 in Table I) as this then necessitates either the rapid physical removal of the  $H_2S$  (high throughput velocities) or the presence of a preferential absorber such as  $CaO$  (reaction 8 in Table II) for chemical removal. Unfortunately, mixing the absorber with the coal introduces subsequent problems of separation. The Cascade Reactor, however, would seem to permit an additional possibility that is something of a compromise between both alternatives: that the coal and absorbent streams can be kept separate while the gas streams are common. The method would be to operate two cascade reactors side by side with two sets of plates to separate the solid streams, but with arrangements to cross-mix the rising gas streams by suitable baffles.

The workability of such a proposal has yet to be demonstrated physically, but the advantages accruing from it, should it prove workable, are so substantial that it encouraged analysis to establish the energy requirements for a complete scheme based on this cross-mix reactor. The gross energy requirements have been examined by constructing a Sankey (Energy Flow) Diagram for the system (see below). The complete scheme is based, as explained, on the cross-mix reactor, but regeneration of the  $CaO$  with sulfur recovery is also included by incorporating two additional reactors: (1) for conversion of  $CaS$  to  $CaCO_3$  and (2) for calcination to reform  $CaO$ .

The complete scheme is illustrated in the block diagram of Figure 2. This diagram shows a total of six chambers comprising one preparation unit

for drying and preoxidation, and four reactors. Their functions are as follows:

R0: Drying and Preoxidation (Preparation unit).

R1: Pyrolysis and Hydrogenation of sulfur-containing-coal, and including gas preheat of recycled fuel-gas by cooling char.

R2: Calcination of  $\text{CaCO}_3$  to form  $\text{CaO}$  for  $\text{H}_2\text{S}$  absorption.

R3: Absorption of  $\text{H}_2\text{S}$  carried across from R1, by  $\text{CaO}$ . The concept requires a design such that the gases in R1 and R3 have equal access to both reactors while the coal and absorbent streams remain separate.  $\text{CaS}$  is formed by absorption.

R4: Regeneration of  $\text{CaS}$  formed by  $\text{H}_2\text{S}$  absorption in R3, utilizing reaction of steam and  $\text{CO}_2$  to reform  $\text{CaCO}_3$ , which is then cycled back to R2 after separation from reformed  $\text{H}_2\text{S}$ .

In selecting reactor types for all these operations, Reactors R1 and R3 are assumed to be Cascades. For the rest, however, the analysis leading to the Sankey Diagram is valid when any continuous counterflow reactor is used.

#### SANKEY DIAGRAM ASSUMPTIONS

In performing the Sankey Analysis a number of assumptions about the system and materials were made, as follows:

##### Sulfur Content and Removal

The coal to be treated is assumed to contain 5% sulfur by weight. This is assumed to be totally removed in Reactor R1 as  $\text{H}_2\text{S}$  by hydrogenation; absorbed in R3 as  $\text{CaS}$ , regenerated in R4 as  $\text{H}_2\text{S}$ , followed by recovery by the Claus Process.

##### Coal Pyrolysis

The maximum temperature of the coal is assumed to reach  $700^\circ\text{C}$  so pyrolysis corresponds to low temperature carbonization. For a 40% V.M. coal a 30% pyrolysis/hydrogenation, loss is assumed of which 5% is sulfur as  $\text{H}_2\text{S}$ . If the coal is such that the pyrolysis/hydrogenation loss is less than this the majority of the calculated energy flows in reactors R2, R3, and R4 are reduced approximately prorata. The balance of material (not pyrolyzed) is a semi-coke that can be assumed to be of higher reactivity than a full coke.

##### Temperature Profiles

In reactors R2, R3, and R4 the temperature profiles are simple, either rising or falling monotonically from one end to the other, with the counterflow material temperature falling or rising correspondingly. The reactor R1 presents a different problem. Its temperature is highest at the center, for both counterflowing materials, so an overall heat balance shows a relatively small net supply of heat,  $Q_{31}$  sufficient for the sensible heats of coal char and pyrolysis products and the heat of pyrolysis. This is the heat supply that has been calculated. It is assumed to be carried across from reactor R3 to R1 partly by hot gas transfer, and partly by conduction where the temperature differentials will allow this. In addition, there is a sizable quantity of heat, not included in the diagram, required for the initial sensible heat of the coal to heat

it from input temperature to reactor temperature (700°C). This is recovered in the hot-gas/pyrolysis-products transfer from R1 to R3, so it recycles continuously. It has to be assumed, however, that the appropriate heat transfer mechanisms will so operate that this necessary heat flow cycles properly. This is a substantial assumption.

## REACTOR CONSIDERATIONS

### Reactor Capacities and Reaction Times

These, of course, are not yet determined. The calculations are based on a coal supply of 100 lb. If the process capacity is to be 100 lb/hr. then the material and energy flows shown in the diagram become flow rates (lb/hr. of material CHU/hr. energy). The reactor duty is then specified, and the reactor capacity can be calculated from the reaction time so that the appropriate duty is attained. On the other hand, this may well affect the final choice of reactor. It seems probable that the reaction time for absorber regeneration in R4 at the temperature specified is too long for a cascade reactor to be feasible. However, the temperatures are such that a tunnel reactor, with a belt conveyor in counter-flow to the reactant gases, may be possible, or even an array of fluidized beds.

### Losses and Source of Energy

Losses are initially neglected. The prime source of energy into the reactor set is by combustion of part of the cleaned pyrolysis products leaving reactor R3. This supplies some sensible and mainly potential heat to the reactor R2. On combustion most of this heat enters the CaO which carries it into R3. Some of this heat then exchanges with the cooler recycle gas and pyrolysis products. The balance (the majority) is assumed to be carried into reactor R1 as sensible heat where it is used for pyrolysis. Some of the heat of combustion in R2 leaves in the product gases which are cycled to R4, to provide the CO<sub>2</sub> and part of the H<sub>2</sub>O required for reaction there. The rest is absorbed in the endothermic calcination in R2, but this is recovered again as heat of reaction, a little in R3 but most in R4. In addition, there is the internal cycling of sensible heat referred to in Temperature Profiles above. At present it seems necessary to assume that much of this is supplied by conduction through the construction materials of the dual R1 and R3 reactors, and is returned again to R3 by the pyrolysis products exchange.

Losses (wall; reactor exchange etc.) can then be included at any time by requiring an appropriate increase in the fraction of pyrolysis products burned in R2, with the heat thus generated assigned to losses.

### Sankey Diagram Analysis

The Sankey Analysis is a heat and mass balance on each individual reactor. Based on the assumptions listed above, some of the inlet and exit temperatures could be preselected, as follows:

- R1:  $T_{\max}$ : (near center) not to exceed  $700^{\circ}\text{C}$ .  
 $T_{\text{inlet}}$ : assumed to be  $50^{\circ}\text{C}$  (following drying and light preoxidation).  
 $T_{\text{outlet}}$ : unspecified - to be determined ( $T_c$ ).
- R2:  $T_{\text{inlet}}$ : selected as  $500^{\circ}\text{C}$  to match outlet temperature of R4 (see R4).  
 $T_{\text{outlet}}$ : specified as  $1000^{\circ}\text{C}$  to assure adequate calcination rate of  $\text{CaCO}_3$ .
- R3:  $T_{\text{inlet}}$ : selected as  $1000^{\circ}\text{C}$  to match outlet temperature of R2.  
 $T_{\text{outlet}}$ : unspecified - to be determined ( $T_e$ ).
- R4:  $T_{\text{inlet}}$ : Selected to match outlet temperature of R3 after this (R3) determination ( $T_e$ ).  
 $T_{\text{outlet}}$ : because of the heat of reaction this exceeds  $T_{\text{inlet}}$ . Because of reaction requirements the peak temperature (which is  $T_{\text{outlet}}$ ) must be lower than  $600^{\circ}\text{C}$ . A temperature of  $500^{\circ}\text{C}$  was selected for calculation to allow some margin for adjustment.

In then setting up the energy balances for the individual reactors there are four equations, one for each reactor, but with a total of five unknowns, only two of which are the unknown temperatures listed above.

1.  $T_c$ : the exit temperature of the semi-coke leaving R1.
2.  $Q_{31}$ : the heat transferred from reactor 3 to R1.
3.  $T_e$ : the exit temperature of the solids leaving R3 to enter R4, the solids being  $\text{CaS}$ ,  $\text{CaO}$ , and inert.
4.  $M$ : the solids quantity cycling round reactors R2, R3, and R4, to temperate R4 and supply heat from R2 to R3.
5.  $P$ : the quantity of pyrolysis gas required to heat the  $\text{CaCO}_3$  and inert in R2 to  $1000^{\circ}\text{C}$ .

The four reactors are treated separately. In all calculations input and output enthalpies are determined with respect to  $0^{\circ}\text{C}$  as zero. Atmospheric pressure is assumed so specific heats are all at constant pressure, where this is relevant.

Completing the heat and mass balances then led to sufficient information to complete the Sankey Diagram when a final item of information was included since the system was otherwise indeterminate with five unknowns but only four equations. The calculations showed that, if the physical mechanisms would allow it, heat could flow either from R1 to R3, or from R3 to R1. However, we know that the temperatures in R1 must always be less than those in R3 since otherwise net heat would not flow from R3 to R1, and the system would not work. If the mechanism of heat transfer is by conduction through the brickwork of the adjacent reactors, then a substantial temperature difference must be maintained between the two. This immediately limits the exit temperatures of R1 and R3 to  $225^{\circ}\text{C}$  or less (determined by the analysis); indeed it must be substantially less than  $225^{\circ}\text{C}$  if the temperature difference between the two reactors is also to be substantial. This restriction is less stringent, however, if the heat exchange between the two reactors is mainly convective. In the limit, in fact, if gaseous exchange between the two reactors is extremely fast - which is also highly desirable from the absorption point of view - the gas temperatures can be almost equal (the "stirred reactor" condition), and this is, in fact, the condition assumed. It is possible under good design conditions for this to be not unrealistic, at least for the lower half of each of the two reactors (R1 and R3), though it will not be true

at the top of each reactor. Here, the coal enters cold ( $50^{\circ}\text{C}$ ) and the  $\text{CaCO}_3$  and inert enter hot ( $1000^{\circ}\text{C}$ ) and this is expected to provide sufficient temperature differential to generate the heat flow required to heat the incoming coal to  $700^{\circ}\text{C}$ .

Adopting the "stirred reactor" or equivalent temperatures condition for  $T_e$  and  $T_c$ , these have equal values at  $225^{\circ}\text{C}$ . The value of  $M$  required is then about 150 lb/100 lb. coal, and  $P$  is 3.8 lb. of volatiles/100 lb. coal. Finally, the net heat flow required for the coal pyrolysis at a coke exit temperature of  $225^{\circ}\text{C}$  is 32,500 CHU. In summary, therefore, the values adopted for the five unknowns are as follows:

1. and 2.  $T_e = T_c = 225^{\circ}\text{C}$
3.  $M = 150$  lb. inert/100 lb. coal.
4.  $P = 3.8$  lb. volatiles/100 lb. coal.
5.  $Q_{31} = 32,500$  CHU/100 lb. coal.

These are the values used for constructing the Sankey Diagram.

#### THE SANKEY DIAGRAM

The specific objectives in constructing the Sankey Diagram are restated below:

1. To determine the process feasibility in terms of the energy requirements.
2. To establish the expected reactor temperatures.
3. To establish the material flow requirements.

The prime conclusion drawn from the diagram is that the material and energy flows are acceptable and compatible with realistic reactor temperatures, so long as the simplifying assumptions are not too unrealistic. This is assessed to some extent in the following commentary.

1. Taken at its face value the Sankey Diagram summarizing the calculations supports the feasibility of the proposed process. Specifically, if the assumptions made are realistic, then the quantities of materials to be handled are not excessive, the temperatures involved are reasonable and well within limits of many current industrial processes. Perhaps most important of all, the energy self-consumption of the process is relatively small. As calculated it is under 13% of the energy of the cleaned pyrolysis products, and about 4% of the total potential thermal energy in the raw coal. This must, of course, be a somewhat optimistic estimate since the analysis excludes heat losses and power requirements for fans, pumps, transfer machines etc. Allowing for these by an increase of 50% in the self-consumption, then this becomes 6% of the potential energy.

2. This estimate of 6% self-consumption may at first sight seem a little high compared with the typical figure for a modern power station of 4 to 5%. This means that an additional 6% could be too high a penalty to pay; however, of the 6%, only 2 or 3% represents unrecoverable losses. This will be clear from examining the Sankey Diagram where the bulk of the 33,000 CHU supplied to the system by burning 3.8 lb. of pyrolysis products reappears in three ways:

(1) as sensible heat of the pyrolysis products, totalling 8,500 CHU; (2) as sensible heat of the char, totalling 6,300 CHU; and (3) as enthalpic heat of pyrolysis, totalling 20,000 CHU, but which reappears as slightly increased heat of combustion per pound of both char and pyrolysis products so it is recovered on combustion (These are the figures for Reactor R1 above: a further 2,300 CHU are supplied by the sensible heats of coal and hydrogen, and the  $H_2/S$  heat of reaction).

This means that about 2/3 of the energy supplied by combustion of the pyrolysis products is automatically recoverable on combustion of the cleaned output. Even more can be recovered if the char and pyrolysis products can be burned immediately without any wastage from cooling since this will recover most of the sensible heat in the output. The system is, therefore, potentially conservative from the energetics point of view.

3. There might still be problems in recovering the sensible heats in the two outputs. For the pyrolysis products this should be the simpler problem of the two since the gases only have to be mixed with air to provide a stable flame - at 1000°C flame holding is no problem - so these could be burned directly in a boiler. Problems would arise primarily as materials problems in confining the high temperature gases till they enter the boiler. Some degree of pre-cooling might, therefore, be required to a temperature where the gases can be handled in metal pipes. There might even be some reason to cool the gases completely and use them as a make-up source for pipeline gas (although the Btu/cu. ft. volume is a little low for this).

4. The problems in handling the char could be greater although the temperatures are initially very much lower. The char should be in much the same form that the coal is originally introduced. If the reactor is a cascade, the coal should be crushed. The char will, therefore, be relatively coarse and certainly unsuitable for immediate use in a conventional pulverized coal boiler: indeed, even if fine enough, conventional belief is that there would then be flame holding problems. The char would otherwise be nominally suitable for direct use in an axial-fired cyclone combustor, but this is only possible if the ash fusion characteristics are also appropriate.

This, unfortunately, indicates that some other combustor may have to be devised. One interesting possibility would be to construct another cascade unit, with water-cooled cascade plates, to burn the char in; however, this would require the development of an entirely new technology. The alternative is only a little better since it again requires a new technology. The char would be suitable for combustion in a fluid bed. Here the necessary technology is being developed. It is not yet commercial, but it is now in a usefully advanced research stage.

5. Development of new technology of a fairly complex character is also a factor militating somewhat against the proposed scheme. The problem that should be borne in mind is that current utility plants for the most part have a high reliability, and utility engineers for the most part are likely to expect additions to existing plants of similar reliability. This is also likely to be a serious matter in view of the current small margin of reserve generating capacity over increasing demand. Unscheduled outages at peak demand could result in brown-

outs or black-outs over appreciable regions. For these reasons it would obviously be desirable to develop the cleaning system in stages. This would mean completing reactors R1 and R2, using precalcined lime and not attempting sulfur recovery and regeneration in the first place. Recovery can then be developed on an open cycle basis, and if this proves successful, the closed cycle operation can be completed.

6. The success of the whole concept, however, is predicated upon certain key assumptions that are still somewhat marginal in our present state of information. The most important of these is the assumption that the gases will exchange with sufficient speed between reactors R1 and R3 that  $H_2S$  absorption by  $CaO$  will be reasonably rapid after the  $H_2S$  has been formed, and that resorption by coke will always be a minor process. If this is true then it is also likely to satisfy the second assumption that the temperatures in R1 and R3, at least in the lower sections of the two reactors, are much the same. A third critical assumption is that the reactors can be built tall enough, but without being excessively high, for the residence times to be long enough for both desulfurization and desorption. Finally, there are the closely related assumptions (1) that the heat exchange between R1 and R3 assumed to take place in the upper sections, that provides the sensible heat for the coal to reach  $700^\circ C$ , will take place; and likewise (2) that the heat recovery in the lower sections that will reduce the material temperatures to  $225^\circ C$  will also be possible.

Definitive information on these assumptions is still lacking. This will require experiments on cascade operation. If, however, experiments should show them to be valid, then the cleaning process can be operated at least on an open cycle basis. Energetically this may be less satisfactory, but as mentioned above, the technological complexity will be reduced substantially.

7. There are, finally, two respects in which the Sankey Diagram is not quite complete:

(a) As already mentioned, sensible heat required to raise the incoming coal to  $700^\circ C$  will be recovered from R1 and returned to R3 (if the assumed energy recovery in the lower sections occurs). Since this is continued exchange from R3 to R1 and back again, it should appear on the diagram as a closed loop of sensible heat. The actual quantity required for this is not very high: 16,250 CHU/100 lb. coal; and its omission is not mechanistically important if the system works as envisaged. For if it works, then this exchange occurs; if the exchange does not occur, then the system has failed as so far described. This, however, should only mean that alternative methods of injecting the necessary energy into R1 must be used. Appropriately modified for this, the scheme should still be operable although the overall energy balance may not look quite so good.

(b) The second omission is again a closed loop, this time of material. To make sure that sulfur is removed at an adequate rate the R1 reactor should contain as high a hydrogen concentration as possible, particularly in the lower sections for sulfur recovery from  $H_2S$  resorbed by the coke. Since most of the volatiles (containing the hydrogen) will be released near the center of the reactor, and will then rise, the lower section is likely to be deficient. An appropriate fraction of the cleaned pyrolysis products must, therefore, be

cooled (to allow handling) and injected into the bottom of reactor R1. Since this is a mass flow cycling internally there is no net decrease in the volatiles output; for complete representation, however, the diagram should include a closed loop to represent this recycle.

## CONCLUSIONS

From the considerations discussed above, desulfurization of coal by hydrogenation before combustion appear to be feasible, energetically and materially. The kinetic data obtained by the non-isothermal method of Juntgen are quite adequate for making preliminary estimates of reactor size. From these it would appear that the reaction times for the desulfurization and for the H<sub>2</sub>S absorption may be compatible with residence times in a reasonably sized cascade reactor. The regeneration and calcination on the other hand is problematical, but for these more conventional methods such as shaft reactors may be quite suitable. The possibility of making such judgments, therefore, illuminates the value and necessity of adequate kinetic data, such as were obtained by the non-isothermal method, to enable design of reactors in the rapid development of a new technology.

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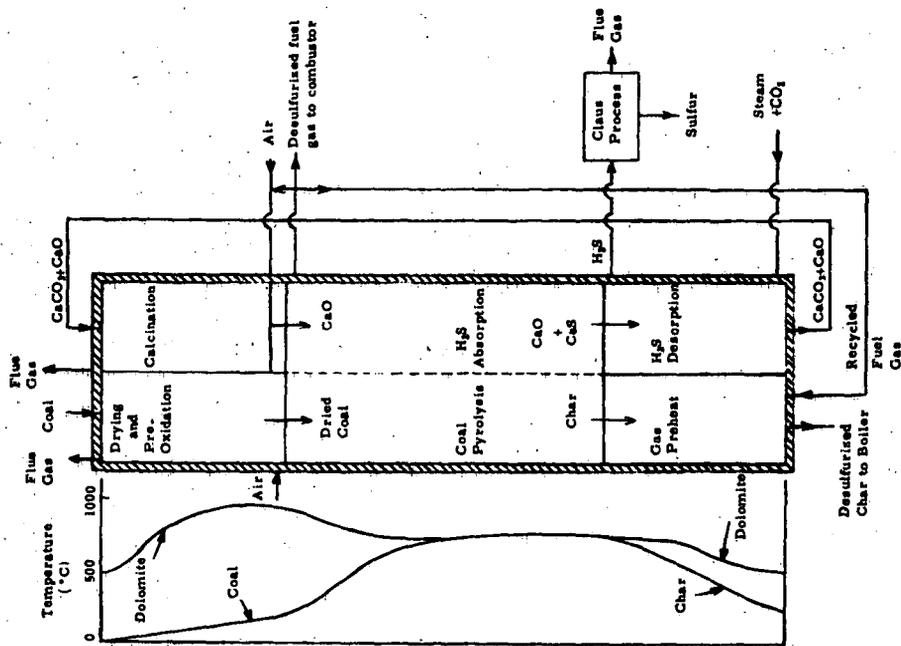


Figure 2. Simplified Block Diagram of Complete Conceptual Desulfurisation System

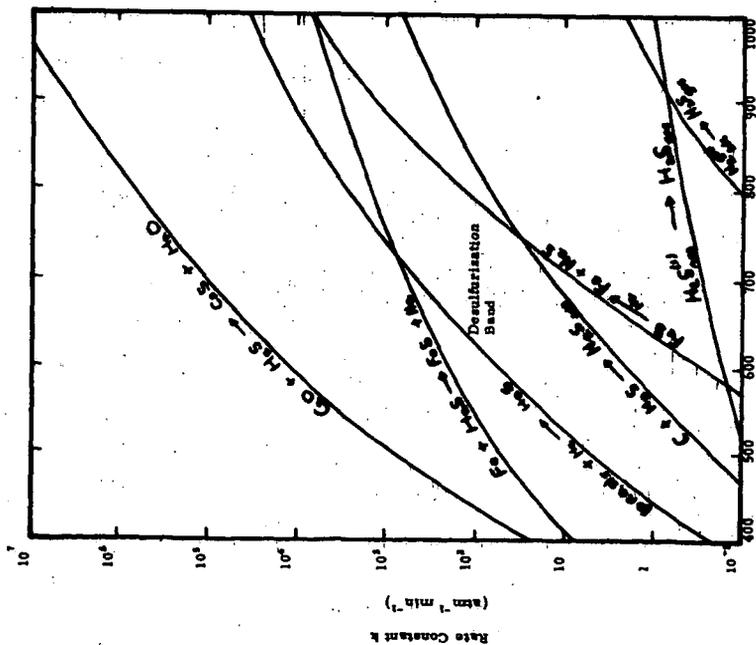


Figure 1. Rate constants for coal desulfurisation reactions and for important back reactions as functions of temperature.

