

The use of sulfur to extract hydrogen from coal

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Abstract

The world's recoverable coal reserves contain about 3×10^{10} tons of hydrogen. The reaction of sulfur vapor with medium-volatile bituminous coal produces hydrogen sulfide in yields up to 97% (based on sulfur), and utilizes 70–75% of the hydrogen from the coal. The conversion of hydrogen sulfide to hydrogen can be effected through commercially proven processes; several laboratory-scale processes could also be scaled up for future use. The solid by-product of the coal-sulfur reaction meets or exceeds specifications for fixed carbon, ash, and friability of conventional metallurgical coke, though produced at lower temperatures than typical by-product coke ovens. A conceptual process is presented in which sulfur is converted to hydrogen sulfide by reaction with coal, the hydrogen sulfide in turn is converted to the desired hydrogen and to sulfur, and the sulfur is recycled through the reactor. The by-product is a good quality coke, but may also have other applications as a carbon material.

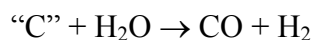
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1. Introduction

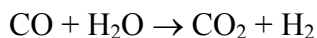
The use of hydrogen as an energy source, whether on a broad scale in the so-called hydrogen economy or in localized niche markets, presents technical challenges in three areas: production; transportation, storage, and handling; and utilization. Strategies for the production of hydrogen focus mainly on water as the feedstock. The approaches for splitting the water

molecule involve electrolysis, thermolysis at extreme temperatures, or chemical reactions. Many substances are capable—depending on reaction temperature—of reducing water to liberate hydrogen. For large-scale or wide-spread commercial application, forms of carbon are likely the most advantageous economically. Of these carbon sources, coal is the cheapest and among the most abundant.

The reaction of coal with water (in the form of steam) is the basis of coal gasification technology, and has been practiced in some fashion since about the 1860s (Berkowitz, 1979). If we use “C” as a symbol for coal, recognizing that coal is not of course pure carbon, the reaction is



The mixture of carbon monoxide and hydrogen that is the primary product can then be “shifted” by further reaction with steam



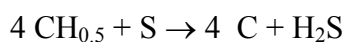
Various techniques—physical dissolution, chemical absorption, membrane separation, or cryogenic separation—are available for removing the carbon dioxide (Kohl and Reisenfeld, 1985), leaving hydrogen as the desired product. (The many details of both chemistry and engineering practice of coal gasification are discussed in various useful references, e.g. Schora, 1967; Berkowitz, 1979; von Fredersdorff and Elliott, 1963; Hebden and Stroud, 1981.) Coal gasification, followed by shifting the CO/H₂ mixture and removal of the CO₂, represents a strategy for production of hydrogen that is often referred to as “hydrogen from coal.” In fact, in this context the term is a misnomer, because here the hydrogen comes mainly from water, and not from the coal.

In contrast to the approach of using coal as a reductant to obtain hydrogen from water, we have developed a reaction scheme that actually extracts hydrogen from the coal itself. Based on recent estimates, the world’s recoverable coal reserves amount to 1.09 x 10¹² tons (Schobert and Song, 2002). If we were to assume that the average hydrogen content of the world’s coal, as it exists in the seam (i.e., complete with mineral matter and moisture), this coal represents a source of 3.26 x 10¹⁰ tons of hydrogen.

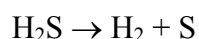
Our process is based on the use of sulfur to facilitate the dehydrogenation of coal. Sulfur was selected for two reasons. First, it is relatively inexpensive, though we anticipate the possibility of recycling the sulfur through the process. Second, sulfur is a good reagent for

dehydrogenation of organic compounds, the hydrogen being removed as H₂S. One formerly used preparative method for H₂S was the heating of sulfur with paraffin (Bloxam, 1913; Kleinberg et al., 1960). Among the other kinds of compounds known to be dehydrogenated with sulfur include abietic acid (Fieser and Fieser, 1944), butane (Rasmussen et al., 1946), cyclohexane (Szmant, 1957), methyldecalins (Cram and Hammond, 1964), various sesquiterpenes (Bordwell, 1963) (e.g., the conversion of cadinene to isocadinene and selinene to eudalene (Fieser and Fieser, 1944)), and tetralin (Turner, et al., 1936; Fuson, 1950). A third reason for initially considering sulfur, though it later proved not to be important in our work, is that many of these dehydrogenation reactions proceed at comparatively low temperatures, usually below 300°C, and typically 230–250°C (Fieser and Fieser, 1957). The mechanism of the reaction is not well understood (House and Orchin, 1960; Silverwood and Orchin, 1962).

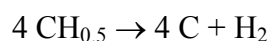
The process can be represented as



where we use CH_{0.5} as a simplified empirical formula for coal. Processes for splitting hydrogen sulfide to sulfur and hydrogen



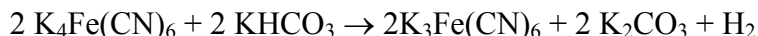
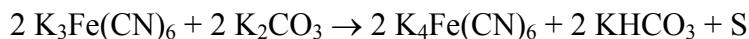
are known, but were not investigated as part of the present work. They are discussed below. The net reaction obtained by summing these two equations is the desired



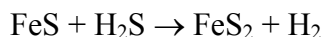
Since the sulfur can be recycled, there is little reagent cost, except for make-up sulfur to replace any losses in the recycle loop. More attractively, the highly carbonaceous solid by-product offers two possibilities: First, it could be returned to the earth as a strategy for sequestering carbon. Second, the carbon may have significant economic value as a precursor to production of premium-value carbon materials. By-product credits from sale of the carbon could offer an economic incentive for this process. Indeed, we will show here that the solid product from our experiments has characteristics of good-quality metallurgical coke, despite having been produced at temperatures below those of conventional slot-type coke ovens.

Several methods are available for producing H₂ from H₂S. The Fischer process (Müller, 1931; Thau, 1932) was used at an industrial scale in Germany prior to World War II. The chemistry is somewhat complex, involving absorption of H₂S in a solution of potassium

carbonate and potassium hexacyanoferrate(III), followed by electrolysis to liberate hydrogen and regenerate the reagents:



Thus the net process is the desired $\text{H}_2\text{S} \rightarrow \text{H}_2 + \text{S}$. The Appleby-Frodingham process (Reeve, 1958) has also been used on a commercial scale to absorb H_2S in a bed of iron(II) oxide. Though not part of the commercial process, the further reaction of iron(II) sulfide with H_2S to iron(II) disulfide is well known (e.g., Wächtershäuser, 1992).



Thus the addition of a second absorber unit to the Appleby-Frodingham process would yield the desired H_2 , albeit not elemental sulfur for recycling. In addition to these processes, several laboratory methods are known to decompose H_2S into the elements. The most straightforward is pyrolysis, although the temperature at which the reaction proceeds is not clear from the literature: as low as 400–500°C (Sneed and Maynard, 1944; Sidgwick, 1950) up to “white heat” (Roscoe and Schorlemmer, 1911). H_2S is reported to be decomposed at “ordinary temperatures” by electric discharge (Sneed and Maynard, 1944). H_2S also acts as an oxidizing agent on many metals, even relatively unreactive ones, converting the metal to the respective sulfide and liberating hydrogen.

2. Experimental methods

The coal used in this work was a medium-volatile bituminous coking coal from western Virginia, USA. The sample and the proximate analysis data were kindly supplied by Mr. R.W. Schoenberger, U.S. Steel Applied Research Laboratory, Monroeville, PA. On an as-received basis, this coal is 1.22% moisture, 22.89% volatile matter, 74.78% fixed carbon, 1.11% ash, and 0.71% sulfur, with a calorific value of 15,375 Btu/lb. The free-swelling index is approximately 5.5, based on Seyler’s chart (Berkowitz, 1979). The coal was selected in part for its low ash yield and sulfur content, so that coal minerals or sulfur would not confound the results of the reaction of sulfur with the coal.

The reactor was made of one-inch (25-mm) diameter Vycor glass or ceramic tubing heated in an electric furnace. A diagram of the apparatus is given in Figure 1. The ends of the reactor were closed with stoppers, having provisions for an inert gas sweep inlet tube, an exit gas tube, and a thermocouple. The purpose of the inert gas was simply to sweep the sulfur vapor, as it formed, through the bed of coal, and prevent the vapor from diffusing in the wrong direction, away from the coal. This procedure also allowed the hydrogen sulfide produced to be swept out of the reactor and into two gas washing bottles that contained an ammoniacal solution of cadmium chloride. This solution was used to determine the amount of hydrogen sulfide generated, as explained below.

Three sources of sulfur were used: reagent-grade sulfur from a commercial laboratory-supply vendor; essentially pure sulfur recovered from a hydrometallurgical process in which H_2S was used to reduce MnO_2 ; and the sulfur-rich residue from that process. There was no discernable difference in reactor performance for any of these feedstocks.

For some experiments, coal and sulfur were mixed together and heated at reaction temperatures of 250–400°C (below the normal boiling point of sulfur, which is 445°C) so that the process involved a liquid phase of sulfur reacting with the coal. Most reactions, however, used sulfur vapor passing through a bed of coal that was undergoing devolatilization. Prior to starting an experiment using sulfur vapor, a weighed quantity of sulfur was introduced into the reactor in a ceramic combustion boat. A weighed amount of coal was also placed in the reactor, and held in place by loose plugs of Pyrex glass wool. The reactor was then heated to the desired test temperature and allowed to run for the desired test duration. At the end of the reaction, the inert gas was swept through the reactor for several additional minutes, to insure that all hydrogen sulfide in the reactor was swept through into the gas washing bottles. When the reactor had cooled, the weights of the unvolatilized sulfur and of the remaining coal were determined.

The contents of the gas washing bottles were filtered to remove precipitated cadmium sulfide. The amount of cadmium remaining in solution was determined by atomic absorption spectroscopic analysis of the filtrate. Given the known amount of cadmium in solution at the start of a test, and that remaining in solution at the end, the amount of cadmium sulfide formed, and hence the amount of hydrogen sulfide generated, could easily be determined by straightforward stoichiometric calculations.

A limited number of scouting studies was done to assess the possibility of scaling up this process. For those studies, a reactor system consisting of two tubular furnaces was assembled. The reaction chamber, contained in one furnace, consisted of a 50-mm diameter piece of type 330 stainless steel pipe nominally 60 cm long. The second furnace was used as a sulfur vaporizer, and was constructed of a 30-cm length of 25-mm diameter pipe of the same kind. The sulfur vapor passed through the bed of coal in the larger reactor. The exit gas stream was then quenched by passing through a 30-cm length of 19-mm diameter titanium pipe, through which the aqueous H₂S solution was recirculated.

3. Results and discussion

3.1 Reactions of coal with liquid sulfur

Fifteen reactions were performed with coal-sulfur mixtures. These reactions encompassed a range of conditions, including temperatures from 220° to 400°C and coal-to-sulfur weight ratios from 0.6 to 3.2. All but two were carried out for an hour; reaction times of one-half and five hours were also tested. The results of this body of work showed that H₂S yields were invariably low, the highest observed being 37% and, in most cases, <10%. We cannot rule out the possibility of obtaining much higher H₂S yields with a different coal, such as a highly aliphatic coal. However, with the medium-volatile bituminous coal used in this work, there seemed little prospect for a significant increase in H₂S yield in this system. For the thirteen reactions done at a nominal 1 h reaction time, the highest H₂S yields were observed midway through the range of temperatures tested, that is, at 300–330°C. Yields were lower at higher temperatures, e.g. 360–390°C. We speculate that this decrease in yield is the result of sulfur vaporizing from the reactor before it has a chance to react with the coal or with volatiles emitted from the coal. This effect would be exacerbated by increasing reaction temperature to increase the thermal decomposition of the coal. Therefore, the reaction system was redesigned to effect the interaction of sulfur vapor with the coal as it is undergoing devolatilization. The results discussed in the subsections below all pertain to reactions of this sort, i.e., sulfur vapor with coal.

3.2 Effect of coal particle size in reactions with sulfur vapor

The effect of coal particle size is illustrated by the results shown in Table 1. The results for the -28/+70 mesh size appear to be an anomaly from an otherwise increasing trend of higher H₂S yield from using finer particle size coal. The highest yield was obtained with the mixture of particle sizes corresponding to 33% +28 mesh, 33% +70 mesh, and 33% +100 mesh. This blend of particle sizes was used in all subsequent work, except for some preliminary scale-up experiments to be discussed later in subsection 3.7.

It should be recognized that the reactor used in this part of the work was a very small one, and the particle-size effects observed here might not necessarily hold in larger reactors. The grinding of coal to fine particle sizes that provide high yields of H₂S may not be required in reactors of larger size. (For example, the feed to a slot-type coke oven, which itself may be 15–17 m high, 6–7 m long, and 45–50 cm wide (Berkowitz, 1979), can be sized 50 mm x 0 (2 inches x 0) when a single coal is coked (Denig, 1945) although common practice is to size to 80% less than 3 mm (Denig, 1945; Álvarez and Díaz-Estébonez, 2000).) In fact, preliminary scale-up studies, discussed below, show that in larger reactors it is possible to achieve good results with coal particles of 25–50 mm.

3.3 Effect of reaction parameters on sulfur conversion

In the experiments performed in this work, sulfur is the stoichiometrically limiting reagent. The yield of H₂S was calculated in terms of the amount of sulfur vaporized and swept through the hot coal bed. In 77 reactions conducted to explore the effect of various reaction parameters (e.g., time, temperature, heat-up rate) H₂S yields varied from 1 to 97%. In this total set of reactions, conducted as a scouting study, many of the parameters were deliberately changed through wide ranges, and one or more of the parameters often was not optimized. To assess the effect of reaction parameters, only those runs for which the H₂S yield was $\geq 60\%$ were considered. The experimental results are summarized in Table 2.

The reaction temperature had no effect on H₂S yield, provided that it was maintained above the normal boiling point of sulfur (445°C). As an example, for two reactions that were comparable other than temperature, yields of 94.5% at 460°C and 96.7% at 600°C were obtained. If the only consideration in this process were the H₂S yield, then the system could be

operated at a temperature just high enough to insure that the sulfur would vaporize readily and not condense in the interior of the reactor. However, this does not take into account the prospect of also converting the reacted coal into a useful by-product. This latter point is discussed below in subsection 3.7.

In the batch reactor system that was used in this work, there is a slight negative effect of increasing reaction time on H₂S yield. Reaction times greater than 1 h are counterproductive in terms of the yield of H₂S, suggesting that most of the available hydrogen comes out of the coal relatively early, in, say, 1 h. This is consistent with the work of van Krevelen and co-workers (van Krevelen et al., 1956), who showed that, for pyrolysis of a coking coal a plot of loss in weight as a function of reaction time has a steep vertical slope in the initial reaction period of ≈ 1 –1.5 h.

A sharp increase in the heat-up rate of the reactor diminishes the H₂S yield. This observation, combined with that on the effect of reaction time, suggests that the early reaction in this system is that of sulfur with hydrogen in the coal volatiles, rather than with hydrogen in the coal itself. It is well established that, under the temperature and heating-rate conditions used in this work bituminous coals undergo so-called active thermal decomposition at ≈ 350 – 550°C (Berkowitz, 1979). In this region, about 75% of all the material that would eventually be measured as volatile matter is released. Virtually all of the lighter hydrocarbons and tar are released at these temperatures. If the rate of volatile release is mis-matched with the rates of sulfur vapor transport through the system or the rate at which sulfur can react (or both), then the net effect is that sulfur cannot react fast enough to make effective use of the hydrogen available in the volatiles.

After reaction with the coal volatiles, a second, slower reaction between sulfur vapor and hydrogen in the coal can occur, but with much less efficiency than a vapor-phase reaction of sulfur and volatiles. Reactions in this post-plastic stage likely involve the removal of hydrogen from the periphery of large aromatic ring systems, and the dehydrogenative oligomerization of those systems (Álvarez et al., 1989). These reactions could be facilitated by the sulfur, and would be consistent with some of the known behavior of sulfur when used as a dehydrogenating reagent with pure compounds. For example, a dehydrogenation of, e.g. cyclohexane at 500°C would yield benzene, but at higher temperatures (650 – 800°C), the principal product is biphenyl (Fieser and Fieser, 1944). 2,2'-Dimethylbiphenyl dehydrogenated with sulfur produces phenanthrene

(Short et al., 1936). Even at the comparatively low temperature of 200°C, toluene undergoes dehydrogenation with sulfur to yield stilbene (Whitmore, 1951).

3.4 Effect of reaction parameters on utilization of coal hydrogen

Although the reactions reported here were conducted with sulfur as the limiting reagent, there was nevertheless sufficient variation among the reaction parameters so that it was possible to assess their effect on the utilization of hydrogen in the coal. Knowing the amounts of H₂S produced, the amount of coal charged, and the hydrogen content of the coal, calculation of the amount of coal hydrogen utilized was straightforward. In most experiments, except for a special series described later in this subsection, the percentage of the hydrogen originally in the coal accounted for in the H₂S product ranged from 1% to 38%.

Longer holding times at the reaction temperature increase utilization of coal hydrogen. This behavior is also consistent with the work of van Krevelen et al. (1956). In addition to showing a relatively fast initial rate of devolatilization in the time up to ≈ 1 –1.5 h, this work also showed that coal continued to devolatilize, albeit at much slower rate if held at temperature for times approaching 24 h.

An increase in heating rate tends to diminish the use of coal hydrogen. Data from volatile matter analyses of the residual solids (discussed below in subsection 3.6) show that, the higher the heat-up rate, the greater the amount of residual volatile matter remaining in the solid. These volatiles that were not released were thus not available for reaction with the sulfur.

The greater the sulfur vaporization rate, the more coal hydrogen is used. We consider this to be an effect of insuring an adequate supply of sulfur vapor over the devolatilizing coal to insure that an adequate amount of sulfur is present in the reaction zone itself.

Two other effects follow directly from the fact that sulfur was the limiting reagent in this system: First, the higher the coal-to-sulfur ratio (and, consequently, the higher the hydrogen-to-coal ratio), the lower is the percentage of total hydrogen utilized. Second, the higher the H₂S yield for approximately comparable coal-to-sulfur ratios, the greater is the percentage of hydrogen utilized.

Since the ultimate aim is to produce hydrogen from coal (via the intermediate H₂S), it is important to determine how much of this hydrogen might ultimately be liberated. Two

approaches were taken to explore this point, one based on calculations, and the other experimental. The weight of hydrogen sulfide produced per unit weight of coal is plotted in Figure 2 as a function of the reciprocal weight of sulfur. The curve is plotted in this way so that extrapolation to zero—corresponding to an infinite weight of sulfur—provides a measure of the maximum amount of H₂S that can be obtained per unit weight of *this coal*. This value is 0.6 H₂S/coal, which corresponds to a S/coal ratio of 0.56, or coal/S ratio of 1.77. These results were calculated on the basis of as-received coal, as charged to the reactor. On a dmmf coal basis, the coal/S ratio would be 1.73.

In H₂S, the H/S weight ratio is 0.063. The hydrogen content of the coal used in this study was determined, from Mott's classification chart (Berkowitz, 1979) to be 4.9% on a dmmf basis. This corresponds to 0.085 g H charged to the reactor. Based on the H/S ratio in H₂S, this result shows that about 75% of the hydrogen originally in the coal is abstracted by the sulfur to form H₂S. It is important to recognize that our numerical results pertain specifically to this coal. For coals of different hydrogen contents, the value of the coal/S ratio reported here would likely change. Although our work focused on this single medium-volatile bituminous coal, this effective dehydrogenation of the coal by sulfur vapor suggests that it would be worth exploring the use of sapropelic coals of high hydrogen content in this process.

In most of the experiments, hydrogen was present in large stoichiometric excess, and no more than 38% of the hydrogen was used in producing H₂S. A series of experiments was designed to determine if this amount of hydrogen utilization could be increased by reacting successive batches of sulfur with the same amount of coal. This was achieved by cautiously opening one end of the reactor, removing the boat that had contained the sulfur, and replacing it with a new boat containing a fresh charge of sulfur. The best result obtained from these "multiple-sulfur" runs was an experiment in which three charges of sulfur were used with reaction temperature of 510°, 530°, and 515°C and a coal-to-sulfur ratio of 2.5, 2.6, and 2.7 in the three stages (based on the total amount of sulfur in the three charges, the total coal-to-sulfur ratio was 0.88). The amount of coal hydrogen accounted for in the total H₂S produced in the three stages was 71%, in very good agreement with the estimate of 75% maximum from the graphical analysis discussed above. This behavior is consistent with the ability of partially dehydrogenated products to be dehydrogenated further in a subsequent reaction with more sulfur.

An example is the dehydrogenation of butane, in which a recycling of primary unsaturated products (the butenes) enhances the yields of butadiene and thiophene (Fuson, 1950).

3.5 Kinetic analysis of reactions of coal with sulfur vapor

Twenty-seven sets of data were selected from the total collection of experimental data, being selected on the criteria of a full compliment of data being obtained in the experiment and no mechanical or operating problems experienced with the reactor throughout the experiment. These 27 data sets were then tested by Chauvenet's criterion (Holman, 1971) to eliminate outliers. Fitting of the data to kinetic equations was done by testing zero-th, first, second, and third order equations. The most reasonable fit was obtained for the equation

$$R_{H_2S} = k[S]$$

where R_{H_2S} is the rate of hydrogen sulfide production and k is $2.93 \times 10^{-3} \text{ min}^{-1}$ for reaction at 500°C .

It was assumed that the system could be modeled as a plug-flow tubular reactor. No data were available on the viscosity of sulfur vapor as a function of temperature, so the viscosity was estimated from the Chapman-Enskog equation (Reid and Sherwood, 1966). The Reynolds number for flow of sulfur vapor in this reactor was calculated to be 7400, consistent with the assumption of plug flow. The space-time, that is, the ratio of reactor volume to the volumetric flow rate of the reactor feed, i.e., sulfur vapor (Levenspeil, 1972), was determined for volumes of the coal bed being $75\text{--}100 \text{ cm}^3$, and assuming that sulfur vapor began to flow when the reactor temperature was above 450°C and then continued for the duration of the experiment. Calculations were done for those reactions for which the H_2S yield was $\geq 90\%$. Space-times calculated in this way were $\approx 4 \times 10^{-2} \text{ sec}$. This compares reasonably with the value of 10^{-1} sec typical for the butane dehydrogenation rereaction (Schmidt, 1998)

3.6 Factors affecting quality of the by-product coke

The cokes* from eleven runs were characterized; the results are provided in Table 3. There is no correlation of the volatile matter or fixed carbon (on a daf basis) of these products

with the reaction temperature. This is consistent with the concept of a “two-stage” devolatilization in which the primary devolatilization is complete by $\approx 550^{\circ}\text{C}$ and the secondary devolatilization begins around $\approx 700^{\circ}\text{C}$. However, the higher the heat-up rate, the greater the volatile matter remaining. This is consistent with the observation mentioned above, that higher heating rates diminish the utilization of coal hydrogen. The higher the rate of sulfur vaporization, which corresponds to the rate of sulfur vapor transport through the coal bed, the lower the amount of volatile matter in the coke. The greater the fraction of coal hydrogen that appears in the H_2S product, the lower the

*Strictly speaking, the solid residues from the reactions at temperatures below $\approx 600^{\circ}\text{C}$ are semicokes; however, to avoid possibly confusing changes in terminology throughout the text, the solids are, for convenience, referred to as cokes regardless of the specific reaction temperature.

volatile matter. This last observation is consistent with the fact that, as hydrogen is removed from the coal, the residual product necessarily becomes increasingly carbon-rich. Hence one would expect lower volatile matter (or higher fixed carbon).

The sulfur content of the product coke was generally low, except for runs 25, 49, and 59. Although a flow of nitrogen was maintained through the reactor at the end of each experiment, to try to sweep any last trace of sulfur vapor out of the reactor, we cannot rule out the possibility that these high-sulfur products were contaminated by condensed elemental sulfur. Standard statistical tests for the rejection of outliers (Belz, 1973) did not allow discarding any of these data. No correlations of the sulfur content (dry basis) with any of the reaction parameters were found.

3.7 Preliminary scale-up studies and assessment of coke quality

The results described in the previous subsections show that it is indeed possible to convert sulfur into high yields ($\approx 95\%$) of H_2S while at the same time extracting some 70–75% of the hydrogen from this coal. Although it is possible to obtain good results by operating the reactor at temperatures just sufficient to insure that the sulfur vaporizes and remains in the vapor state (e.g., $460\text{--}500^{\circ}\text{C}$), the production of a metallurgical coke by-product remained an

intriguing possibility, since the by-product credits from sale of the coke could provide an economic “driver” for this process. Metallurgical coke production would require operation at temperatures above the 460–500°C range. It was also of interest to determine if some of the necessary coal crushing could be eliminated, by being able to feed lumps of, say, 25-50 mm (1 to 2 inches) to the reactor.

To test these two possibilities, at the end of the experimental program a larger reactor was assembled for the first steps toward scale-up. The reaction chamber itself was a 50-mm (2-inch) diameter type 330 stainless steel pipe approximately 60 cm (2 feet) long. A sulfur vaporizer was constructed of the same material, but only 25 mm (1 inch) diameter and 30 cm (1 foot) long. The gases leaving the reactor chamber were conducted through a quench tower made of 19 mm (3/4-inch) titanium pipe 30 cm (1 foot) long, where they were sprayed with a recirculating stream of water (which, as the run progressed, would have become an aqueous solution of H₂S).

Three test runs were performed, using coal in the nominal 50-mm size range and reactor temperatures of 700–800°C. Analyses of the product coke were provided by U.S. Steel, with comparative analyses of standard metallurgical coke as a control. Results are shown in Table 4. Also, the friability of the coke produced from our reactor was identical with that of a sample of standard metallurgical coke. Other properties of coke—e.g., reactivity toward CO₂, resistance to alkali attack, and mechanical strength (Álvarez and Díaz-Estébonez, 2000)—would need to be assessed as part of further scale-up work. However, these preliminary results show that it is possible to make a coke product comparable, in several important aspects, to metallurgical coke. It is noteworthy that this coke was produced at temperatures below those of a typical slot-type by-product coke oven, which are typically in the range 800–1000°C (Camp and Francis, 1951); temperatures of 950–1050°C are recommended for good quality blast-furnace coke (Gibson, 1979). Also, given present interest in production of premium carbon products from coal (Song and Schobert, 2000; Schobert and Song, 2002; Schobert, 2003; Andrésen et al., 2003), other applications of this coke—e.g., as filler for aluminum-smelting anodes or for synthetic graphites—merit investigation. Sulfur incorporation in the coke would of course be a concern, since sulfur in metallurgical coke is known to affect the quality of both the molten metal and the slag (Loison et al., 1989). For alternative high-tonnage use, such as in manufacture of electrodes, sulfur is known to cause “puffing”, an irreversible expansion of the carbonaceous artifact during graphitization (Fitzer et al., 1978). Although we did not study sulfur incorporation in this work,

related information from the literature suggests that sulfur incorporation into the coke might be significant only at the last stages of reaction (Larsen and Li, 1998; Larsen et al., 2001).

The tests in this scaled-up reactor were the first in which noticeable quantities of coal tar were formed. The tar collected and settled in the quenching tower. As is well known, coal tar can represent a valuable by-product providing additional economic benefit to a sulfur-based coal-from-hydrogen process. From a different perspective, though, the coal tar has also carried out of the system some of the hydrogen from the coal, which is then “lost” in terms of being available for the desired product. Tests in the smaller reactor, described above, suggest that the reaction of sulfur vapor with coal volatiles is important in the overall production of H_2S . A careful matching of the rate of sulfur vapor transport through the coal bed with the rate of coal devolatilization could reduce, and perhaps eliminate, the formation of by-product tar via the reaction of sulfur vapor and coal volatiles.

3.8 Conceptual design of a sulfur-based hydrogen-from-coal process

In Figure 3 a block flow diagram for a process that leads to the production of hydrogen from coal. As mentioned above, we did not test the conversion of hydrogen sulfide to hydrogen. H_2S -to- H_2 conversions are known (Thau, 1933; Reeve, 1958); their operation would be independent of the source of the H_2S . The coal tar stream is tagged with a question mark because of the potential that its formation could be suppressed by adjustment of the rates of sulfur flow and coal devolatilization. (An alternative, which was outside the scope of this investigation, would be the reaction of coal tar with sulfur vapor in a separate reactor.)

Another potential advantage of this process, as opposed to the use of coal gasification to produce hydrogen, is that there should be much less hot-gas clean-up needed. Ash particles would be retained within the coke. Sulfur-containing gases, specifically H_2S are in the case, the desired primary product, and would be destroyed upon conversion to H_2 and a recycle stream of sulfur vapor.

4. Conclusions

This laboratory-scale investigation has shown that sulfur vapor will react with medium-volatile bituminous coal to produce abundant amounts of H₂S. Up to 97% of the sulfur, which was the stoichiometrically limiting reagent in this work, is converted to H₂S. About 70–75% of the hydrogen in the coal is removed as H₂S. The H₂S can be fed to known processes for its facile conversion to the desired H₂. The by-product coke could be buried as means of sequestering carbon. However, this coke also meets ash, fixed carbon, volatile matter, and friability specifications for metallurgical coke, even though it has been produced at temperatures lower than a conventional by-product coke oven. Credits from the sale of the coke could provide a benefit to the economics of making hydrogen from coal.

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Table 1

The relationship of yield of H₂S and rate of H₂S formation to coal particle size.

Run number	Particle size	Yield of H ₂ S, %	Rate, g H ₂ S/min
69	+ ¹ / ₄ inch	48.3	0.029
73	- ¹ / ₄ inch/+9 mesh	68.5	0.029
74	-9/+28 mesh	80.0	0.030
75	-28/+70 mesh	68.5	0.029
44	(a)	96.7	0.031

Note (a): This reaction used a mixture blended of 33% each of +28, +70, and +100 mesh particles.

Table 2

Summary of experimental results for all reactions of coal with sulfur vapor that provided H₂S yields $\geq 60\%$.

Run number	Maximum Temp. °C	Time at T _{max} , min.	Heat-up time, min.	Heat-up rate, °C/min.	Total rxn. time, min.	Weight of coal, g.	Coal wt. loss, g.	Wt. sulfur vaporized, g.	H ₂ S yield, %
28	730	45	160	4.6	286	34.4	— (b)	0.84	94.9
40	500	60	130	3.8	190	33.9	—	4.58	66.2
41	570	60	115	4.8	182	44.0	0.6	4.47	91.4
42	580	65	78	7.4	138	37.5	—	5.47	68.5
43	680	60	233	2.8	298	42.5	—	6.13	64.1
44	600	60	103	5.2	130	35.3	8.9	4.66	96.7
45	500	60	100	5.0	165	40.7	—	5.41	94.5
46	460	67	113	4.1	180	55.0	—	5.09	96.2
49a	540	73	97	4.5	170	62.3	—	6.31	68.4
49b	560	61	154	3.6	215	62.3 (a)	—	6.50	64.5
56	510	74	97	5.3	173	53.2	—	4.04	73.5
72	540	215	173	3.0	328	39.0	4.3	13.3	60.7
73	550	175	165	3.0	340	53.3	4.5	14.7	68.6
74	530	207	163	3.1	370	55.6	4.7	16.2	80.0
75	550	180	155	3.2	335	40.3	3.3	17.0	68.5

Notes: (a) The same charge of coal was reacted with two batches of sulfur. (b) The symbol — indicates that the value was not measured in this experiment.

Table 3

Analyses of cokes produced from selected runs, as received basis.

Run	Moisture	Volatile matter	Fixed carbon	Ash	Sulfur	Heating value, Btu/lb
25	0.93	19.48	76.78	2.81	2.46	14,766
33	0.86	13.05	83.24	2.85	0.60	14,835
34	0.77	12.92	84.33	1.98	1.32	14,761
36	1.81	16.97	76.81	2.61	0.72	14,448
41	2.65	18.78	77.23	1.34	1.12	15,018
43	4.63	10.33	81.24	3.80	0.96	14,149
44	1.64	6.45	89.40	2.51	1.00	14,407
45	2.82	13.35	80.97	2.86	0.84	14,398
49	7.01	11.34	78.13	3.52	2.20	14,135
56	0.99	15.44	81.56	2.01	0.72	14,675
59	0.31	11.26	85.23	3.20	3.42	14,291

Table 4

Comparison of coke produced in this work in scale-up reactor with reference sample of metallurgical coke. Results from this work are the average of analyses of three samples.

Sample	Volatile matter	Fixed carbon	Ash
<i>Reference</i>	0.78	87.7	12.3
<i>This work</i>	0.76	90.8	8.0