ENERGY

Kinetics of Direct Oxidation of H_2S in Coal Gas to Elemental Sulfur

Annual Technical Progress Report for the Period
October 1, 2002 to September 30, 2003

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January 2004

Work Performed Under Contract No
DE-FG26-00NT40835

For
U.S. Department of Energy
National Energy Technology Laboratory
Pittsburgh, PA 15236-0940

By
Tuskegee University
Tuskegee, Alabama 36088

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DISCLAIMER

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SUMMARY

The direct oxidation of H_2S to elemental sulfur in the presence of SO_2 is ideally suited for coal gas from commercial gasifiers with a quench system to remove essentially all the trace contaminants except H_2S. This direct oxidation process has the potential to produce a super clean coal gas more economically than both conventional amine-based processes and the hot-gas desulfurization using regenerable metal oxide sorbents followed by Direct Sulfur Recovery Process. The objective of this research is to support the near- and long-term process development efforts to commercialize this direct oxidation technology. The objectives of this research are to measure kinetics of direct oxidation of H_2S to elemental sulfur in the presence of a simulated coal gas mixture containing SO_2, H_2, and moisture, using 160-μm C-500-04 alumina catalyst particles and a micro bubble reactor, and to develop kinetic rate equations and model the direct oxidation process to assist in the design of large-scale plants. This heterogeneous catalytic reaction has gaseous reactants such as H_2S and SO_2. However, this heterogeneous catalytic reaction has heterogeneous products such as liquid elemental sulfur and steam.

To achieve the above-mentioned objectives, experiments on conversion of hydrogen sulfide into liquid elemental sulfur were carried out for the space time range of 1 – 6 milliseconds at 125 - 155°C to evaluate effects of reaction temperature, moisture concentration, reaction pressure on conversion of hydrogen sulfide into liquid elemental sulfur. Simulated coal gas mixtures consist of 70 v% hydrogen, 2,500 – 7,500-ppmv hydrogen sulfide, 1,250 - 3,750 ppmv sulfur dioxide, and 0 – 15 vol % moisture, and nitrogen as remainder. Volumetric feed rates of a simulated coal gas mixture to a micro bubble reactor are 100 cm^3/min at room temperature and atmospheric pressure. The temperature of the reactor is controlled in an oven at 125 - 155°C. The pressure of the reactor is maintained at 40 - 170 psia.

INTRODUCTION

Coal is our most abundant energy resource. It is strategically important to our nation to increase coal use as an energy source in an environmentally acceptable manner. Coal gasification, a primary step in advanced coal utilization processes, produces a coal gas, containing hydrogen (H_2) and carbon monoxide (CO) as the fuel components. Raw coal gas, however, also contains a number of major and trace contaminants including hydrogen sulfide (H_2S), carbonyl sulfide (COS), ammonia (NH_3), hydrogen chloride (HCl), alkali, heavy metals, and particulate. Thus, this gas must be cleaned before further use. H_2S is a major coal gas contaminant that can range from 1000 to 10,000 ppm, depending on the sulfur content of the coal. Removal of H_2S from coal gas and sulfur recovery are key steps in the development of advanced gasification plants combining a power plant and a refinery based on coal and natural gas to co-produce electricity and clean transportation-grade liquid fuels. These gasification plants will require highly clean coal gas with H_2S below 1 ppm and negligible amounts of other contaminants such as COS, HCl, NH_3, alkali, heavy metals, and particulate.

The conventional method of removing H_2S and sulfur recovery involves a number of steps including amine scrubbing at low temperature followed by amine regeneration using steam to produce a concentrated H_2S-containing gas. This concentrated H_2S-containing gas is then combusted to produce a gas with a H_2S to sulfur dioxide (SO_2) ratio of 2 to 1 in a Claus furnace. This is followed by up to three (3) stages of Claus reaction at temperatures of around 250-280^oC over an alumina catalyst to recover elemental sulfur:

The Claus reaction is exothermic and equilibrium limited. To circumvent equilibrium limitations, the reaction is conducted in up to three (3) reaction stages with interstage cooling/ sulfur condensation followed by interstage re-heating. However, even with three (3) stages, the reaction is not complete due to thermodynamic limitations at 250^oC. The Claus tail gas contains sulfur that must be further treated in an expensive tail gas treatment plant (e.g., SCOT) before discharge. Thus, overall H_2S removal and sulfur recovery using this conventional sequence are extremely cumbersome, equipment intensive, and expensive.

A second generation approach for sulfur removal/recovery involves three steps:

(i) hot-gas desulfurization (HGD) using regenerable zinc oxide-based sorbents

$$ZnO + H_2S \leftrightarrow ZnS + H_2O \quad \text{(HGD)}$$

(ii) sorbent regeneration using air to produce SO_2

$$ZnS + 3/2\, O_2 \leftrightarrow SO_2 + ZnO \quad \text{(regeneration)}$$

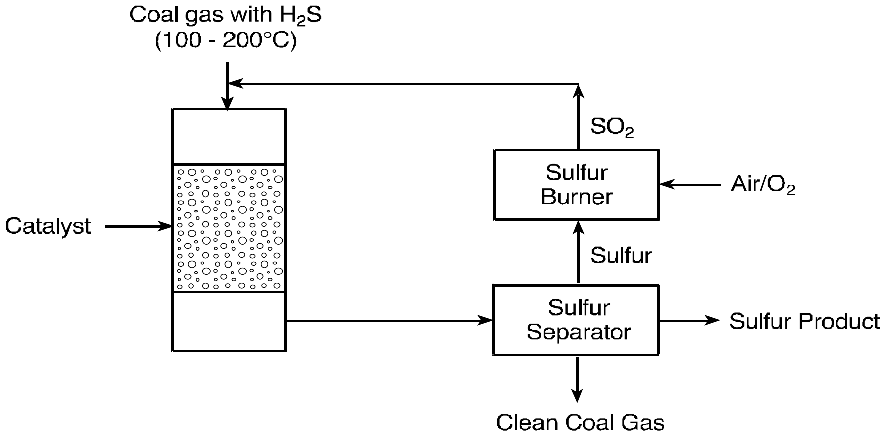
(iii) catalytic reduction of SO_2 using a small portion of the coal gas, to elemental sulfur by the Direct Sulfur Recovery Process (DSRP):

$$SO_2 + 2H_2 \text{ (or } 2CO) \leftrightarrow S + 2H_2O \text{ (or } 2CO_2) \quad \text{(DSRP)}$$

This approach integrates well with a coal gasifier in an integrated gasification (IGCC) system because the raw coal gas does not have to be cooled all the way down to near room temperature as is the case with the conventional amine/Claus/tail-gas treatment method. However, the overall process scheme requires solid sorbent handling/circulation, and three separate reactors. Also, there is a small energy penalty associated with the use of coal gas to reduce SO_2 by DSRP. Furthermore, since trace contaminants e.g. NH_3 and HCl are not removed by the zinc-based sorbents. This approach is primarily targeted towards the development of advanced IGCC plants that produce electricity only (but do not coproduce both electricity and clean transportation grade fuels).

There is an immediate as well as long-term need for the development of clean processes that produce highly clean coal gas for next generation gasification plants producing both electricity and transportation-grade liquid fuels. To this end, Research Triangle Institute (RTI) is developing a novel process in which the H_2S in coal gas is directly oxidized to elemental sulfur over a selective catalyst using sulfur dioxide (SO_2) produced by burning a portion of the sulfur produced as shown in Figure 1.

Figure 1: RTI proposed direct oxidation process



The direct oxidation process shown in Figure 1 is ideally suited for coal gas from a commercial gasifier with a quench system. During quench, the trace contaminants (except sulfur) are essentially completely removed and H_2S (with some COS) remains as the only contaminant. The gas contains all of the major coal gas components including H_2, CO, CO_2 and H_2O.

The objectives of this research are to measure kinetics of direct oxidation of H_2S to elemental sulfur in the presence of a simulated coal gas mixture containing SO_2, H_2, and moisture, using 160-µm C-500-04 alumina catalyst particles and a fluidized-bed micro bubble reactor fabricated with perfluoroalkoxy (PFA), and to develop kinetic rate equations and model the direct oxidation process to assist in the design of large-scale plants. Experiments on conversion of hydrogen sulfide to elemental sulfur were carried out for the space time range of 1 – 6 milliseconds (ms) at 125 - 155°C and 40 - 170 psia to evaluate effects of reaction temperature, moisture concentration, reaction pressure on conversion of hydrogen sulfide to elemental sulfur. Simulated coal gas mixtures consist of 70 v% hydrogen, 2,500 – 7,500-ppmv hydrogen sulfide, 1,250 - 3,750 ppmv sulfur dioxide, and 0 - 15 vol % moisture, and nitrogen as remainder. Volumetric feed rates of a simulated coal gas mixture to the reactor are 100 cm^3/min at room temperature and atmospheric pressure.

EXPERIMENTAL SETUPS

A fluidized-bed micro bubble reactor was fabricated with PFA (perfluoroalkoxy). The amount of a C-500-04 alumina catalyst packed in the reactor is 0.002 - 0.008 g. The C-500-04 alumina catalyst in the form of 160-µm spherical particles was examined. A simulated coal gas mixture containing H_2S and SO_2 was reacted with the aid of the catalyst in the differential fluidized-bed micro bubble reactor at 125 - 155°C. Conversion of hydrogen sulfide to elemental sulfur was analyzed with a gas chromatograph. The range of space (residence) time of the reaction gas mixture in the reactor was 1 – 6 milliseconds under the reaction conditions. Space times are obtained by dividing the bulk volume of catalyst particles with the volumetric flow rate of a feed gaseous mixture at reaction conditions.

Figure 2. Schematic diagram of the experimental set-up

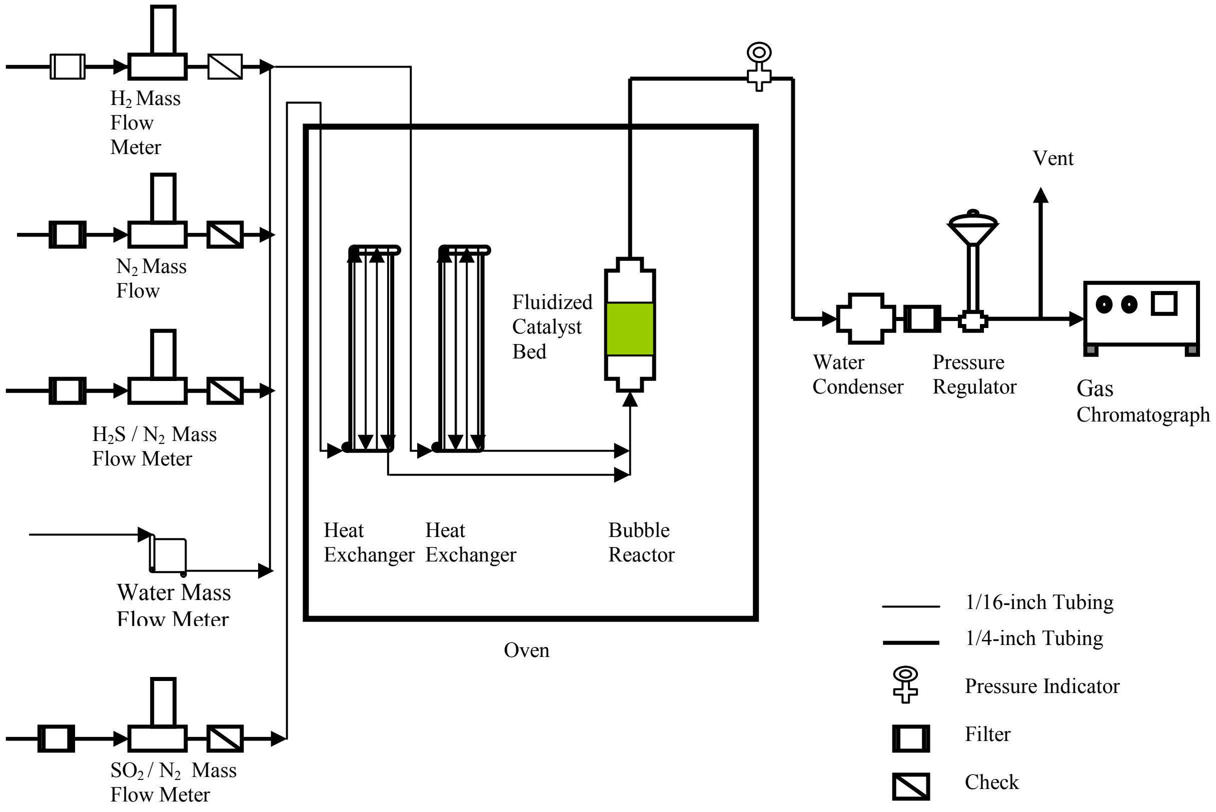


Table 1. Experimental conditions for the reaction of hydrogen sulfide with sulfur dioxide.

Amounts of catalyst particles in the reactor, g	0.02 – 0.08
Temperature, ^{o}C:	125 - 155
Reaction Pressure, psia	40 - 170
Space Time under the reaction conditions, millisecond:	1 – 6
Mean Particle Size, μm	160
Gas Flow Rate, cc/min at room temperature and 1 atm (SCCM)	100 - 105
Hydrogen, vol %	70
Moisture, vol %:	0 -15
Concentration of H_2S, ppmv	2,500 – 7,500
Concentration of SO_2, ppmv	1,250 – 3,750
Nitrogen, vol %	Remainder

A micro bubble reactor assembly mainly consists of four mass flow meters for gases, one micro bubble reactor, two preheaters, one high pressure liquid pump for water, one four-way switch valve, one oven, five filters for gases, four check valves, and one water condenser (see Figure 2). The preheaters are made of 1/16-inch PFA tubing. The reactor, loaded with the C-500-04 alumina catalyst particles, was placed inside the oven to be heated at a desired temperature. Nitrogen was introduced into the catalyst-loaded reactor during preheating the reactor. When the temperature of the reactor was raised at the desired temperature, one simulated coal gas mixture stream containing H_2S and another feed stream containing SO_2 were introduced into the reactor, by switching nitrogen with the simulated coal gas mixture. The typical reaction conditions are shown in Table 1. The properties of the catalyst are shown in Table 2.

Table 2. Properties of the C-500-04 alumina catalyst from the Research Triangle Institute (RTI).

BET Area, m^2/g	227
Bulk Density, g/cm^3	0.8346
Pore Volume, cm^3/g	0.6211
Mean Particle Size, μm	160
Composition	Alumina

Table 3. Conversion of 2,500 – 7,500 ppmv hydrogen sulfide with 1,250 – 3,750 ppmv sulfur dioxide in the presence of 70 v-% hydrogen, 0 – 15 v-% moisture, and 0.02 – 0.08 g catalyst at 125 - 155 °C, 40 - 170 psia, and 1 - 6 millisecond space time.

Run Number	Temperature, °C	Pressure psia	Catalyst Amount, g	Total Feed scc/min	Space Time, s	Feed Composition, v%					Conversion
						H_2	H_2S	SO_2	moisture	N_2	
B1	140	121	0.02	100	0.0014	70	0.498	0.25	10	19.252	0.092
B2	140	121	0.04	100	0.0028	70	0.498	0.25	10	19.252	0.190
B3	140	120	0.02	100	0.0014	70	0.498	0.25	10	19.252	0.097
B4	140	119	0.04	100	0.0028	70	0.498	0.25	10	19.252	0.218
B5	140	122	0.06	100	0.0043	70	0.498	0.25	10	19.252	0.272
B6	140	119	0.06	100	0.0042	70	0.498	0.25	10	19.252	0.294
B7	140	121	0.06	100	0.0043	70	0.498	0.25	10	19.252	0.272
B8	140	121	0.08	100	0.0057	70	0.498	0.25	10	19.252	0.358
B9	140	123	0.08	100	0.0058	70	0.498	0.25	10	19.252	0.283
B10	140	118	0.08	100	0.0056	70	0.498	0.25	10	19.252	0.362
B11	140	120	0.04	100	0.0028	70	0.647	0.175	10	19.178	0.146
B12	140	122	0.04	100	0.0029	70	0.647	0.175	10	19.178	0.157
B13	140	124	0.04	100	0.0029	70	0.349	0.325	10	19.326	0.161
B14	140	121	0.04	100	0.0028	70	0.349	0.325	10	19.326	0.254
B15	140	121	0.04	100	0.0028	70	0.349	0.325	10	19.326	0.266
B16	150	122	0.04	100	0.0028	70	0.498	0.25	10	19.252	0.123
B17	150	121	0.04	100	0.0028	70	0.498	0.25	10	19.252	0.180
B18	150	120	0.04	100	0.0028	70	0.498	0.25	10	19.252	0.203
B19	130	122	0.04	100	0.0029	70	0.498	0.25	10	19.252	0.136
B20	130	119	0.04	100	0.0029	70	0.498	0.25	10	19.252	0.250
B21	130	122	0.04	100	0.0029	70	0.498	0.25	10	19.252	0.139
B22	125	120	0.04	100	0.0029	70	0.498	0.25	10	19.252	0.172
B23	125	120	0.04	100	0.0029	70	0.498	0.25	10	19.252	0.166
B24	155	121	0.04	100	0.0027	70	0.498	0.25	10	19.252	0.153
B25	155	120	0.04	100	0.0027	70	0.498	0.25	10	19.252	0.179

Table 3. Continued-1

Run Number	Temperature, ºC	Pressure psia	Catalyst Amount, g	Total Feed scc/min	Space Time, s	Feed Composition, v%					Conversion
						H_2	H_2S	SO_2	moisture	N_2	
B26	155	121	0.04	100	0.0027	70	0.498	0.25	10	19.252	0.143
B27	145	121	0.04	100	0.0028	70	0.498	0.25	10	19.252	0.110
B28	145	120	0.04	100	0.0028	70	0.498	0.25	10	19.252	0.334
B29	145	119	0.04	100	0.0028	70	0.498	0.25	10	19.252	0.096
B30	145	119	0.04	100	0.0028	70	0.498	0.25	10	19.252	0.096
B31	140	91	0.04	100	0.0021	70	0.498	0.25	10	19.252	0.142
B32	140	90	0.04	100	0.0021	70	0.498	0.25	10	19.252	0.149
B33	140	61	0.04	100	0.0014	70	0.498	0.25	10	19.252	0.127
B34	140	62	0.04	100	0.0015	70	0.498	0.25	10	19.252	0.094
B35	140	62	0.04	100	0.0015	70	0.498	0.25	10	19.252	0.132
B36	140	41	0.04	100	0.0010	70	0.498	0.25	10	19.252	0.102
B37	140	42	0.04	100	0.0010	70	0.498	0.25	10	19.252	0.197
B38	140	150	0.04	100	0.0035	70	0.498	0.25	10	19.252	0.274
B39	140	149	0.04	100	0.0035	70	0.498	0.25	10	19.252	0.164
B40	140	150	0.04	100	0.0035	70	0.498	0.25	10	19.252	0.157
B41	140	149	0.04	100	0.0035	70	0.498	0.25	10	19.252	0.161
B42	140	166	0.04	100	0.0039	70	0.498	0.25	10	19.252	0.228
B43	140	171	0.04	100	0.0040	70	0.498	0.25	10	19.252	0.344
B44	140	121	0.04	100	0.0028	70	0.498	0.25	0	29.252	0.087
B45	140	121	0.04	100	0.0028	70	0.498	0.25	0	29.252	0.071
B46	140	121	0.04	100	0.0028	70	0.498	0.25	0	29.252	0.074
B47	140	122	0.04	100	0.0029	70	0.498	0.25	5	24.252	0.126
B48	140	118	0.04	100	0.0028	70	0.498	0.25	5	24.252	0.177
B49	140	119	0.04	100	0.0028	70	0.498	0.25	5	24.252	0.184
B50	140	118	0.04	100	0.0028	70	0.498	0.25	15	14.252	0.163
B51	140	122	0.04	100	0.0029	70	0.498	0.25	15	14.252	0.154
B52	140	147	0.04	100	0.0035	70	0.498	0.25	10	19.252	0.340
B53	140	146	0.04	100	0.0034	70	0.498	0.25	10	19.252	0.331
B54	140	151	0.04	100	0.0036	70	0.498	0.25	10	19.252	0.235
B55	140	150	0.04	100	0.0035	70	0.498	0.25	10	19.252	0.256
B56	140	170	0.04	100	0.0040	70	0.498	0.25	10	19.252	0.323
B57	140	171	0.04	100	0.0040	70	0.498	0.25	10	19.252	0.283
B58	140	171	0.04	100	0.0040	70	0.498	0.25	10	19.252	0.308
B59	140	42	0.04	100	0.0010	70	0.498	0.25	10	19.252	0.117
B60	140	42	0.04	100	0.0010	70	0.498	0.25	10	19.252	0.159
B61	140	42	0.04	100	0.0010	70	0.498	0.25	10	19.252	0.147
B62	140	121	0.04	100	0.0028	70	0.249	0.375	10	19.376	0.157
B63	140	122	0.04	100	0.0029	70	0.249	0.375	10	19.376	0.158
B64	140	122	0.04	100	0.0029	70	0.747	0.125	10	19.128	0.051
B65	140	120	0.04	100	0.0028	70	0.249	0.375	10	19.376	0.069

Table 4. Effects of moisture concentration on conversion of H_2S to elemental sulfur with 0.04-g alumina catalyst and a 100-SCCM feed stream containing 4,980-ppmv H_2S and 2,500-ppmv SO_2, 0 – 15 v% moisture, 70-v% H_2 at 140°C, 118 – 122 psia and 2.8 – 2.9 millisecond space time.

						Feed Composition, v%					
Run Number	Temperature, °C	Pressure psia	Catalyst Amount, g	Total Feed scc/min	Space Time, s	H_2	H_2S	SO_2	moisture	N_2	Conversion
B44	140	121	0.04	100	0.0028	70	0.498	0.25	0	29.252	0.0874
B45	140	121	0.04	100	0.0028	70	0.498	0.25	0	29.252	0.0706
B46	140	121	0.04	100	0.0028	70	0.498	0.25	0	29.252	0.0737
B48	140	118	0.04	100	0.0028	70	0.498	0.25	5	24.252	0.1772
B49	140	119	0.04	100	0.0028	70	0.498	0.25	5	24.252	0.1838
B2	140	121	0.04	100	0.0028	70	0.498	0.25	10	19.252	0.1903
B4	140	119	0.04	100	0.0028	70	0.498	0.25	10	19.252	0.2183
B50	140	118	0.04	100	0.0028	70	0.498	0.25	15	14.252	0.1634
B51	140	122	0.04	100	0.0029	70	0.498	0.25	15	14.252	0.1538

Table 5. Effects of reaction temperature on conversion of H_2S to elemental sulfur with 0.04-g catalyst and a 100-SCCM feed stream containing 4,980-ppmv H_2S and 2,500-ppmv SO_2, 10-v% moisture, and 70-v% H_2 at 125 – 155°C, 119 – 122 psia and 2.7 – 2.9 millisecond space time.

						Feed Composition, v%					
Run Number	Temperature, °C	Pressure psia	Catalyst Amount, g	Total Feed scc/min	Space Time, s	H_2	H_2S	SO_2	moisture	N_2	Conversion
B2	140	121	0.04	100	0.0028	70	0.498	0.25	10	19.252	0.1903
B4	140	119	0.04	100	0.0028	70	0.498	0.25	10	19.252	0.2183
B17	150	121	0.04	100	0.0028	70	0.498	0.25	10	19.252	0.1795
B18	150	120	0.04	100	0.0028	70	0.498	0.25	10	19.252	0.2025
B19	130	122	0.04	100	0.0029	70	0.498	0.25	10	19.252	0.1361
B21	130	122	0.04	100	0.0029	70	0.498	0.25	10	19.252	0.1386
B22	125	120	0.04	100	0.0029	70	0.498	0.25	10	19.252	0.1722
B23	125	120	0.04	100	0.0029	70	0.498	0.25	10	19.252	0.1663
B24	155	121	0.04	100	0.0027	70	0.498	0.25	10	19.252	0.1529
B26	155	121	0.04	100	0.0027	70	0.498	0.25	10	19.252	0.1425
B27	145	121	0.04	100	0.0028	70	0.498	0.25	10	19.252	0.1101
B29	145	119	0.04	100	0.0028	70	0.498	0.25	10	19.252	0.0960
B30	145	119	0.04	100	0.0028	70	0.498	0.25	10	19.252	0.0955

Table 6. Effects of reaction pressure on conversion of H_2S with 0.04-g alumina catalyst and a 100-SCCM feed stream containing 4,980-ppmv H_2S and 2,500-ppmv SO_2, 10-v% moisture, and 70-v% H_2 at 140°C, 40 – 170 psia, and 1 – 4 millisecond space time.

Run Number	Temperature, °C	Pressure psia	Catalyst Amount, g	Total Feed scc/min	Space Time, s	Feed Composition, v%					Conversion
						H_2	H_2S	SO_2	moisture	N_2	
B2	140	121	0.04	100	0.0028	70	0.498	0.25	10	19.252	0.1903
B4	140	119	0.04	100	0.0028	70	0.498	0.25	10	19.252	0.2183
B31	140	91	0.04	100	0.0021	70	0.498	0.25	10	19.252	0.1419
B32	140	90	0.04	100	0.0021	70	0.498	0.25	10	19.252	0.1489
B33	140	61	0.04	100	0.0014	70	0.498	0.25	10	19.252	0.1267
B34	140	62	0.04	100	0.0015	70	0.498	0.25	10	19.252	0.0937
B35	140	62	0.04	100	0.0015	70	0.498	0.25	10	19.252	0.1316
B36	140	41	0.04	100	0.0010	70	0.498	0.25	10	19.252	0.1024
B43	140	171	0.04	100	0.0040	70	0.498	0.25	10	19.252	0.3435
B54	140	151	0.04	100	0.0036	70	0.498	0.25	10	19.252	0.2354
B55	140	150	0.04	100	0.0035	70	0.498	0.25	10	19.252	0.2562
B56	140	170	0.04	100	0.0040	70	0.498	0.25	10	19.252	0.3234
B57	140	171	0.04	100	0.0040	70	0.498	0.25	10	19.252	0.2825
B38	140	150	0.04	100	0.0035	70	0.498	0.25	10	19.252	0.2744
B58	140	171	0.04	100	0.0040	70	0.498	0.25	10	19.252	0.3084
B59	140	42	0.04	100	0.0010	70	0.498	0.25	10	19.252	0.1170
B60	140	42	0.04	100	0.0010	70	0.498	0.25	10	19.252	0.1593
B61	140	42	0.04	100	0.0010	70	0.498	0.25	10	19.252	0.1470

Table 7. A reaction model developed with experimental data of conversion of 3,500 -6,500 ppmv hydrogen sulfide with 1,750 – 3,250 ppmv sulfur dioxide in the presence of 70 v-% hydrogen, 10-v % moisture, and 0.04-g catalyst at 140 °C, 40 – 170 psia, and 1- 4 millisecond space time.

Run Number	Temperature, °C	Pressure psia	Catalyst Amount, g	Total Feed scc/min	Space Time, s	Feed Composition, v%					Conversion
						H_2	H_2S	SO_2	moisture	N_2	
B2	140	121	0.04	100	0.0029	70	0.498	0.25	10	19.252	0.1903
B4	140	119	0.04	100	0.0028	70	0.498	0.25	10	19.252	0.2183
B11	140	120	0.04	100	0.0028	70	0.647	0.175	10	19.178	0.1462
B12	140	122	0.04	100	0.0029	70	0.647	0.175	10	19.178	0.1574
B14	140	121	0.04	100	0.0029	70	0.349	0.325	10	19.326	0.2544
B15	140	121	0.04	100	0.0029	70	0.349	0.325	10	19.326	0.2660
B31	140	91	0.04	100	0.0021	70	0.498	0.25	10	19.252	0.1419

Table 7. Continued-1

Run Number	Temperature, ^{o}C	Pressure psia	Catalyst Amount, g	Total Feed scc/min	Space Time, s	Feed Composition, v%					Conversion
						H_2	H_2S	SO_2	moisture	N_2	
B32	140	90	0.04	100	0.0021	70	0.498	0.25	10	19.252	0.1489
B33	140	61	0.04	100	0.0014	70	0.498	0.25	10	19.252	0.1267
B34	140	62	0.04	100	0.0015	70	0.498	0.25	10	19.252	0.0937
B35	140	62	0.04	100	0.0015	70	0.498	0.25	10	19.252	0.1316
B36	140	41	0.04	100	0.0010	70	0.498	0.25	10	19.252	0.1024
B38	140	150	0.04	100	0.0035	70	0.498	0.25	10	19.252	0.2744
B54	140	151	0.04	100	0.0036	70	0.498	0.25	10	19.252	0.2354
B55	140	150	0.04	100	0.0035	70	0.498	0.25	10	19.252	0.2562
B56	140	170	0.04	100	0.0040	70	0.498	0.25	10	19.252	0.3234
B58	140	171	0.04	100	0.0040	70	0.498	0.25	10	19.252	0.3084
B59	140	42	0.04	100	0.0010	70	0.498	0.25	10	19.252	0.1170

Table 8. Experimental surface reaction rates and predicted surface reaction rates of H_2S for conversion of 3,500 - 6,500 ppmv hydrogen sulfide with 1,750 – 3,250 ppmv sulfur dioxide in the presence of 70 v-% hydrogen, 10-v % moisture, and 0.04-g catalyst at 140 ^{o}C, 40 – 170 psia, and 1- 4 millisecond space time.

Run Number	Pressure, psia			Conversion of H_2S	Molar Flow Rate H_2S, g-mole/s	Left-Side Value of Rearranged Reaction Model psia$^{1.5}$ (g-cat-s/g-mole)$^{0.5}$	Surface Reaction Rate, g-mole/s-g-cat	
	Total	H_2S	SO_2				Experimental	Predicted
B2	121	0.4879	0.2452	0.1903	3.3931E-07	190	1.6143E-06	1.9722E-06
B4	119	0.4633	0.2328	0.2183	3.3931E-07	164	1.8518E-06	1.8427E-06
B11	120	0.6629	0.1532	0.1462	4.4084E-07	204	1.6113E-06	1.3390E-06
B12	122	0.6651	0.1514	0.1574	4.4084E-07	196	1.7347E-06	1.3237E-06
B14	121	0.3149	0.3395	0.2544	2.3779E-07	149	1.5124E-06	2.3233E-06
B15	121	0.3100	0.3371	0.2660	2.3779E-07	143	1.5813E-06	2.2907E-06
B31	91	0.3889	0.1953	0.1419	3.3931E-07	157	1.2037E-06	1.4556E-06
B32	90	0.3815	0.1916	0.1489	3.3931E-07	149	1.2631E-06	1.4177E-06
B33	61	0.2653	0.1333	0.1267	3.3931E-07	93	1.0748E-06	8.4151E-07
B34	62	0.2798	0.1405	0.0937	3.3931E-07	118	7.9484E-07	9.1097E-07
B35	62	0.2681	0.1347	0.1316	3.3931E-07	93	1.1163E-06	8.5504E-07
B36	41	0.1833	0.0920	0.1024	3.3931E-07	60	8.6865E-07	4.7024E-07
B38	150	0.5420	0.2725	0.2744	3.3931E-07	185	2.3277E-06	2.2609E-06
B54	151	0.5750	0.2890	0.2354	3.3931E-07	219	1.9969E-06	2.4366E-06
B55	150	0.5556	0.2793	0.2562	3.3931E-07	199	2.1733E-06	2.3333E-06
B56	170	0.5728	0.2881	0.3234	3.3931E-07	186	2.7434E-06	2.4267E-06
B58	171	0.5890	0.2962	0.3084	3.3931E-07	198	2.6161E-06	2.5131E-06
B59	42	0.1847	0.0928	0.1170	3.3931E-07	56	9.9250E-07	4.7629E-07

Table 9. Effects of reaction duration on conversion of H_2S with 0.04-g alumina catalyst and a 100-SCCM feed stream containing 4,980-ppmv H_2S and 2,500-ppmv SO_2, 10-v% moisture, and 70-v% H_2 for 25 – 274 min at 130°C and 120 psia.

Time, min	Conversion of H_2S
25	0.52
85	0.27
114	0.21
144	0.17
187	0.14
216	0.13
245	0.15
274	0.12

Table 10. Effects of catalyst loading on conversion of H_2S to elemental sulfur with 0.02 – 0.08 g catalyst and a 100-SCCM feed stream containing 4,980-ppmv H_2S and 2,500-ppmv SO_2, 10-v% moisture, and 70-v% H_2 at 118 - 123 psia and 140°C.

Run Number	Temperature, °C	Pressure psia	Catalyst Amount, g	Total Feed scc/min	Space Time, s	Feed Composition, v%					Conversion
						H_2	H_2S	SO_2	moisture	N_2	
B2	140	121	0.04	100	0.0028	70	0.498	0.25	10	19.252	0.1903
B4	140	119	0.04	100	0.0028	70	0.498	0.25	10	19.252	0.2183
B1	140	121	0.02	100	0.0014	70	0.498	0.25	10	19.252	0.0924
B2	140	121	0.04	100	0.0028	70	0.498	0.25	10	19.252	0.1903
B3	140	120	0.02	100	0.0014	70	0.498	0.25	10	19.252	0.097
B4	140	119	0.04	100	0.0028	70	0.498	0.25	10	19.252	0.2183
B5	140	122	0.06	100	0.0043	70	0.498	0.25	10	19.252	0.2724
B6	140	119	0.06	100	0.0042	70	0.498	0.25	10	19.252	0.2935
B7	140	121	0.06	100	0.0043	70	0.498	0.25	10	19.252	0.2715
B8	140	121	0.08	100	0.0057	70	0.498	0.25	10	19.252	0.3581
B9	140	123	0.08	100	0.0058	70	0.498	0.25	10	19.252	0.2831
B10	140	118	0.08	100	0.0056	70	0.498	0.25	10	19.252	0.3623

CALCULATIONS

Gaseous samples having a 4-cm^3 volume, obtained from the outlet stream of a micro bubble reactor, are injected into a gas chromatograph to analyze gas chromatography (GC) areas of gaseous samples. Conversion of H_2S is obtained by dividing the GC area of H_2S from a reaction run with that from its blank run (see Equation 1).

$$x_A = \frac{(A_B - A_R)}{A_B} \tag{1}$$

where x_A: conversion of H_2S.

A_B: GC area of H_2S of the 4-cm^3 gaseous sample from a blank run.

A_R: GC area of H_2S of the 4-cm^3 gaseous sample from a reaction run.

$$2H_2S\ (g) + SO_2\ (g) \leftrightarrow 3S\ (\ell) + 2H_2O(g) \tag{2}$$

Experimental surface reaction rate of conversion of H_2S to elemental sulfur in a micro bubble reactor is obtained with amount of the alumina catalyst loaded in the micro bubble reactor, molar feed rate of H_2S to the micro bubble reactor, and conversion of H_2S, as shown in the following equation.

$$-r_A' = \frac{F_{Ao} x_A}{W} \tag{3}$$

where $-r_A'$: surface reaction rate

F_{Ao}: molar flow rate of H_2S in a feed stream to a bubble reactor

x_A: conversion of H_2S to elemental sulfur

W: amount of catalyst particles in a bubble reactor

Space time of gaseous reaction mixtures in the bubble reactor is calculated by dividing bulk volume of catalyst particles with volumetric flow rate of gaseous reaction mixtures fed under reaction conditions, as shown in the following equation.

$$\tau = \frac{V}{v_o} \tag{4}$$

where τ: space time

V: bulk volume of catalyst particles

v_o: volumetric flow rate of gaseous reaction mixture fed under reaction conditions

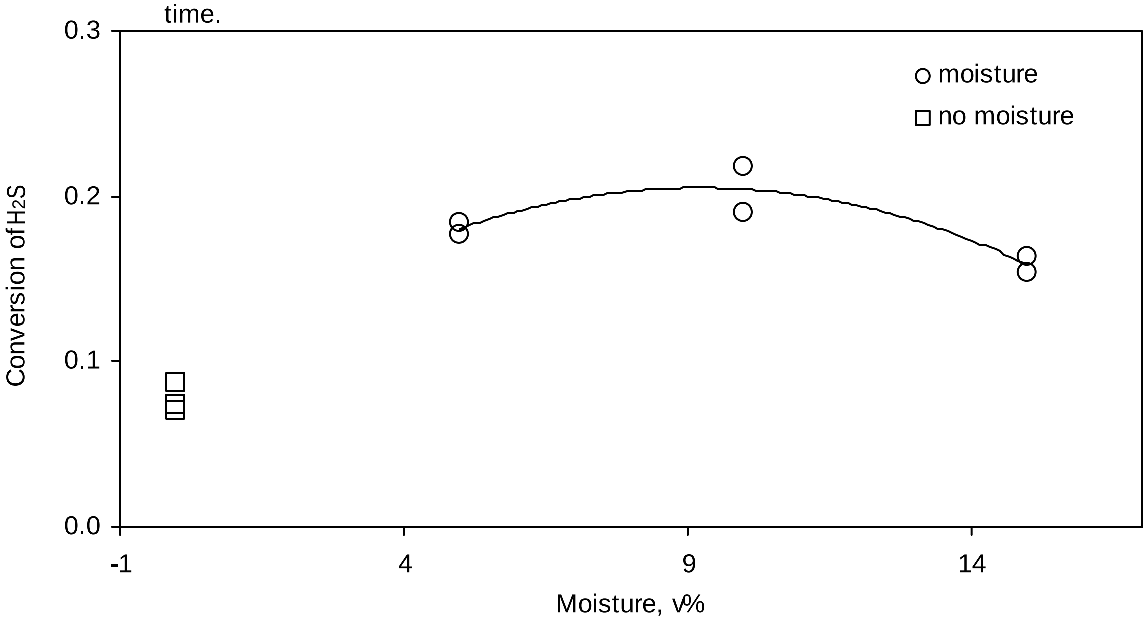
RESULTS AND DISCUSSION

Experiments on conversion of hydrogen sulfide to elemental sulfur were carried out for the space time range of 1 – 6 millieconds (ms) at 125 - 155^oC to evaluate effects of catalyst amount, moisture concentration, and reaction pressure on conversion of hydrogen sulfide to elemental sulfur. Simulated coal gas mixtures consist of 70 v% hydrogen, 2,500 – 7,500 ppmv hydrogen sulfide, 1,250 - 3,750 ppmv sulfur dioxide, and 0 - 15 vol % moisture, and nitrogen as remainder. Volumetric feed rates of a simulated coal gas mixture to a bubble reactor are 100 cm^3/min at room temperature and atmospheric pressure (SCCM). The temperature of the reactor is controlled in an oven at 125 - 155°C. The pressure of the reactor is maintained at 40 - 170 psia, loading 0.02 – 0.08 g catalyst particles in the micro bubble reactor.

Effects of Moisture on Conversion of H_2S to elemental sulfur

Experiments on conversion of hydrogen sulfide to elemental sulfur with 0.04-g catalyst were carried out for the space time range of 2.8 – 2.9 ms to evaluate effects of moisture concentration on conversion of hydrogen sulfide to elemental sulfur at 140°C and 118 – 122 psia. A gas mixture consisting of 70 v% hydrogen, 4,980-ppmv H_2S, 2,500 ppmv SO_2, 0 – 15 v% moisture, and nitrogen as remainder is fed to a micro bubble reactor. Volumetric feed rates of the gas mixture to the micro bubble reactor are 100 SCCM. Conversion of H_2S to elemental sulfur is 0.07 – 0.22.

Figure 3. Effects of moisture on conversion of H_2S with 0.04-g alumina catalyst and a 100-SCCM feed stream containing 4,980-ppmv H_2S and 2,500-ppmv SO_2, 0 - 15 v% moisture, and 70-v% H_2 at 140°C, 118 - 122 psia, and 2.8 - 2.9 ms space time.



Concentration of moisture in the presence of 4,980 ppmv H_2S and 2,500 ppmv SO_2 affects conversion of H_2S to elemental sulfur in the moisture range of 0 - 15 v% in a simulated coal gas mixture at 118 – 122 psia (see Figure 3). However, conversions of H_2S to elemental sulfur in the presence of moisture are higher than those in the absence of moisture. Conversion of H_2S to elemental sulfur in the presence of moisture appears to be not affected significantly by amount of moisture. Conversion of H_2S to elemental sulfur is highest at 10-v % moisture.

Figure 4. Effects of reaction temperature on conversion of H_2S with 0.04-g catalyst and a 100-SCCM feed stream containing 4,980-ppmv H_2S and 2,500-ppmv SO_2, 10-v% moisture, and 70-v% H_2 at 125 - 155°C, 120 psia, and 2.7 - 2.9 ms space time.

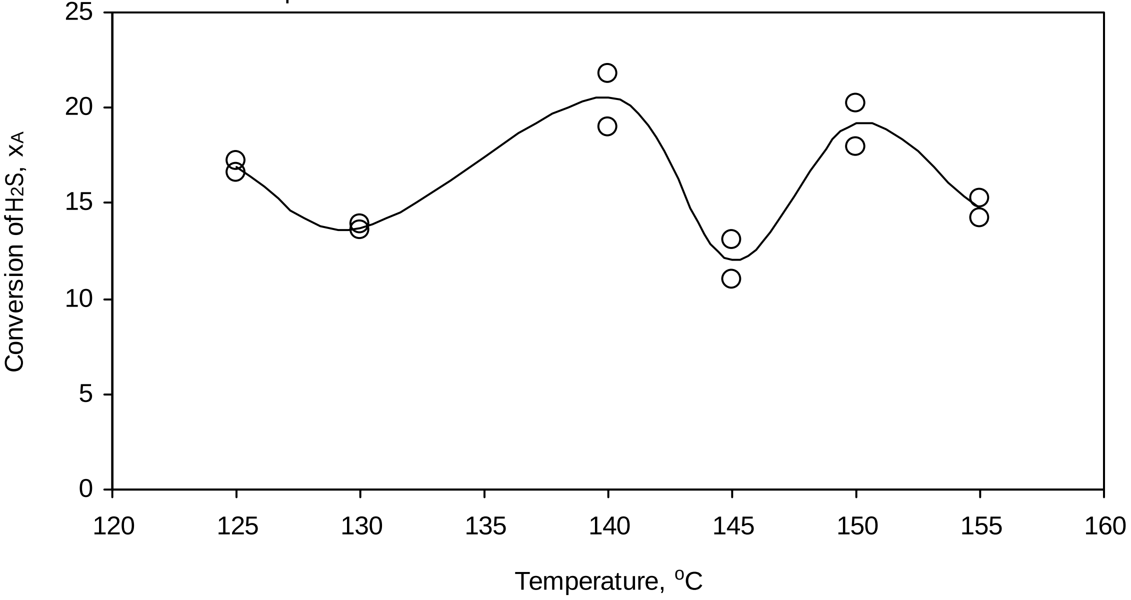
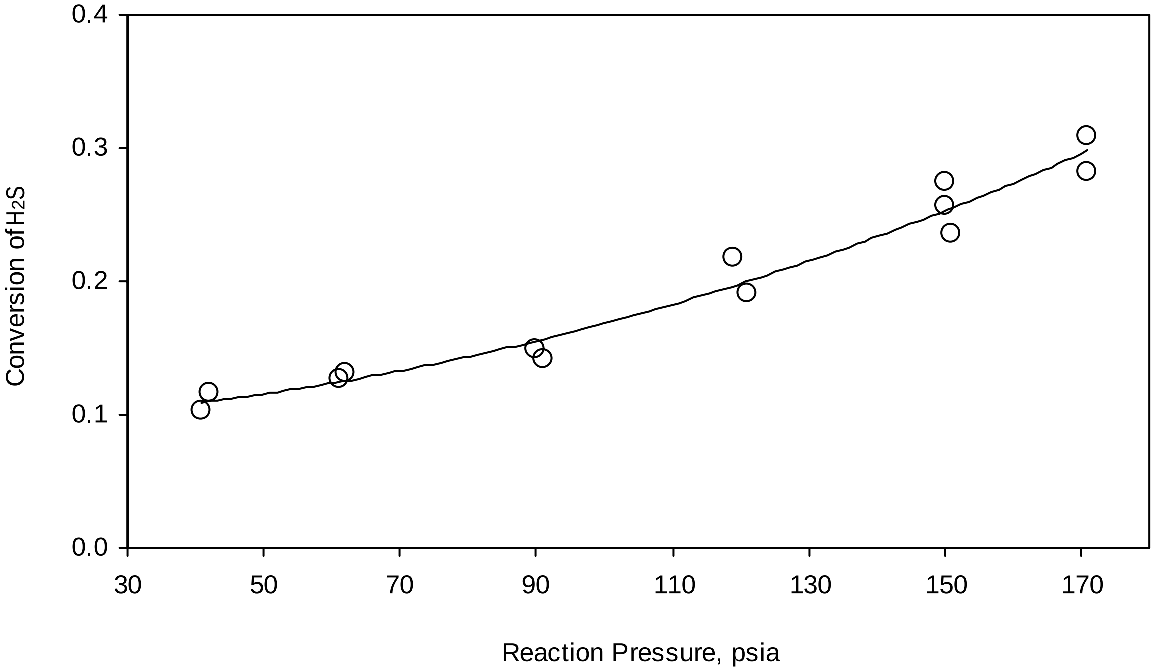


Figure 5. Effects of reaction pressure on conversion of H_2S with 0.04-g alumina catalyst and a 100-SCCM feed stream containing 4,980-ppmv H_2S and 2,500-ppmv SO_2, 10-v% moisture, and 70-v% H_2 at 40 - 170 psia, 140°C and 1 - 4 ms space time.



Effects of Reaction Temperature on Conversion of H_2S to elemental sulfur

Experiments on conversion of hydrogen sulfide to elemental sulfur with 0.04-g catalyst were carried out for the space time range of 2.7 – 2.9 ms to evaluate effects of reaction temperature on conversion of hydrogen sulfide to elemental sulfur at 125 - 155°C and 119 – 122 psia. Gas mixtures are fed to a micro bubble reactor containing 70-v% hydrogen, 4,980-ppmv H_2S, 2,500 ppmv SO_2, 10-v% moisture, and nitrogen as remainder. Volumetric feed rates of gas mixtures to the micro bubble reactor are 100 SCCM . Conversion of H_2S to elemental sulfur is 0.09 – 0.22. Conversion of H_2S to elemental sulfur does not follow the Arrhenius' equation. Reaction temperature affects conversion of H_2S to elemental sulfur. However, conversion of H_2S to elemental sulfur is highest at 140°C, while conversion of H_2S to elemental sulfur is lowest at 145°C over the reaction temperature range of 125 – 155°C (see Figure 4). Conversion of H_2S to elemental sulfur decreases with increased reaction temperature over the temperature ranges of 125 – 130°C, 140 – 145°C, and 150 – 155°C, whereas conversion of H_2S to elemental sulfur increases with increased reaction temperature over the temperature ranges of 130 – 140°C and 145 – 150°C

Effects of Pressure on Conversion of H_2S to elemental sulfur

Experiments on conversion of hydrogen sulfide to elemental sulfur with 0.04-g catalyst were carried out for the space time range of 1 – 4 ms to evaluate effects of reaction pressure on conversion of hydrogen sulfide to elemental sulfur at 140°C and 40 -170 psia. A gas mixture fed to a micro bubble reactor contains 70-v% hydrogen, 4,980-ppmv H_2S, 2,500-ppmv SO_2, and 10-v% moisture, and nitrogen as remainder. Volumetric feed rates of the gas mixture to the micro bubble reactor are 100 SCCM. Conversion of H_2S to elemental sulfur is 0.09 – 0.35. Reaction pressure affects significantly conversion of H_2S to elemental sulfur in the pressure range of 40 - 170 psia. Conversion of H_2S to elemental sulfur increases with reaction pressure over the pressure range of 40 -170 psia (see Figure 5).

Effects of H_2S and SO_2 Partial Pressures on Reaction Rates of H_2S

A reaction rate equation (see Equation 5) was developed with the following surface reaction mechanisms. Gaseous hydrogen sulfide is attached to active sites on the surface of catalyst particles, and then the H_2S attached to active sites on the surface of catalyst particles is reacted with gaseous SO_2 from a bulk gaseous reaction mixture to produce liquid elemental sulfur and water. Water produced from the reaction of H_2S with SO_2 is mostly evaporated into the gaseous reaction mixture.

$$-r_A' = \frac{kP_A^{\,2}P_B}{(1+k_AP_A)^2} \qquad (5)$$

where $-r_A'$: surface reaction rates of H_2S

k: surface reaction rate constant

k_A: equilibrium adsorption constant of H_2S on active sites of catalyst particles

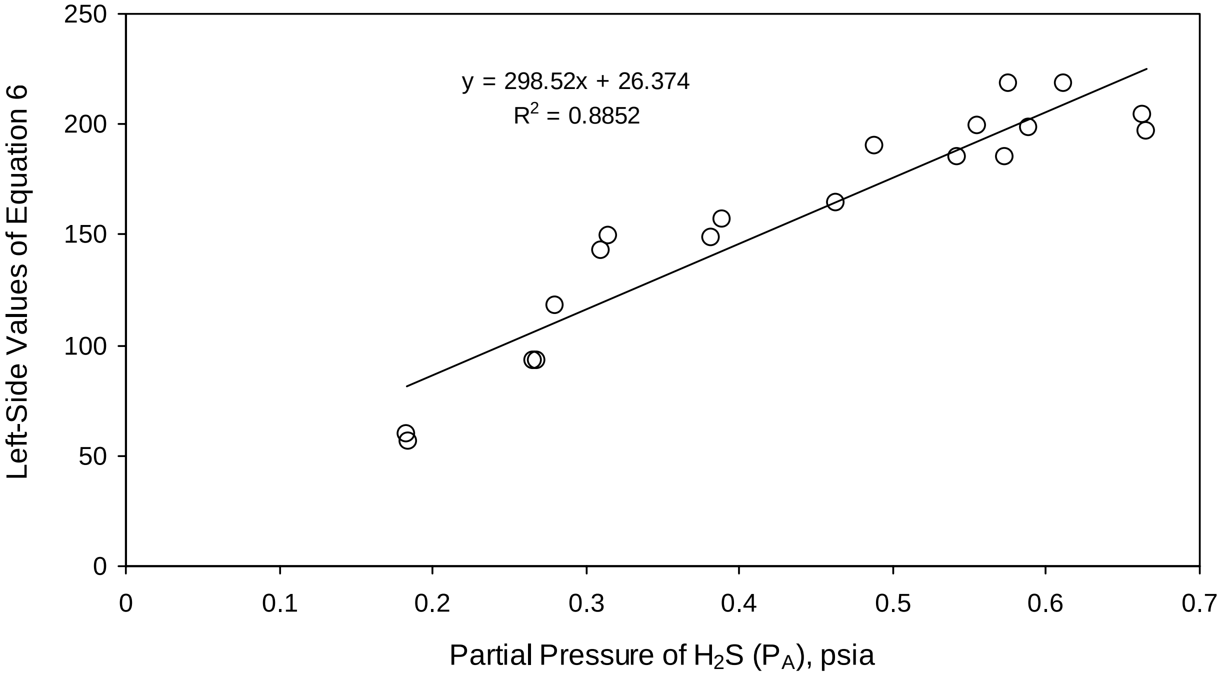
P_A: partial pressure of H_2S
P_B: partial pressure of SO_2

Rearranging Equation 5 produces Equation 6. Experimental data in Table 7 obtained at 140°C, 40 – 170 psia, 1 – 4 ms space time and 100 SCCM feed rate are applied to Equation 6 to determine the surface reaction rate constant k and the equilibrium adsorption constant k_A of H_2S.

$$\left(\frac{P_A{}^2 P_B}{-r_A{}'}\right)^{0.5} = \frac{1}{k^{0.5}} + \frac{k_A}{k^{0.5}} P_A \qquad (6)$$

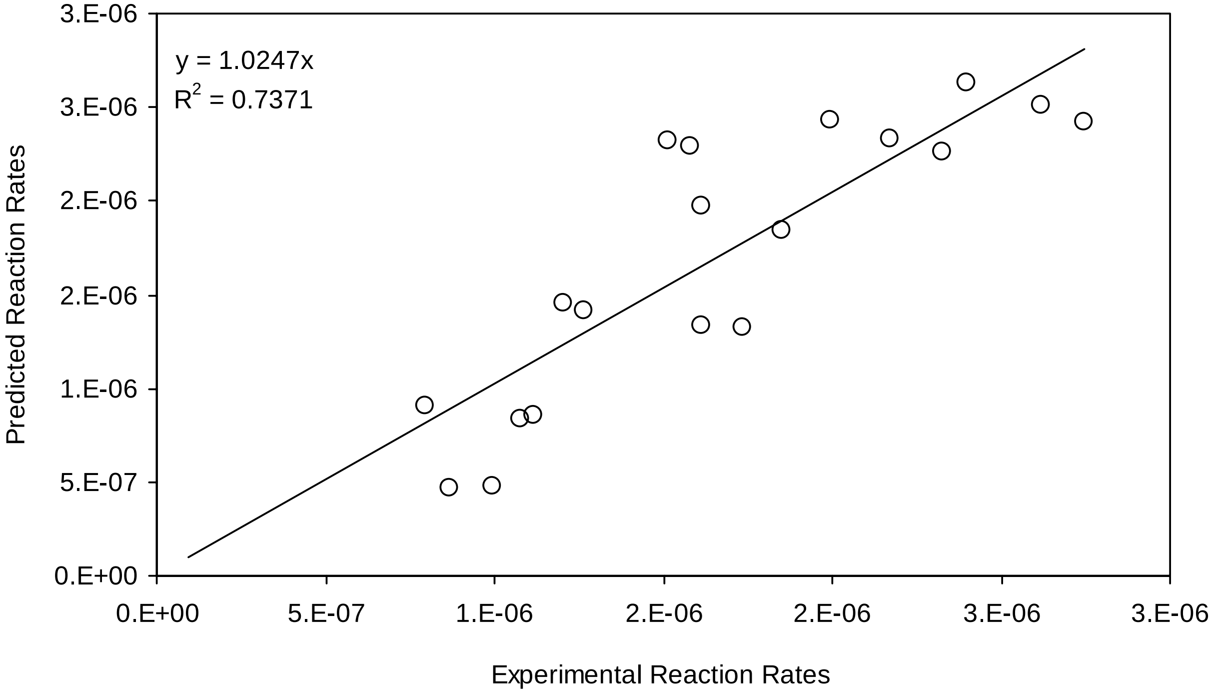
Partial pressures of H_2S and experimental surface reaction rates of H_2S determined with experimental data in Table 7 are applied to Equation 6. Left-side values of Equation 6 are plotted against partial pressures of H_2S, as shown in Figure 6. The value of a surface reaction rate constant k can be calculated from the intercept value of a linear regression line in Figure 6, whereas the value of an equilibrium adsorption constants k_A of H_2S on active sites of catalyst particles can be obtained from the slope value of the linear regression line. The value of the surface reaction rate constant k of H_2S and the value of the equilibrium adsorption constant k_A of H_2S, determined with the experimental data in Table 7, are $1.4376\text{x}10^{-3}$ g-mole/s-g-(psia)^3 and 11.3187 psia^{-1}, respectively. The developed reaction model suggests that H_2S is strongly adsorbed onto active sites of catalyst particles, and the reaction for conversion of H_2S to elemental sulfur is second order with respect to partial pressure of H_2S and first order with respect to partial pressure of SO_2.

Figure 6. Left-side values of the rearranged reaction model vs. partial pressures of H_2S.



Predicted surface reaction rates for conversion of H_2S to elemental sulfur in Table 8 were calculated with the surface reaction rate constant k and the equilibrium absorption constant k_A of H_2S determined by applying experimental data to the reaction model. Predicted surface reaction rates for conversion of H_2S to elemental sulfur were compared with experimental surface reaction rates for conversion of H_2S to elemental sulfur calculated with experimental data of conversion of H_2S, catalyst amount, and molar feed rate of H_2S, as shown in Figure 7.

Figure 7. Predicted reaction rates vs. experimental reaction rates.



Effects of reaction duration on catalyst activities

Effects of reaction duration on conversion of H_2S to elemental sulfur were examined at 130°C and 120 psia. The feed gas mixture to a micro bubble reactor contains 4,980-ppmv H_2S, 2,500-ppmv SO_2, 10-v% moisture, and 70-v% H_2. The volumetric feed rate of the feed gas mixture is 100 SCCM. The amount of fresh catalyst particles in the bubble reactor is 0.04 g. Initially, conversion of H_2S to elemental sulfur decreases drastically with increased reaction duration. Conversion of H_2S to elemental sulfur levels off, as reaction duration increases further, as shown in Figure 8. These observations may suggest that initially reaction takes place on both internal surface and external surface of porous catalyst particles, and then porous catalyst particles are plugged up with produced liquid elemental sulfur, as reaction duration increases further. These observations also indicate that reaction may occur mainly on external surface of catalyst particles rather than internal surface of catalyst particles, when conversion of H_2S levels off.

Figure 8. Effects of reaction duration on conversion of H_2S to elemental sulfur with 0.04-g alumina catalyst and a 100-SCCM feed stream containing 4,980-ppmv H_2S and 2,500-ppmv SO_2, 10-v% moisture, and 70-v% H_2 for 25 - 274 min at 130°C and 120 psia.

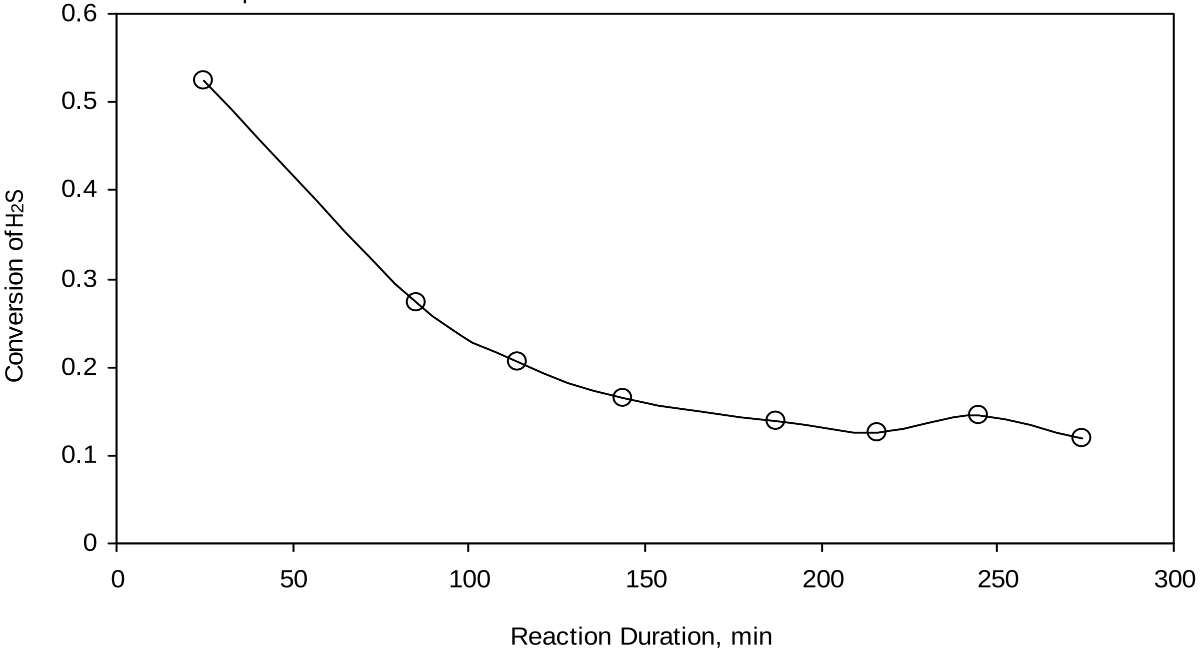


Figure 9. Effects of catalyst loading on conversion of H_2S with 0.02 - 0.08 g catalyst and a 100-SCCM feed stream containing 4,980-ppmv H_2S and 2,500-ppmv SO_2, 10-v% moisture, and 70-v% H_2 at 118 - 123 psia and 140°C.

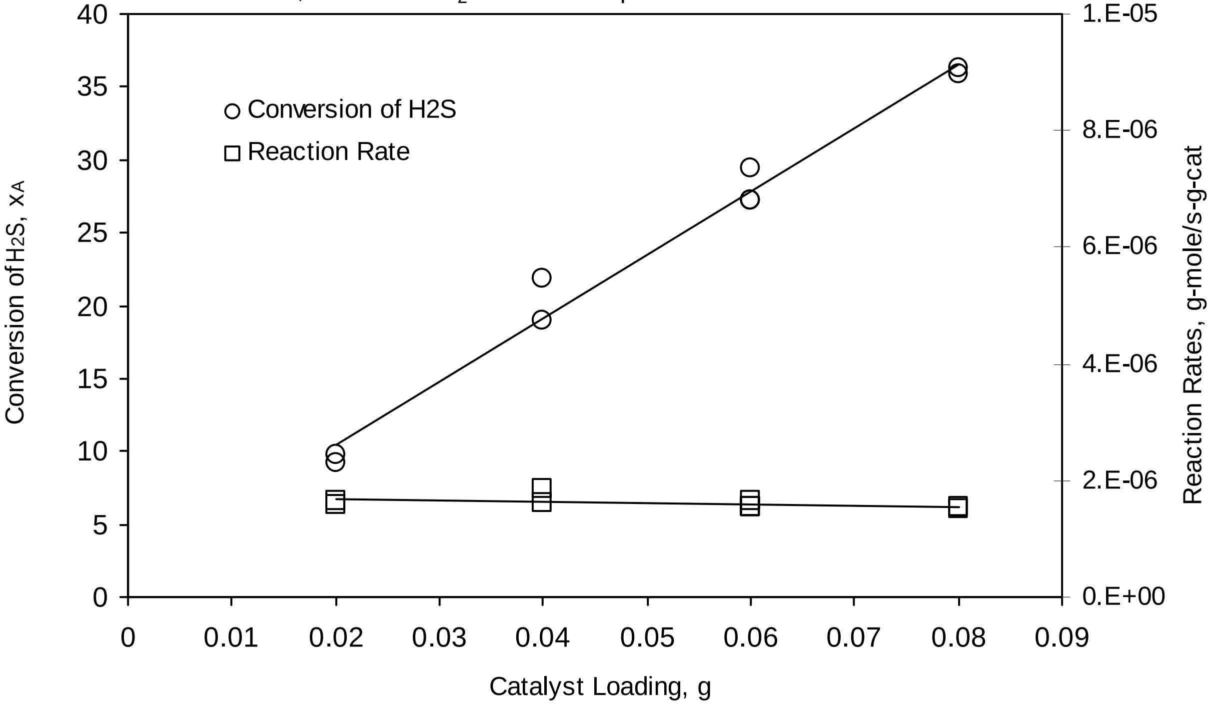
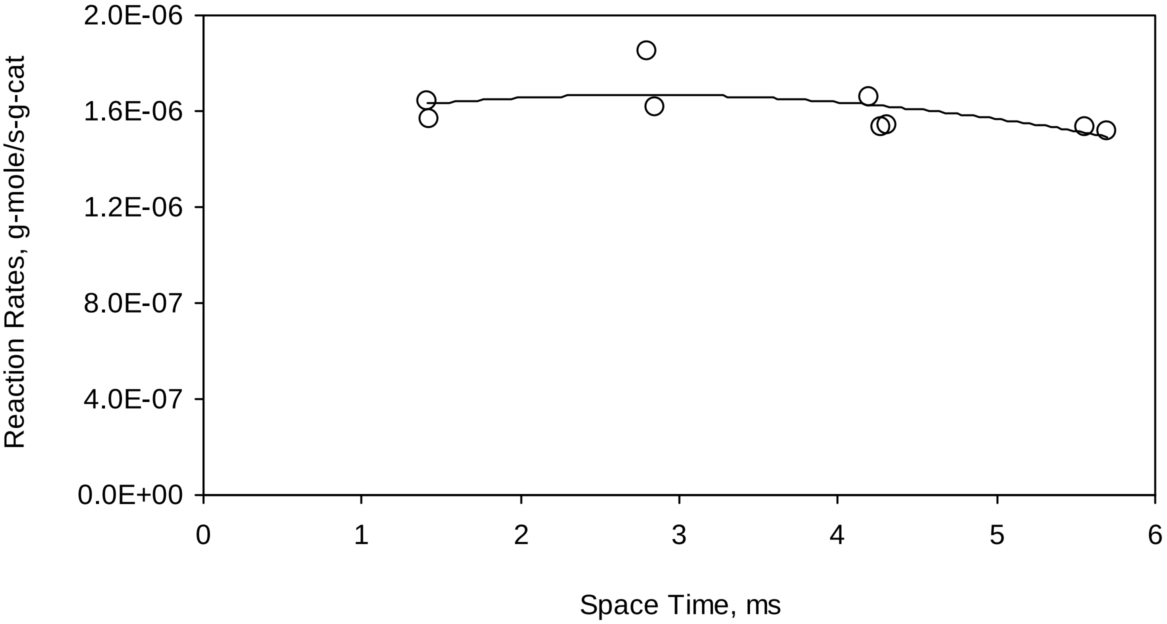


Figure 10. Effects of space time on experimental surface reaction rates of H_2S with 0.02 - 0.08 g catalyst and a 100-SCCM feed stream containing 4,980-ppmv H_2S and 2,500-ppmv SO_2, 10-v% moisture, and 70-v% H_2 at 118 - 123 psia and 140°C.



Effects of catalyst loading on conversion of H_2S

Effects of catalyst loading on conversion of H_2S to elemental sulfur were examined at 140°C and 118 - 123 psia. The feed gas mixture to a micro bubble reactor contains 4,980-ppmv H_2S, 2,500-ppmv SO_2, 10-v% moisture, and 70-v% H_2. The volumetric feed rate of the feed gas mixture to the micro bubble reactor is 100 SCCM. The amount range of fresh catalyst particles loaded in the micro bubble reactor is 0.02 – 0.08 g. Conversion of H_2S increases with catalyst loading. However, experimental reaction rate of H_2S (see Equation 3) is independent of catalyst loading, as shown in Figure 9. This result may indicate that both surface reaction rate k and equilibrium adsorption constant k_A of H_2S for conversion of H_2S with SO_2 to elemental liquid sulfur are not significantly affected by amount of catalyst particles loaded in the micro bubble reactor. These data also indicate that experimental reaction rate of H_2S with SO_2 be independent of space time of gaseous reaction mixtures in the micro bubble reactor, as shown in Figure 10.

CONCLUSIONS

The following conclusions were drawn based on experimental data generated from the micro bubble reactor system, and their interpretations,

- Conversion of H_2S to elemental sulfur does not follow the Arrhenius' equation. Reaction temperature affects conversion of H_2S to elemental sulfur. However, conversion of H_2S to elemental sulfur is highest at 140°C, whereas conversion of H_2S to elemental sulfur is lowest at 145°C over the reaction temperature range of 125 – 155°C.

- Reaction pressure affects significantly conversion of H_2S to elemental sulfur in the pressure range of 40 -170 psia. Conversion of H_2S to elemental sulfur increases with reaction pressure over the pressure range of 40 -170 psia.

- A reaction rate equation for the conversion of H_2S to element sulfur in the presence of SO_2 was developed with the following surface reaction mechanisms. Feed gaseous hydrogen sulfide is attached to active sites on the surface of catalyst particles, and then the H_2S attached to active sites on the surface of catalyst particles is reacted with gaseous SO_2 from bulk gaseous reaction mixtures to produce liquid elemental sulfur and water. Water produced from the reaction of H_2S with SO_2 is mostly evaporated into the gaseous reaction mixture.

- Effects of mass transfer of both H_2S gas and SO_2 gas through bulk gaseous reaction mixtures on reaction rates for the conversion of H_2S to elemental sulfur appear to be negligible according to the developed reaction model.

- Initially, conversion of H_2S to elemental sulfur appears to take place on both external surface and internal surface of porous catalyst particles, and then porous catalyst particles are plugged up with produced liquid elemental sulfur, as reaction duration increases further. Conversion reaction of H_2S to elemental sulfur may occur mainly on external surface of catalyst particles rather than internal surface of catalyst particles, when conversion of H_2S level off.

- Reaction rate of H_2S for conversion of H_2S with SO_2 to elemental sulfur is independent of catalyst loading. Reaction rate of H_2S for conversion of H_2S with SO_2 to elemental sulfur appears to be independent of space time of gaseous reaction mixtures in a bubble reactor.

- Both surface reaction rate k and equilibrium adsorption constant k_A of H_2S for conversion of H_2S with SO_2 to elemental liquid sulfur are not significantly affected by amount of catalyst particles loaded in the micro bubble reactor.

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PUBLICATIONS AND PRESENTATIONS

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STUDENTS ASSIGNED FOR THIS PROJECT

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