TASK II

Project II.9

DEVELOPMENT OF ADVANCED METHODS OF COAL LIQUEFACTION PRODUCT ANALYSIS

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This research program has the goal of developing HPLC methods and techniques to rapidly analyze coal liquids. This involves quantitatively separating them into well defined fractions on the basis of molecular size or type. Developing these methods will reduce analysis times from days to hours and will provide information necessary to assess product quality and to understand coal liquefaction process chemistry.

ACCOMPLISHMENTS

Since the outset of this program in May 1991, workers at West Virginia University have concentrated on separating the oil fraction of coal liquids by molecular type. An HPLC method was developed using three solvents, three columns and a column switching valve to separate a single injection of oil into saturate, aromatic and polar molecules, and further separate the aromatic molecules by ring size (1). Separating these same fractions using ASTM open column methods (2) requires several days work. With this HPLC method, these separations were achieved in just over one hour.

Quantitation of complex mixtures by HPLC is often difficult. The standard uv detector is not proportional to concentration and only sees molecules which absorb uv light. It does not detect saturate molecules at all. This quantitation problem has been solved for low boiling liquids by collecting fractions from the HPLC, adding internal standards for calibration and analyzing them on a gas chromatograph with a flame ionization detector (3). The method works well for distillate samples with molecules smaller than 20 or 25 carbon atoms. The method does not work for undistillable hydrocarbons.

Our solution for analyzing higher boiling hydrocarbons has been to add a mass sensitive, evaporative light-scattering detector to the HPLC system for direct quantitation of product molecules. This detector functions by spraying sample and solvent into a heated tube purged with inert gas. The low boiling components evaporate whereas higher boiling compounds form a mist whose concentration is measured by laser light scattering. The concentration of mist is a function of operating conditions and sample boiling point.

We have found that by operating the evaporative light-scattering detector (ELSD) at 40 °C, molecules with normal boiling points above 280 °C (536 °F) can be detected. On a molecular basis, this includes saturates like hexadecane (B.P. 286 °C) and aromatic hydrocarbons with 3 or more rings (B.P. > 340 °C). On a fuel basis, we can detect components in the heavy diesel range and higher.

Figures 1 and 2 show how the output of the uv and ELSD detectors differ for a mixture of aromatic compounds. Figure 1 shows the uv detector output for a Supelco PAH Test Mix whose components are listed in Table 1. Toluene (peak 1) is the solvent; all of the other components are present at a concentration of 0.06%.

Table 1. Supelco PAH Test Mixture

Peak	Name	Rings	B. P. (°C)
1	Toluene	1	110
2	Phenanthrene	3	340
2	Anthracene	3	340
3	Fluoranthene	4	375
3	Pyrene	4	393
4	Triphenylene	4	425
4	Benzo(a)anthracene	4	---
4	Chrysene	4	448
5	Benzo(e)pyrene	5	495
5	Perylene	5	---
5	Benzo(a)pyrene	5	495

Figure 2 shows the ELSD output for this same sample. Notice that toluene (peak 1) is not detected because it evaporates with the solvent. Peaks 2,3,4 and 5 remain because they have substantially higher boiling points and form a mist whose concentration is measured.

Peaks 2 and 3 each contain 2 components whereas peaks 4 and 5 each contain 3 components. If the ELSD provided a linear response, the peak areas would be in the ratio of 2:2:3:3. Peaks 4 and 5 seem to have about the same area, but the other peaks are much too small. This is the effect of a non-linear detector. The ELSD response as a function of operating conditions is currently being studied.

Examples of separated oil fractions for a Wilsonville heavy diesel (4) are shown in Figures 3 and 4. Figure 3 shows the output from the uv detector set at 254 nm. Polar molecules elute first followed by 1 and 2-ring aromatics. Saturate molecules are not in the figure since they are not detected by uv light.

Figure 4 shows the ELSD response for the same Wilsonville heavy diesel. The polar molecules have been resolved into 4 peaks whereas the saturates and aromatics have been separated into 2 peaks. The identities of the polar molecules are unknown. The first peak in the nonpolars are saturates and 1-ring aromatics that have not been resolved. The last peak is 2-ring aromatics.

The evaporative light scattering detector provides a means of detecting all high boiling molecules eluting from the HPLC and is promising for the analysis of coal liquids. Its response is non-linear but can be corrected with calibration curves. This problem is currently being studied.

REFERENCES

1. E. L. Kugler and S. L. Kugler, CFFLS Program Review, Lexington KY, August 11-14, 1991

2. Annual Book of ASTM Standards, Vol.05.02, ASTM, Philadelphia, PA, 1991, Standard D-2007

3. D. R: Keely, S. L. Kugler and E. L. Kugler, CFFLS Program Review, Wheeling WV, July 28-31, 1992

4. Obtained from V. U. S. Rao, U.S. DOE /Pittsburgh Energy Technology Center, September 1992

Figure 1: Supelco PAH Test Mix
uv Detector at 254 nm

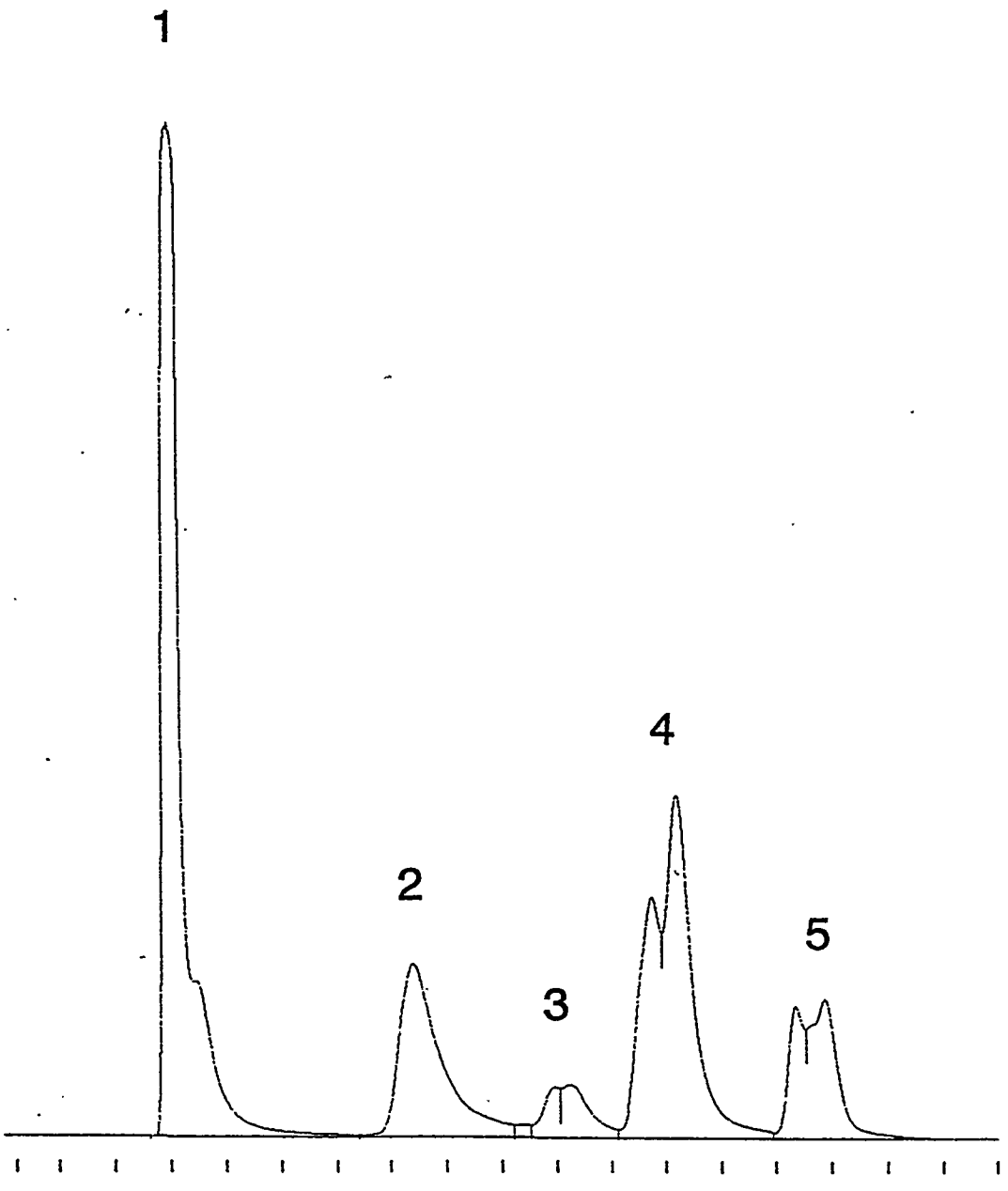


Figure 2: Supelco PAH Test Mix
Evaporative Light-Scattering Detector

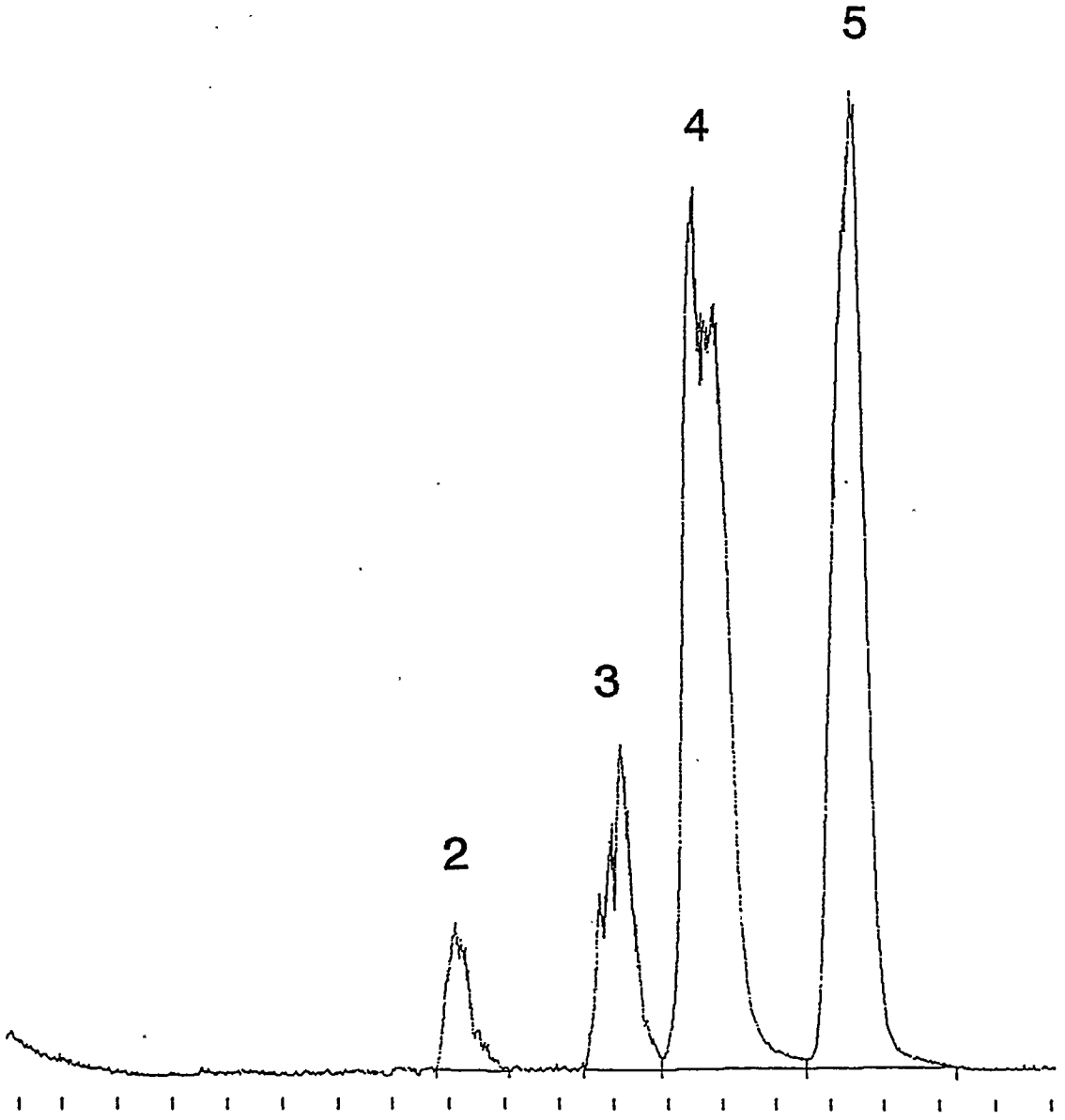


Figure 3: Wilsonville Heavy Diesel uv Detector at 254 nm

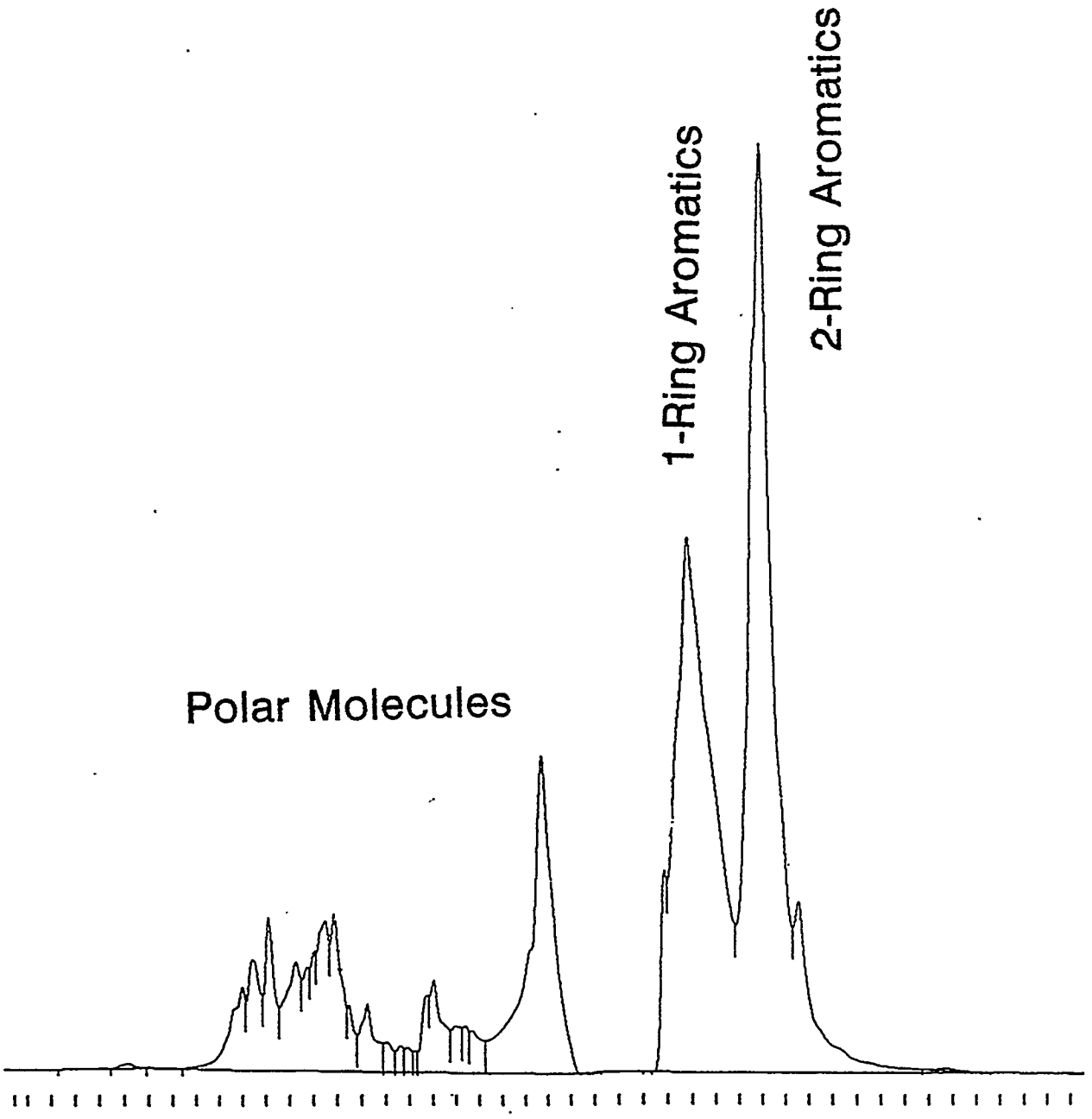
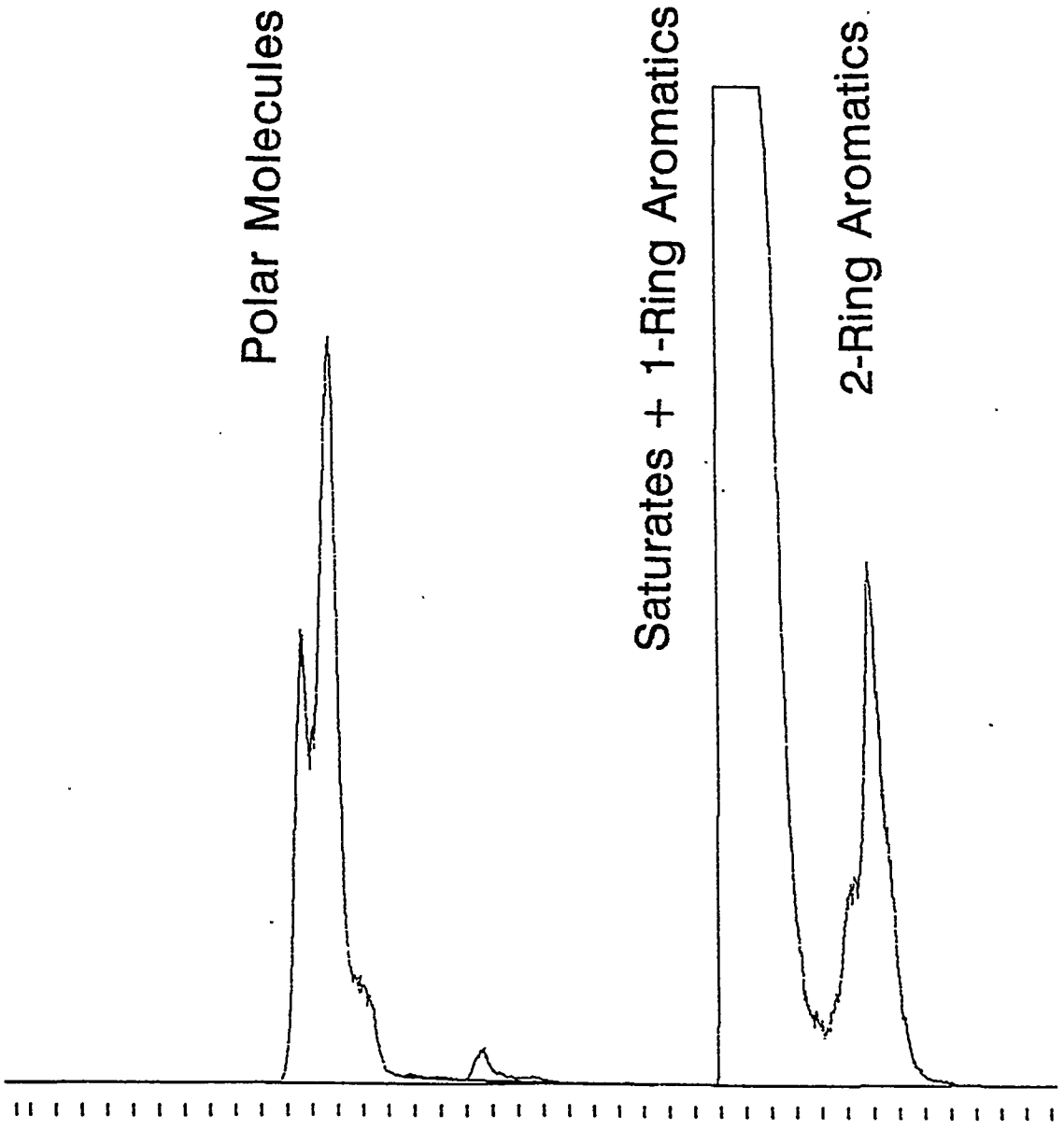


Figure 4: Wilsonville Heavy Diesel Evaporative Light-Scattering Detector



Task III

Novel Coal Liquefaction Concepts

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TASK III

Project III.1

BIOPROCESSING OF COAL

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SUMMARY

The influence of gas pressure on metabolism of *Desulfovibrio desulfuricans* for biohydrogenation of fumarate was studied. In order to overcome the hydrogen limitation, high pressure (5-500 psig) hydrogen gas was applied in a multipurpose bioreactor which was constructed in our laboratory. The study with *D. desulfuricans* under (normal and high pressure) H2 showed complete (~ 100%) reduction of fumarate within 24 hours. The hydrogenation of fumarate was observed only when hydrogen supply was continuous. The effect of organic solvents containing stilbene on *Desulfovibrio vulgaris* under hydrogen gas was also studied. Toluene containing stilbene was treated with the cells of *D. vulgaris* present in an aqueous medium under H2 (5 psig) to dissolve the stilbene and to enhance the solute transport through bacterial cell wall. Net decrease in H2 pressure was 2.0 psig over the controls at the end of 5 days. The results also show that the amount of stilbene present in toluene phase was decreased to 80%. When the concentration of the cells was increased five fold, a 50% decrease in stilbene content was achieved in two days with the utilization of 4 psig H2. Hence, the decrease in the stilbene content was attributed to the biological process.

Variation in liquefaction temperature showed that the direct liquefaction yield of the coal (KCER #91182) treated with *Thiobacillus ferrooxidans* was increased with increase of liquefaction temperature over the raw coal. Mossbauer data showed that all coals containing different high pyrite, high sulfur Illinois coals (IBC #102,105), and pyrite free DECS coal with added pyrite, (with initial pH 2.5) completely removed pyrite in 21 days. In-situ catalyst formation studies with *Acidianus brierleyi* showed

the formation of FeOOH crystals (by Mossbauer analysis). Although the percentage of iron in FeOOH (on DECS #17) was less than that of the other coals, it was clearly evident from IS value (.37) that it is indeed FeOOH. It also showed an increase of the liquefaction conversion of 14% over the control which did not contain *A. brierleyi.*

I. Biohydrogenation Studies Using Sulfate Reducing Bacteria

Microbial activities have been employed as the basis for chemical transformations of various compounds. One promising application involves the use of bacteria containing hydrogen uptake hydrogenase enzyme to hydrogenate coal. We have used *Desulfovibrio desulfuricans, D. vulgaris* and conducted several experiments to investigate the biohydrogenation of several substrates, including the coal-related model compound *trans*-stilbene.

Since hydrogen will be utilized for bioprocessing, the pressure must be increased in order to enhance the solubility of the gas in a liquid medium (e.g., it is known that at 50°C, for a change in pressure from 1 to 34 atmospheres, the solubility of hydrogen in water increases approximately 60 times). This research is also looking at the effect of pressure on the bacterial culture and hydrogenation reaction. The solubility of coal-related model compounds is also a limiting factor for biohydrogenation. The solubility of coal-related model compounds can be enhanced using nonaqueous (e.g., toluene) media for biohydrogenation.

a) **Effect of Pressure on *Desulfovibrio desulfuricans***

Experimental Setup

For each experiment, 1-2 grams (wet weight) of bacteria were needed. The bacteria were cultured in 15 liter glass batch fermenters. The solution medium contained the following compounds in amounts scaled to grams per 1 liter of solution: 0.5 K2HPO4; 1 NH4Cl; 5 Na2SO4; 0.02 CaCl2.2H2O; 0.2 MgSO4.7H2O; 18 60%(w/w) DL-sodium lactate; 0.5 ferric ammonium citrate; 0.1 sodium thioglycollate; 0.1 ascorbic acid; and 0.05 yeast extract. After mixing up the chemical medium, the pH was adjusted to 7.7 for optimum growth. Then we sterilized the medium and fermenter and sparged nitrogen through the system overnight to attain sterile

anaerobic conditions. The next day, we inoculated the medium with 1-2 liters of solution from a previous batch. The incubation period for growth was about 1 week.

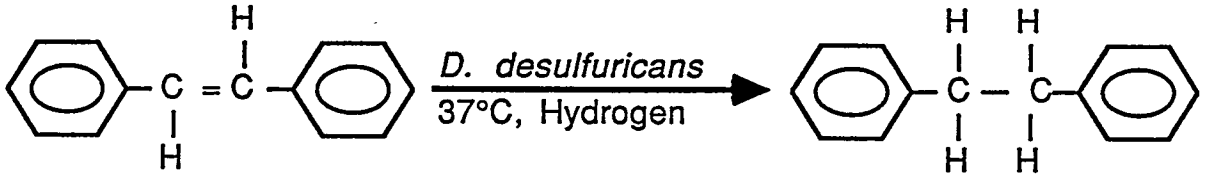
After the culture matured, it was centrifuged to collect the bacteria. Ferrous sulfide precipitate is also collected in the process. The generation of this precipitate is important since it removes sulfide from solution that would otherwise inhibit the reaction. The solid pellet of bacteria and sulfide precipitate was repeatedly washed and centrifuged to separate out and purify the bacterial culture. Once purified, the culture was ready to use. It was very important to keep the bacteria away from open air at all times and to maintain anaerobic conditions because the bacteria are very sensitive to oxygen.

We constructed a 350 ml stainless steel batch reactor system (Figure 1). The reactor was equipped with a magnetic stirrer control and an electric temperature control to maintain a homogeneous medium at the optimum growth temperature (36°C). A constant overhead pressure could be applied to the reactor system. This configuration was used for the first two experiments involving stilbene hydrogenation.

The reactor was then modified to allow a known, steady stream of hydrogen gas to be sparged through the system. Further modifications included the addition of a high pressure sample port and a low (atmospheric) pressure reactor in series with the high pressure reactor. This would allow atmospheric pressure experiments to be simultaneously conducted for a comparison (Figure 2).

Hydrogenation of *trans*-Stilbene

Two experiments were conducted to determine if granular stilbene could be hydrogenated to form bibenzyl in an aqueous medium containing bacteria in the presence of hydrogen gas. A GC/MS spectra of stilbene and bibenzyl is shown in Figure 3. The desired reaction is given as



A constant overhead pressure of 500 psig was maintained. The reactor medium contained only the nutrients that the bacteria needed for stabilization. One gram of stilbene was added to 220ml of this medium and placed in the reactor. One to two grams (wet weight) of cells were added and stirred in while sparging with hydrogen to maintain anaerobic conditions. The system was then pressurized to 500 psig and maintained for five days. After depressurization, the medium was analyzed according to procedures outlined in the analysis section. A GC/MS analysis of the first two reactor runs with constant hydrogen pressure has revealed that no significant hydrogenation was detected (Figure 4) with 80% of the stilbene recovered.

After the reactor had been modified for gas sparging and sample removal, we ran a third experiment with stilbene at low and high pressure simultaneously. Samples of the medium were taken every day. This medium contained two additional nutrients, lactate and sulfate, previously left out of the first two runs. In the earlier experiments, lactate was not added since it also acts as the source of hydrogen and we desired to utilize hydrogen gas. The addition of lactate was initiated to help drive the reaction to the right. A small amount of sulfate was also added to the medium. This was added with the idea of initiating the hydrogenation reaction, then observing a substrate transfer from sulfate to stilbene.

Upon analysis, it was found that both the low and high pressure samples contained no significant degree of hydrogenation with 90% and 95% of the stilbene recovered, respectively. The bacteria, however, did retain its viability for all runs even after five days of high pressure exposure to stilbene. It was decided that the low conversion might be due to the low solubility of stilbene in water. Steps to enhance solubility would include dissolving the stilbene in an organic solvent and contacting it in a two phase system with bacteria in an aqueous medium.

Reduction of Sulfate

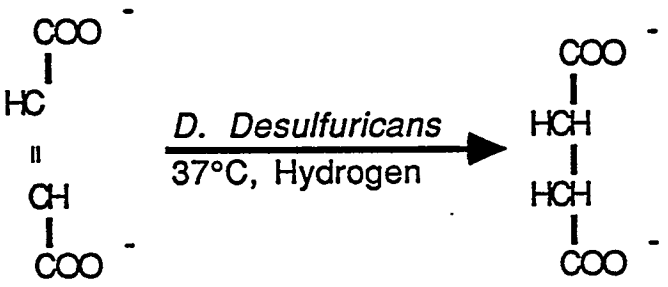
In order to characterize the effect of pressure on sulfate reducing bacteria, it was desirable to run experiments using the bacteria's natural substrate. The bacteria reduces sulfate to sulfide by the following reaction.

$$2\,CH_3CHOHCOO^- + SO_4^{2-} \xrightarrow[37°C,\ Hydrogen]{D.\ desulfuricans} 2(CH_3CO^-) + 2CO_2 + HS^- + 2OH^-$$

Both the high and low pressure batch reactors were filled with 300 ml of medium containing sulfate (0.65 g/L), lactate (1.29 g/L), and other necessary nutrients. After inoculation with *D. desulfuricans*, the reactor was pressurized to 250 psig with inert nitrogen gas. Samples taken over a six day time period were analyzed for cell growth, reduction of sulfate, and reaction of lactic acid. The conversion of sulfate was 78% and 88% for the low and high pressure, respectively. Similarly, the lactate was consumed with conversions of 99.8%. Figure 5 shows the concentration profile of lactate for both low and high pressure with time. Figure 6 shows the change in absorbance as related to cell protein for low and high pressure. It is important to note that both the lactate and protein analysis indicate that the hydrogenation reaction was initiated in the high pressure reactor well before the low pressure system. Since the gas used was inert nitrogen, we concluded that the high pressure aided in maintaining anaerobic conditions. *D. desulfuricans*, under high pressure (250 psig of nitrogen), not only survived, but also increased the cell protein with concomitant utilization of lactate. This experiment indicates that *D. desulfuricans* may be used under high pressure of hydrogen for the hydrogenation studies of the organic compounds.

Hydrogenation of Fumarate

The bacteria used to hydrogenate sulfate in the previous section was found to be very active. We decided to use this bacteria in an experiment to investigate hydrogenation of a soluble organic under low and high pressure hydrogen gas. Fumaric acid (.636 g/L) was added to medium containing basic nutrients. After inoculation, samples were taken every twelve hours. The hydrogenation reaction of fumarate to succinate is



After one day, the conversion of fumarate was 97.5% in the low pressure reactor and 96.2% in the high pressure reactor (Figure 7). The reaction occurred quickly due to the high activity of the hydrogenase enzyme in the bacteria. Results from the protein analysis show that the bacteria did not grow during this period (Figure 8). An analysis of the succinate in the medium is also being done to verify hydrogenation.

b) Analysis of the Bioreaction Materials

Several analytical techniques have been researched and developed to analyze the various compounds being tested. For the solid stilbene experiments, the reaction mixture is separated into liquid and solid phases and treated as in Figure 9. After washing and cleaning as shown in the figure, an extraction is carried out for both phases to dissolve all of the stilbene in methylene chloride (Figure 10). The resulting solutions are analyzed in a GC/MS against known standards.

Bacterial growth rates are analyzed by determining the amount of protein in the medium as described by Lowry1. The protein was correlated to a standard curve of bovine serum albumin. Lactate is an important hydrogen donor and carbon source for sulfate reducing bacteria. We are using an accurate colorimetric method used by Lawrence 2,3 to determine lactate concentrations in our experiments. Sulfate concentrations are determined using the gravimetric method4. We might also employ a turbidimetric method5-7 to determine sulfate concentrations as a function of time in future experiments. Fumarate concentrations were analyzed using a spectrophotometer at 210nm. The analysis of succinate will be done using either enzyme colorimetry or HPLC analysis.

c) Influence of Organic Solvents on Biohydrogenation of Stilbene by *Desulfovibrio vulgaris*

In order to solubilize stilbene and to mediate transfer of hydrogen, toluene was used for biohydrogenation experiments. A new culture, *D. vulgaris*, was used based on the highest activity and stability of the hydrogenase. The hydrogenation of the stilbene was carried out by supplementing the nutrients (e.g., lactate and iron) in limited quantities. These nutrients are required for the growth of the organism and to improve the activity of the hydrogenase which contains iron, nickel, and sulfur. In order to determine the requirements of any of these nutrients, individual experiments with different nutrients were done along with suitable controls. At the beginning of the reaction, all the vials were pressurized to 4.5 psig with hydrogen. In the presence of toluene, the head-space pressure decreased significantly when compared to all the other set of controls (Figure 11). Total protein content of the test with toluene was increased from 101 µg/ml to 251 µg/ml by the end of 12 days (Table 1). The increase in protein content also indicates that *D. vulgaris* can tolerate the presence of a minimum of 35% toluene. Toluene is also known to permeate the bacterial cells, which might allow for the transport of larger molecules into the cells.

The GC-MS analysis of the reaction mixture was carried out to determine the transformation of stilbene. With the analysis of the toluene phase obtained so far, stilbene present in test (with bacteria) solution with toluene decreased from 25 ng/ml to 4.7 ng/ml. Whereas the control with initial 25 ng/ml was recovered up to 24.5 ng/ml at the end of the reaction (Table 2). The control reaction system was identical in every respect with the test solution composition with the exception of the bacterial cells. Although 80% of stilbene decreased from the test solution, we did not find significant formation of bibenzyl as an end product. This may indicate that bibenzyl might have been dispersed in the inter-phase or it was not an end product but acted as an intermediate. In the present analytical method of the toluene phase, first six minutes were not analyzed due to the solvent (toluene) delay operation. Moreover, the inter-phase and the aqueous phase analysis have to be analyzed in search of any product formation.

When the initial cell protein concentration was increased to 498 µg/ml (~5 fold), approximately 50% of the stilbene content in the toluene phase was decreased in two days under hydrogen gas and toluene. This rate of decrease of stilbene clearly shows that it is due to the metabolic activity of *D. vulgaris* in the presence of hydrogen. The presence of tetralin containing stilbene showed only 0.2 psig hydrogen utilization in 24 h. Tetralin is toxic for the cells of *D. vulgaris* since, the cells were lysed and lost the original grayish-black pigmentation within 6 h. of the reaction. The cells recovered from the medium treated with the tetralin did not produce sulfide in the sulfate reducing medium.

A two phase hydrogenation experiment (under high pressure) contacting a solution consisting of stilbene dissolved in toluene with an aqueous medium containing *D. desulfuricans* is under way.

II. Precipitation of Active Iron Catalyst on Coal Surface Under Aerobic/Anaerobic Conditions

This part of the work deals with the improvement on the formation of ultra-fine active iron particles and to substantially reduce the time required for the deposition of the fine FeOOH crystals on the surface of coal by using iron/pyrite utilizing microorganisms. We reported earlier that the archaebacterium *Acidianus brierleyi* can bring about significant changes in the iron forms of biotreated coals (KCER #91182) with enhanced liquefaction yield (25%).

a) Effect of Temperature on Direct Liquefaction yield of the *Thiobacillus Ferrooxidans* Treated Coal

Coal (KCER #91182) was treated with *T. ferrooxidans* in a fermenter maintaining at constant pH 2.8, temperature 30°C and sparged with CO2 plus O2 followed by H2. The biotreated and raw coal were subjected to direct liquefaction using DMDS at different temperatures for 15 min. under hydrogen (initial pressure 800 psig). With the increase of temperature, the biotreated coal showed higher conversion than that of raw coal (Ref. Half yearly report 1992-93). Approximately 10% increase in liquefaction yield was observed at 385°C over the raw coal.

Therefore, the present study clearly indicates the increase in conversion was solely due to biological treatment but not due to any abiotic process.

b) Biological Reaction Variations During the Processing of IBC and DECS Coals in the presence of *Acidianus brierleyi* and Effect on Direct Liquefaction of the Biotreated Coals

Different coal samples (IBC #101, #102, #105 equivalent to Argon premium coal and DECS #17), with varying amounts of iron and sulfur, were used for the catalyst formation. IBC #101, #102, and #103, which have very high pyrite (1.2 to 2.4% dry basis) and total sulfur (3.4 to 4.4% dry basis) were subjected to biotreatment with *A. brierleyi* at pH 2.5 and 65°C under aerobic conditions. DECS #17 which has a negligible quantity of pyritic and non-pyritic iron, was mixed with pyrite (2500 ppm). This mixture was then subjected to biotreatment with *A. brierleyi* at pH 2.5 and 68°C. Of the four biotreated coals studied, IBC #105 (with 2.4% pyrite dry basis) showed significant release of iron (220 ppm, at the end of 15 days) into the aqueous phase and then started to decrease the liquid phase iron concentration. Whereas the control showed only increase of liquid phase iron (148 ppm, at the end of 21 days) (Figure 12).

The amount of sulfate released by the biotreated coals into the aqueous phase was measured by the gravimetric method. Biotreated IBC #105 showed complete utilization of the pyritic sulfur (2.4% dry basis) as sulfate in the aqueous phase (Figure 13). DECS coal with added pyrite showed only traces of liquid phase iron (Figure 14) and the sulfate was not detectable in liquid phase even at the end of 21 days. The biotreated coals were analyzed using Mossbauer spectroscopy (by Dr. Huffman's group) to further elucidate the effect of biotreatment particularly to determine the forms of iron. It showed that pyrite was completely oxidized in all coals which were treated with *A. brierleyi* (Table 3). This analysis also revealed that the formation of the percentage of iron (36) as FeOOH (of IBC #105) was higher than that of DECS #17 (12% Fe of FeOOH) with predominant formation of jarosite (88% Fe) (Table 3). However, the liquefaction conversion went up by 14% only in the case of DECS coal treated with *A. brierleyi* (Table 4). This might be due to the formation

of FeOOH, which showed an IS value of .37, exactly the same as pure FeOOH. Whereas in other coals the IS value was away from .37 and thus resulted as an inefficient catalyst to influence the liquefaction yield. It is also interesting to note that FeSO4 was utilized in the presence of *A. brierleyi.* The implication of this property is yet to be determined.

Further work will be focussed on DECS #17 with the addition of pyrite and IBC #105 with controlled pH at 2.5. This will enable *A. brierleyi* to oxidize pyrite rapidly. Then the pH will be increased to 2.8 for the reprecipitation of the liquid phase iron.

References

1. Lowry, O.H., Rosebrough, N.J., Farr, A.L., and Randal, R.J., J. Biol. Chem., 193:265-275 (1951).

2. Lawrence, A.J., Austral. J. Dairy Technol., 25:198-200 (1970).

3. Barker, S.B., Summerson, W.H., J. of Biol. Chem., 38:535-554 (1941).

4. APHA 1989. Standard methods for the examination of water and waste water, 19th edition. APHA, Washington, D.C.

5. Herrera, L., Hernandez, J., Ruiz, P., and Gantenbein, S., Environmental Toxicology and Water Quality, 6:225-237 (1991).

6. Okabe, S., Characklis, W.G., Biotech. Bioeng., 39:1031-1042 (1992).

7. Okabe, S., Nielsen, P.H., and Characklis, W.G., Biotech. Bioeng., 40:725-734 (1992).

Table 1. Analysis of Protein Content of *D. vulgaris* Cells Present in Aqueous phase (initial H2 pressure = 4.5 p.s.i., pH = 7.6)

Treatment	Initial protein µg/ml	Protein (12th day) µg/ml
Test* (no toluene)	92	215
Aqueous medium only	0	0
Cells alone (aqueous medium)	98	123
Test* (35% toluene)	101	251
Toluene only	0	0

* Test was treated with *D. vulgaris*

Table 2. Decrease of Stilbene content (determined by GC-MS) in Two-phase System Containing 35% Toluene (pH = 7.6, temp. = 37°C, time = 12 days)

Sample	Area count* (of stilbene)	Mass (of Stilbene) ng/µl
Standard	221 377 764	50
Control (no bacteria)	108 649 612	24.5
Test (with bacteria)	20 765 469	4.7

* Area count was obtained from an average of three concurrent values (injections0. This observation was also replicated in three different experiments.

Table 3. Composition and Phases of Iron Determined by Mossbauer Analysis of Different Illinois and DECS #17 Coals (5%) Treated with and without *Acidianus brierleyi* with an Initial pH of 2.5 at 68°C Incubated in Flasks Kept on a Rotary Shaker for 21 Days.

	% Fe			
Coal type	Pyrite	FeOOH[a]	Jarosite	$FeSO_4$
IBC #101T	-	36 (IS .38)	64	-
IBC #101C	11	-	89	-
IBC #105T	-	22 (IS .36)	77	1.0
IBC #105C	12	-	85	2.5
DECS #17[b]T	-	12 (IS .37)	88	-
DECS #17[b]C	80	-	14	5

T - Test or coal was treated with *A. brierleyi*

C - Control or coal was treated without *A. brierleyi*

- - Not detectable

[a] - The IS value for FeOOH is .37

[b] - Pyrite (2500 ppm) was added to the pyrite free coal

Table 4. Direct Liquefaction Conversion and Oil Content of Different Illinois and DECS #17 Coals (5%) Treated with and without *Acidianus brierleyi* with an Initial pH of 2.5 at 68°C Incubated in Flasks Kept on a Rotary Shaker for 21 Days.

Coal type	Total conversion	Oil yield
IBC #101T	50	17
IBC #101C	47	16
IBC #105T	52	20
IBC #105C	46	17
DECS #17*T	79	25
DECS #17*C	65	20

T - Test or coal was treated with *A. brierleyi*

C - Control or coal was treated without *A. brierleyi*

* - Pyrite (2500 ppm)was added to the pyrite free coal

Liquefaction Conditions:

Temp. 385°C

Time 15 min.

Pressure 800 p.s.i., H_2 gas (cold)

DMDS 20% in access of iron in coal

Figure 1. Schematic Diagram of High Pressure Biological Hydrogenation Unit

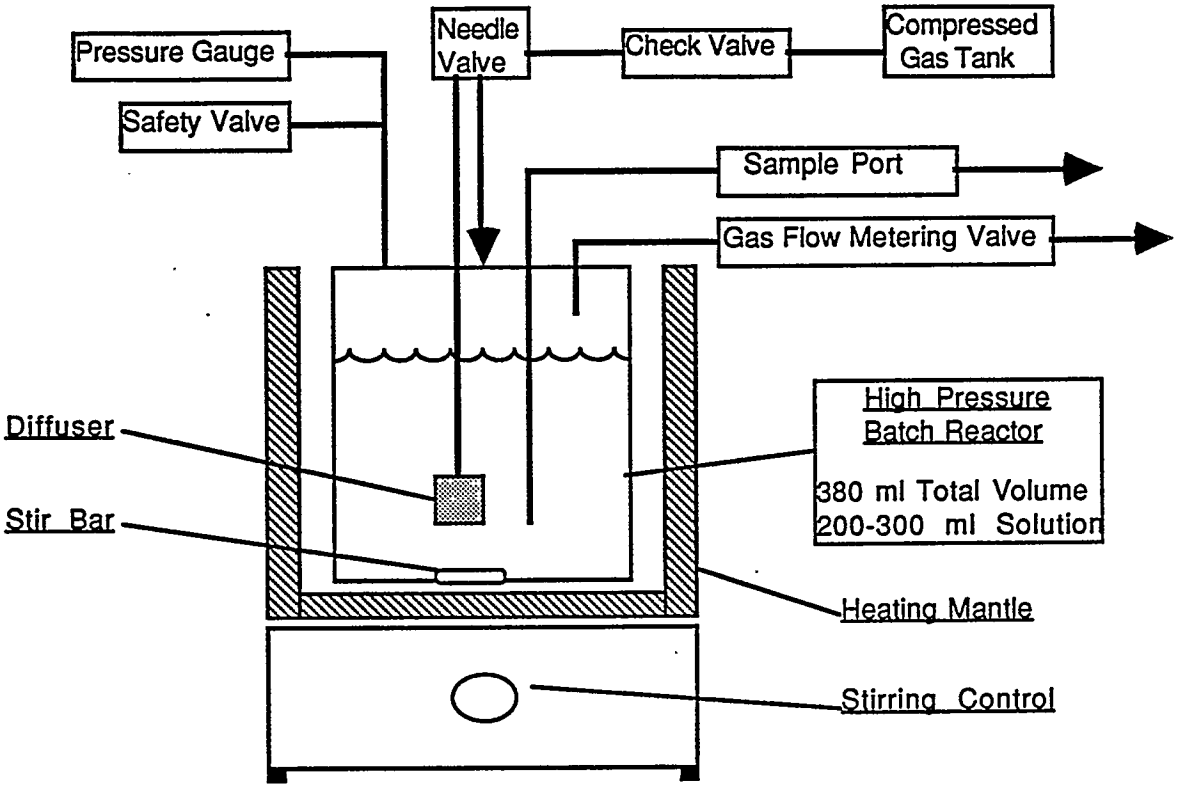


Figure 2. Schematic Diagram of Low Pressure Biological Hydrogenation Unit

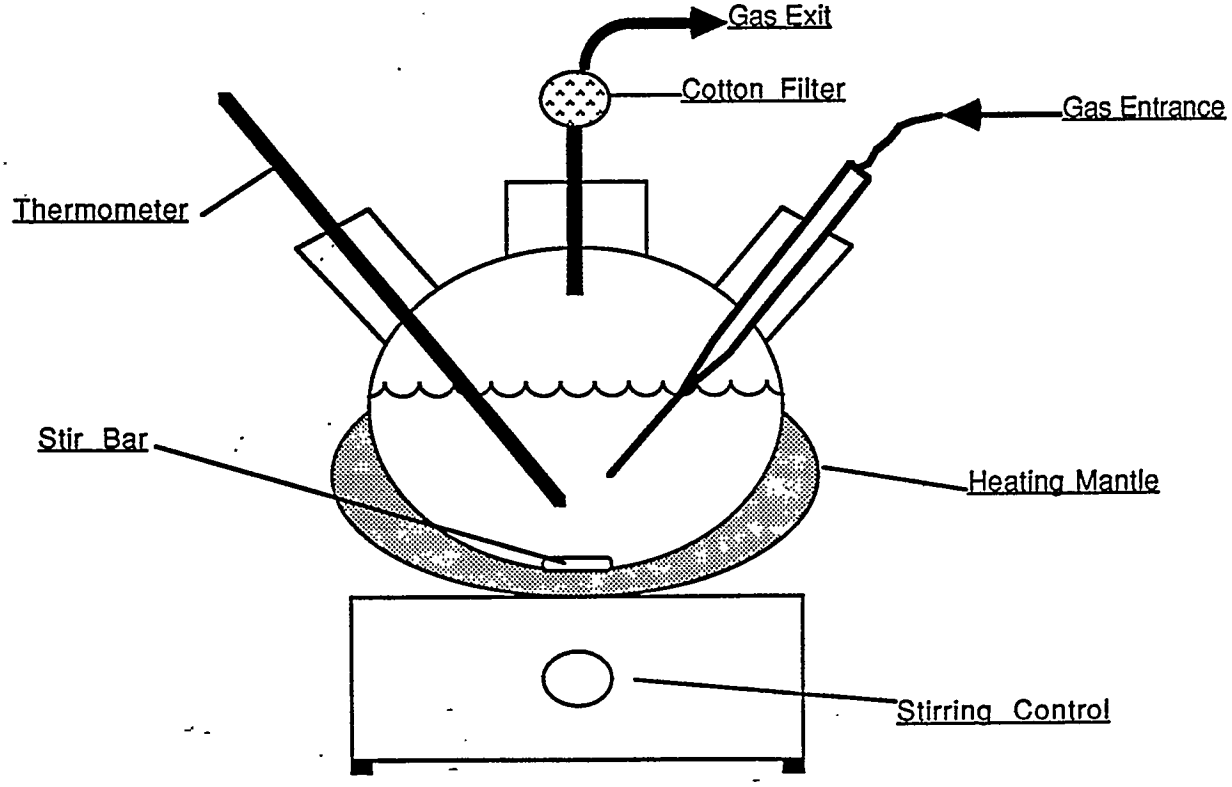


Figure 3. GC/MS Analysis of *trans*-stilbene (20.0 min.) and Bibenzyl (17.6 min.)

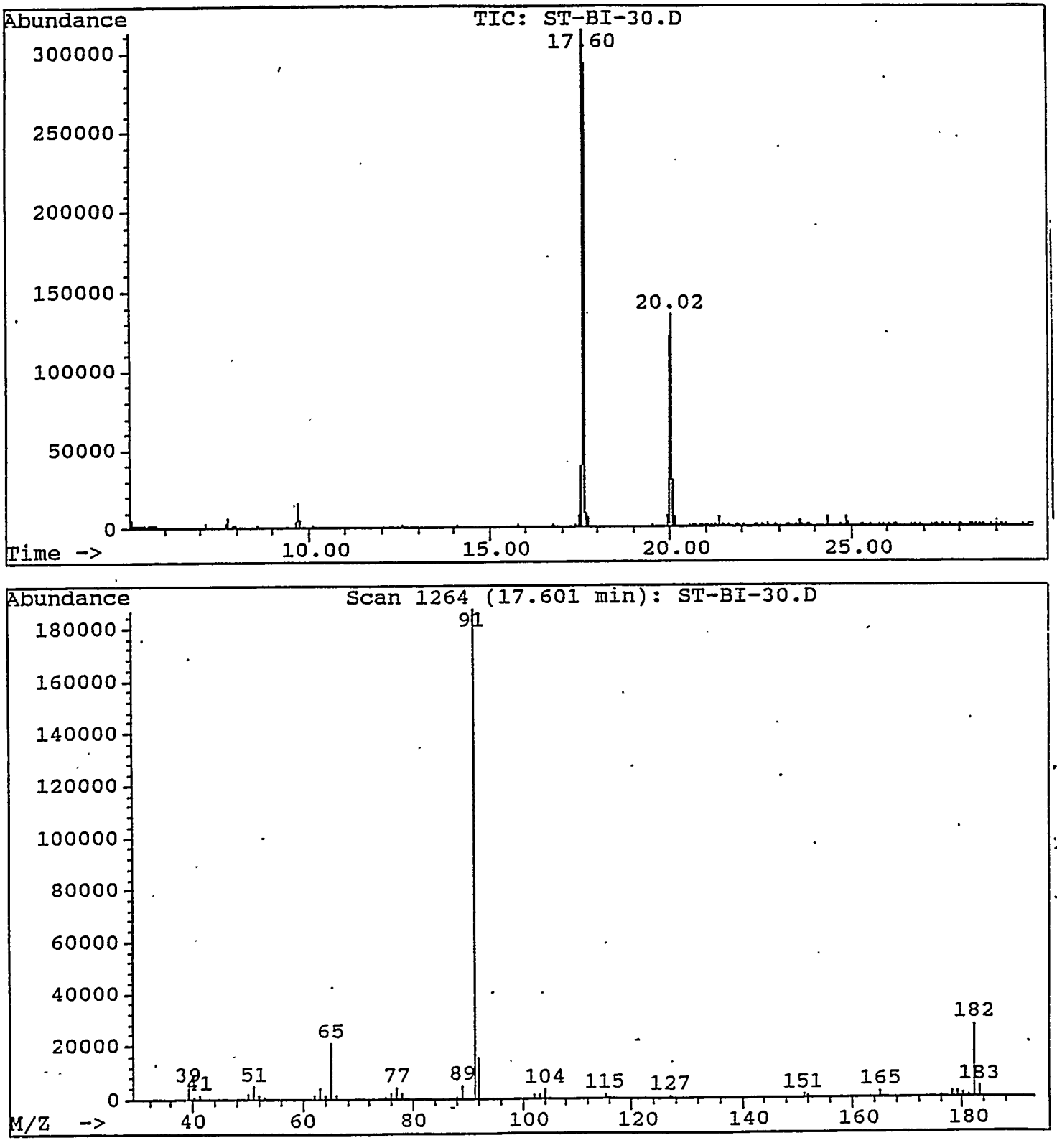


Figure 4. GC/MS Analysis of *trans*-stilbene Treated with *D. desulfuricans*, 34 atm, 36°C, (Stilbene Peak Masked)

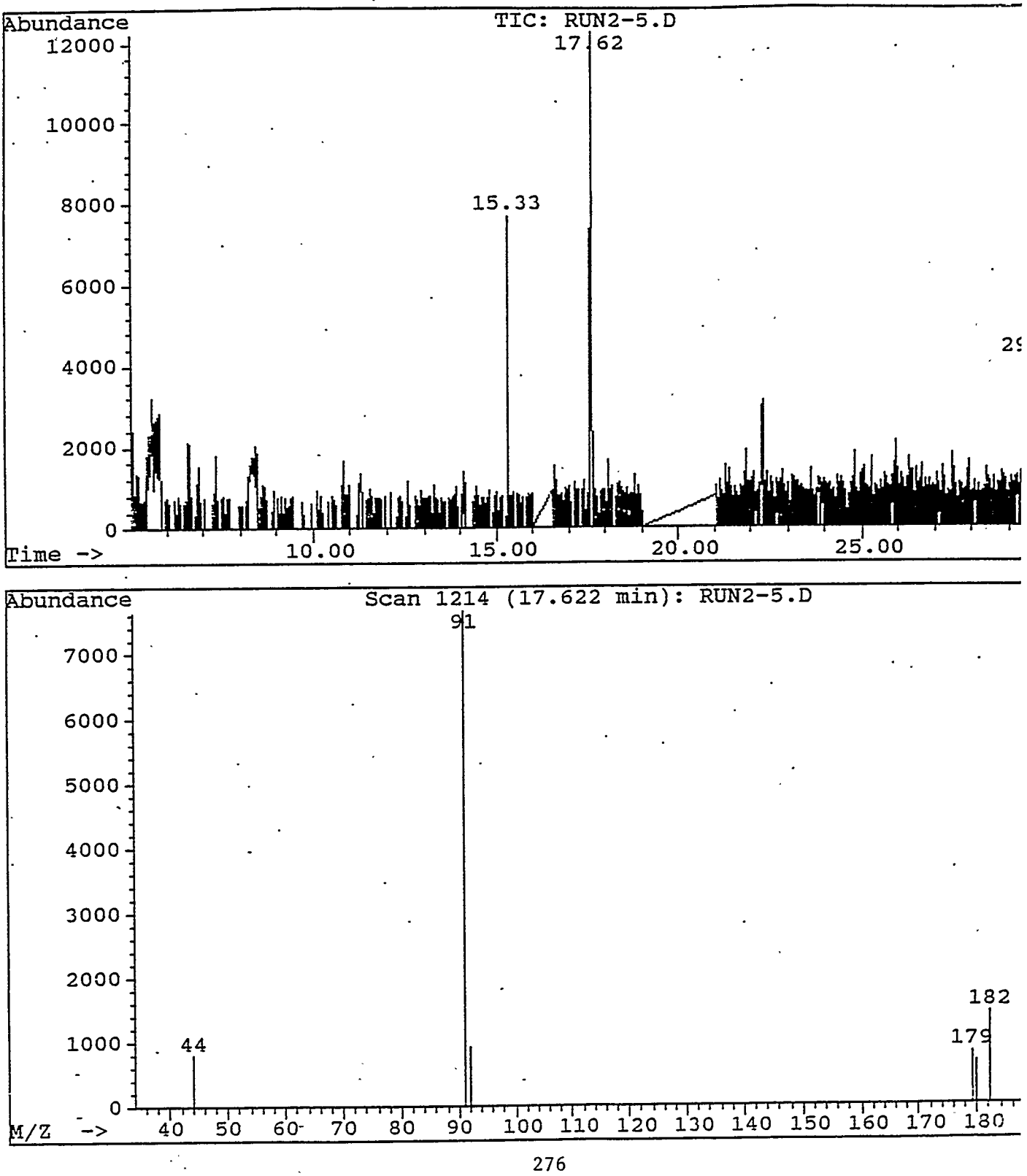


Figure 5. Lactate Concentration vs. Time Sulfate and Lactate Treated with D. desulfuricans at 1 and 34 atm, 36°C

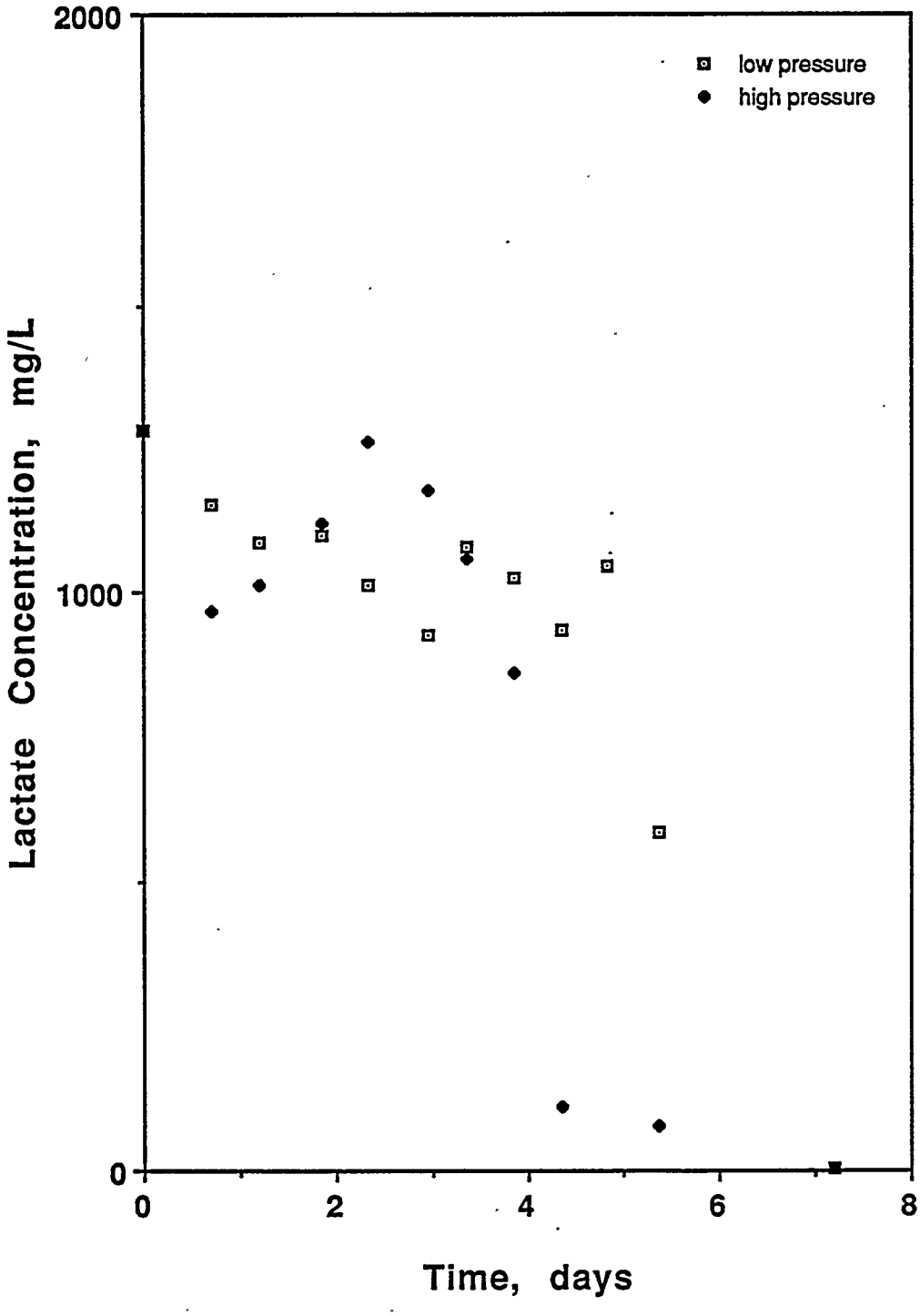


Figure 6. Protein Concentration vs. Time Sulfate and Lactate Treated With D. desulfuricans at 1 and 34 atm, 36°C

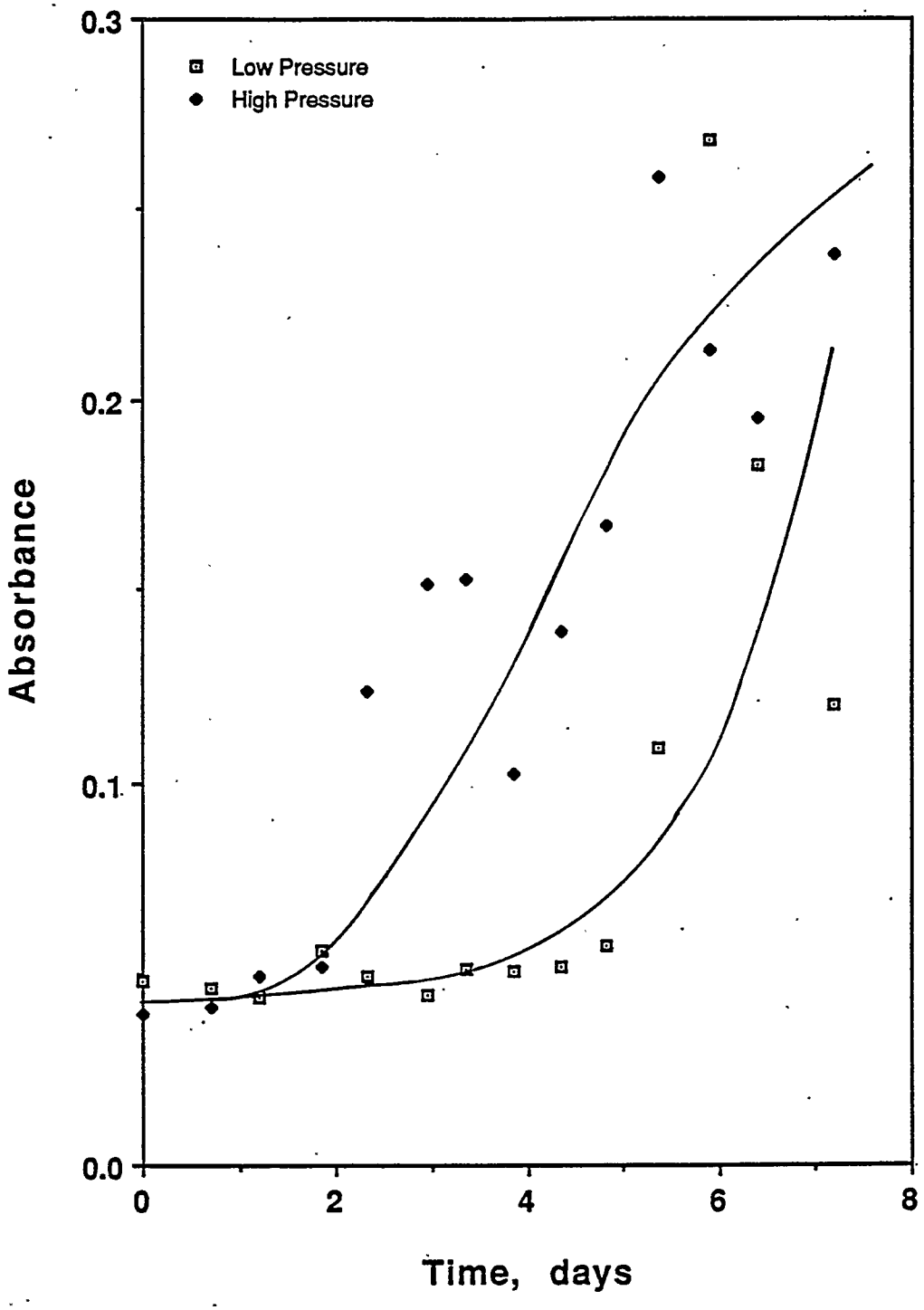


Figure 7. Fumarate Concentration vs. Time Fumarate Treated with D. desulfuricans at 1 and 34 atm, 36°C

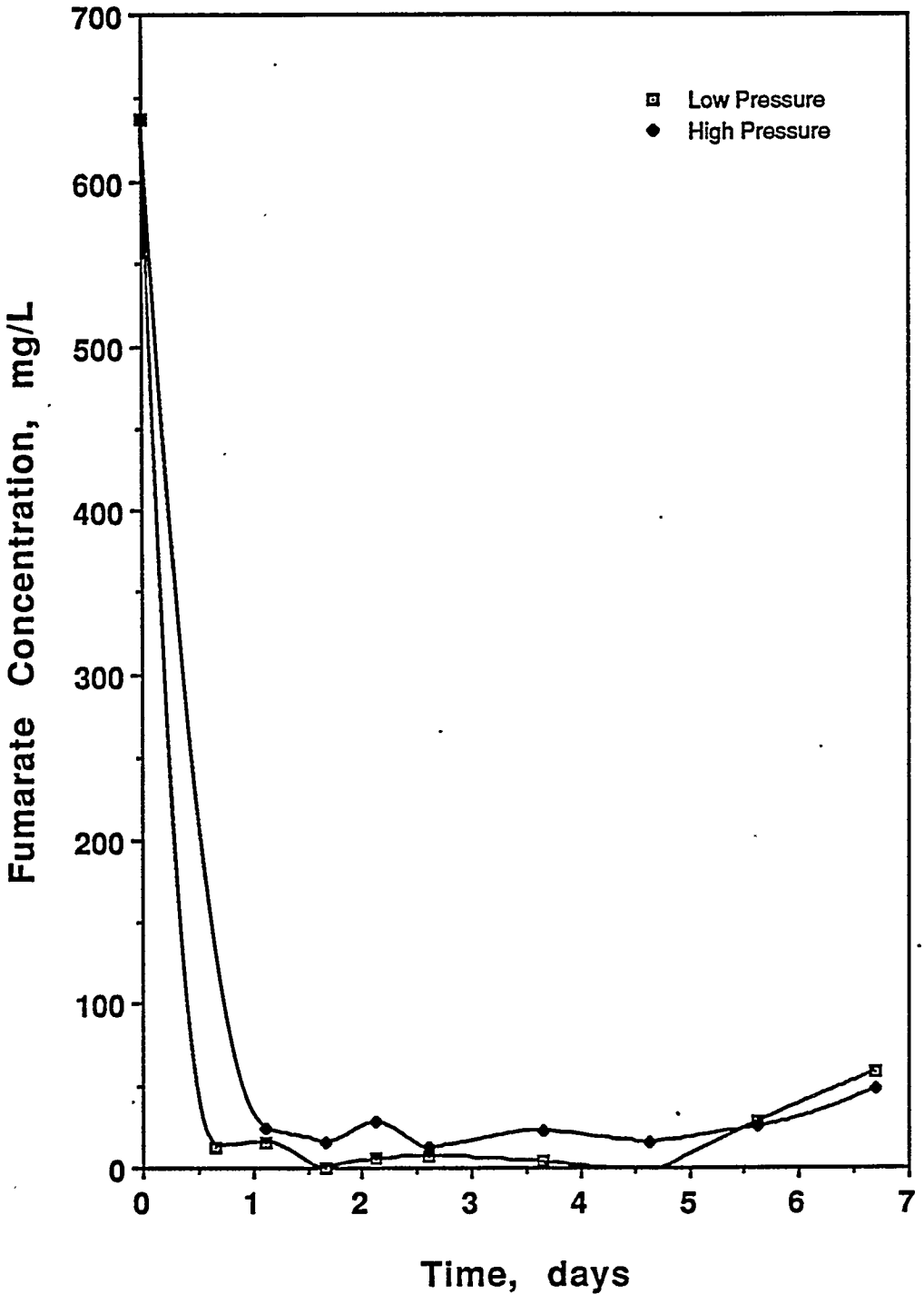


Figure 8. Protein Concentration vs. Time Fumarate Treated With D. desulfuricans at 1 and 34 atm, 36°C

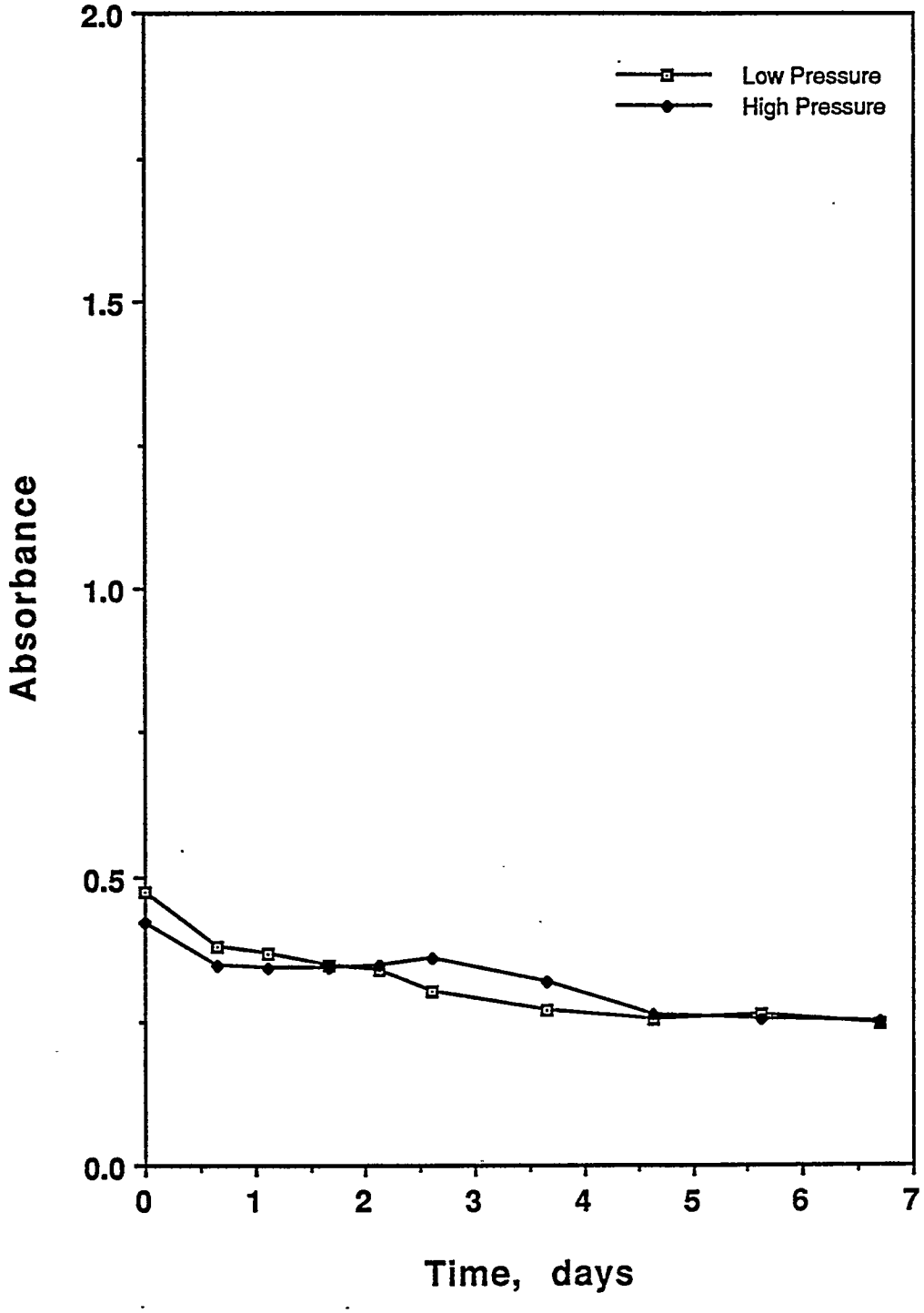


Figure 9. Hydrogenation Analysis Flowsheet

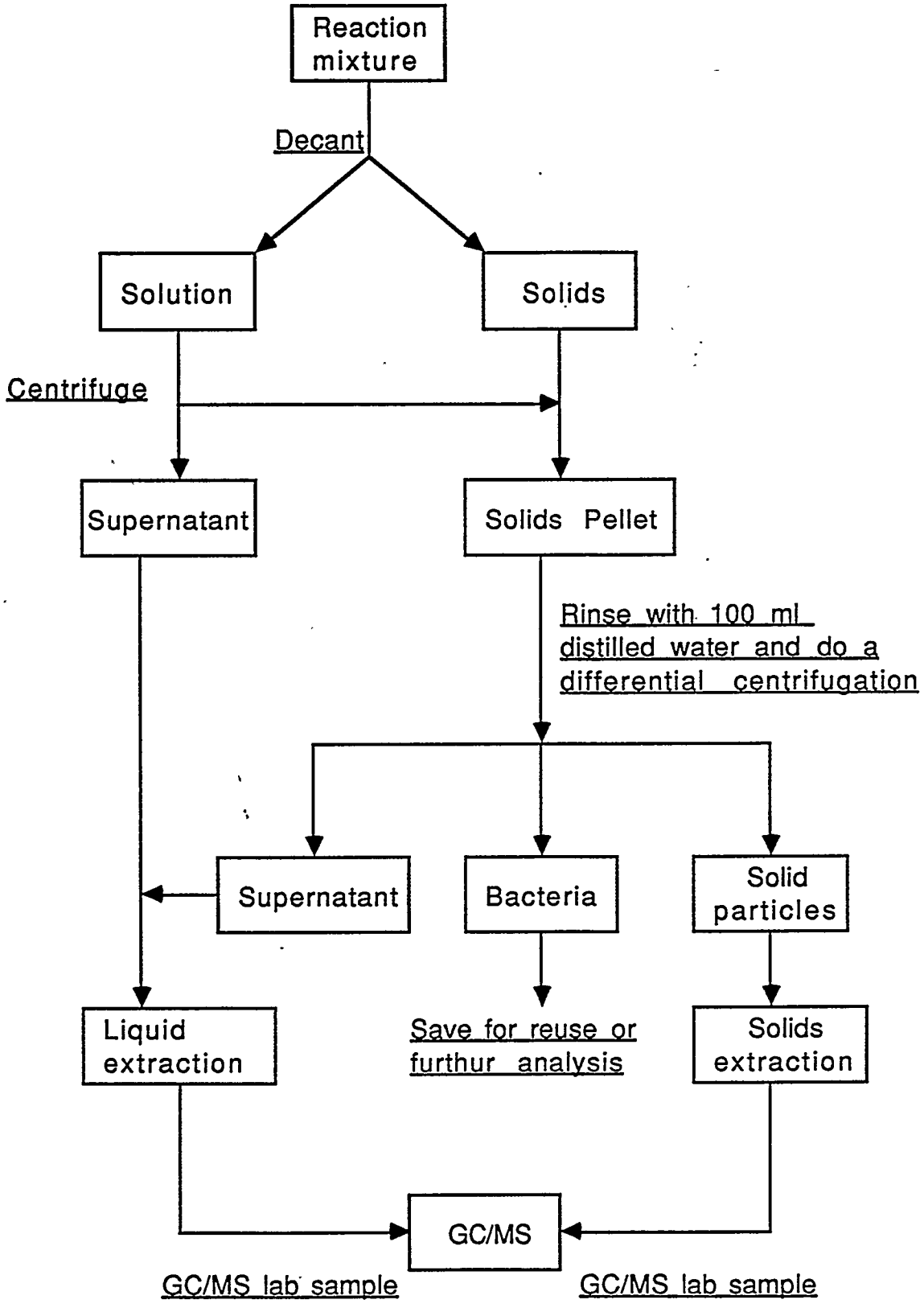
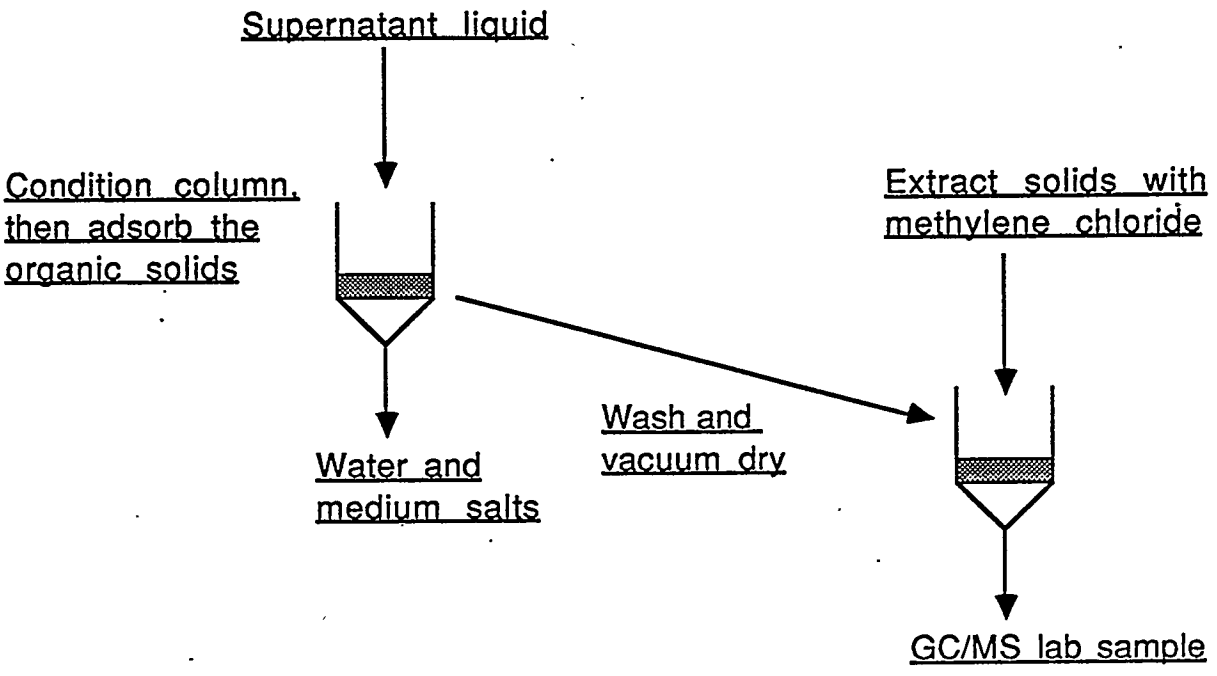


Figure 10. Liquid Extraction Process



Solids Extraction

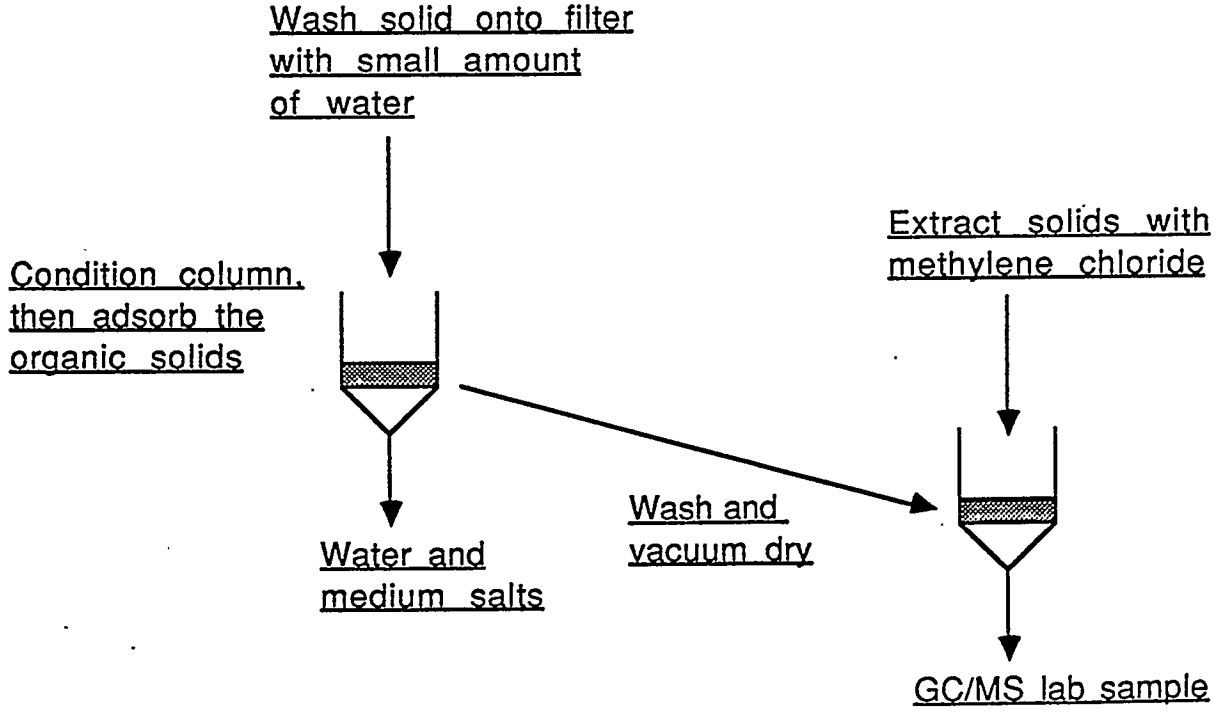


Figure 11. Measurement of Head-space Hydrogen Pressure of Vials Containing Stilbene Medium Treated with Desulfovibrio vulgaris at 37°C and pH7.6 (Initial H2 pressure = 4.5 p.s.i., experiment was repeated 3 times)

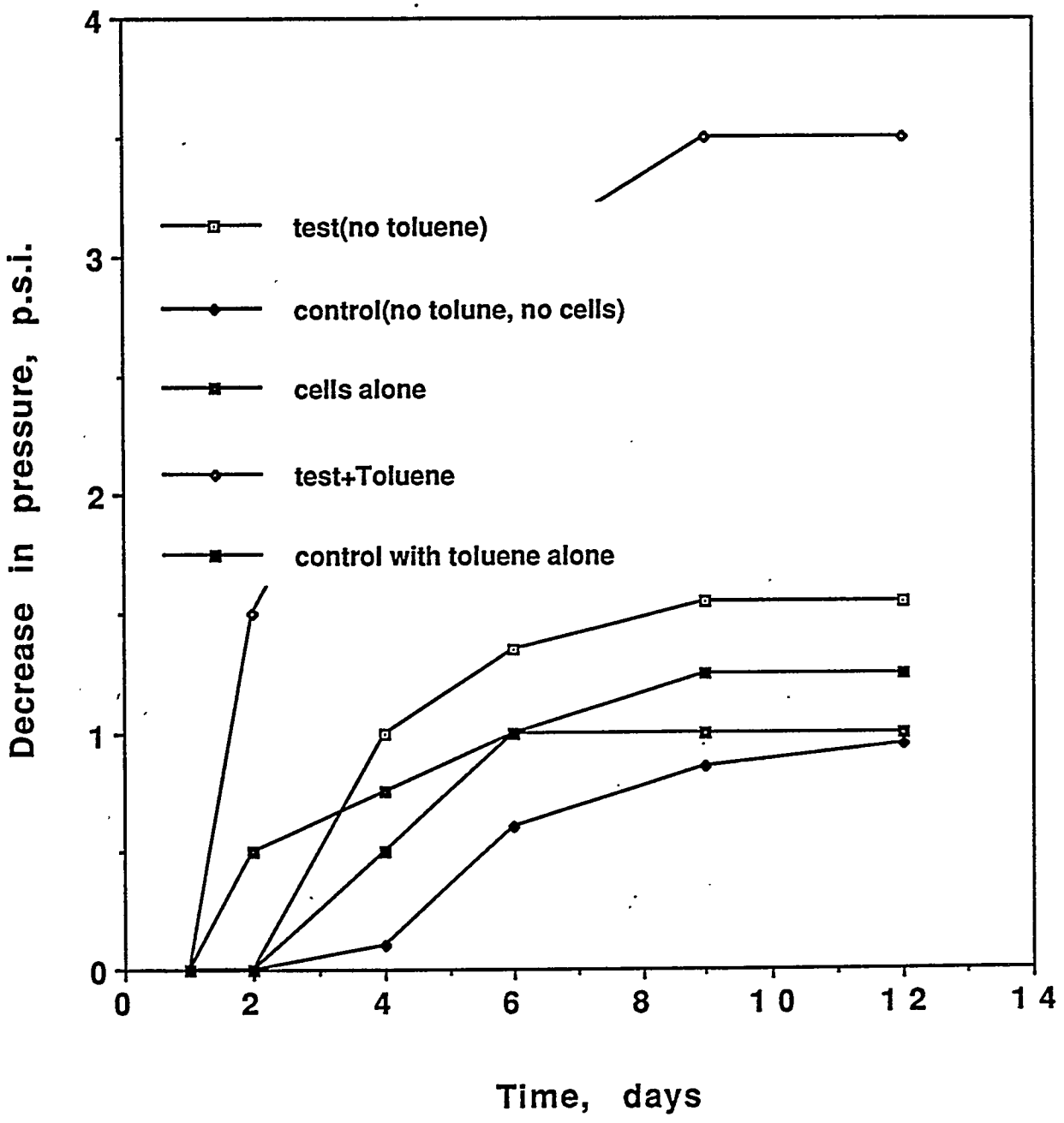


Figure 12. Variation of Liquid Phase Iron Released from IBC # 105 (5% coal) When Treated with A. brierleyi with an Initial pH of 2.5 at 68°C Incubated on Flasks Kept on a Rotary Shaker

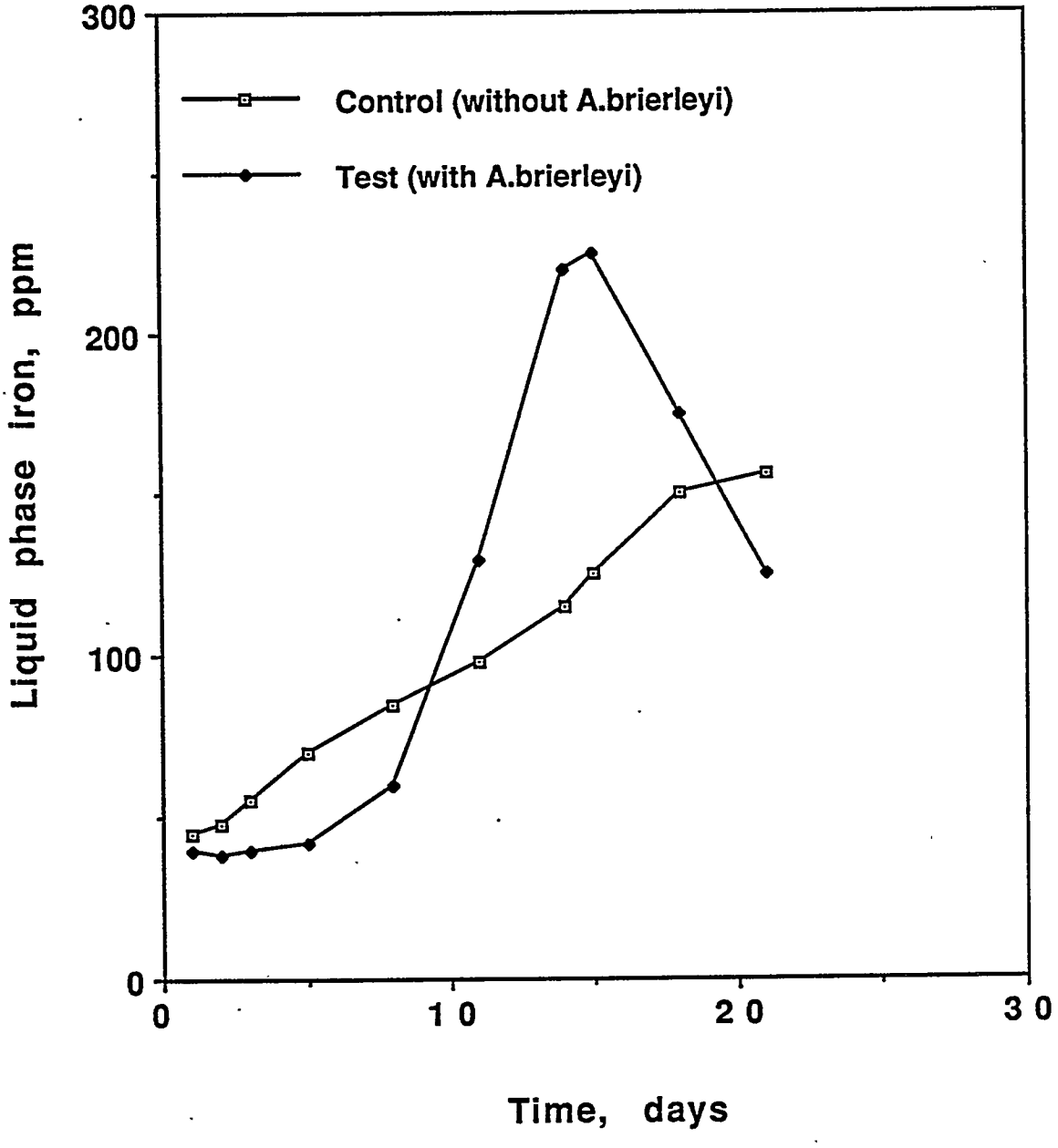


Figure 13. Sulfate Released from IBC #105 (5% coal) When Treated with Acidianus brierleyi with an Initial pH of 2.5 at 68°C Incubated in Flasks Kept on a Rotary Shaker

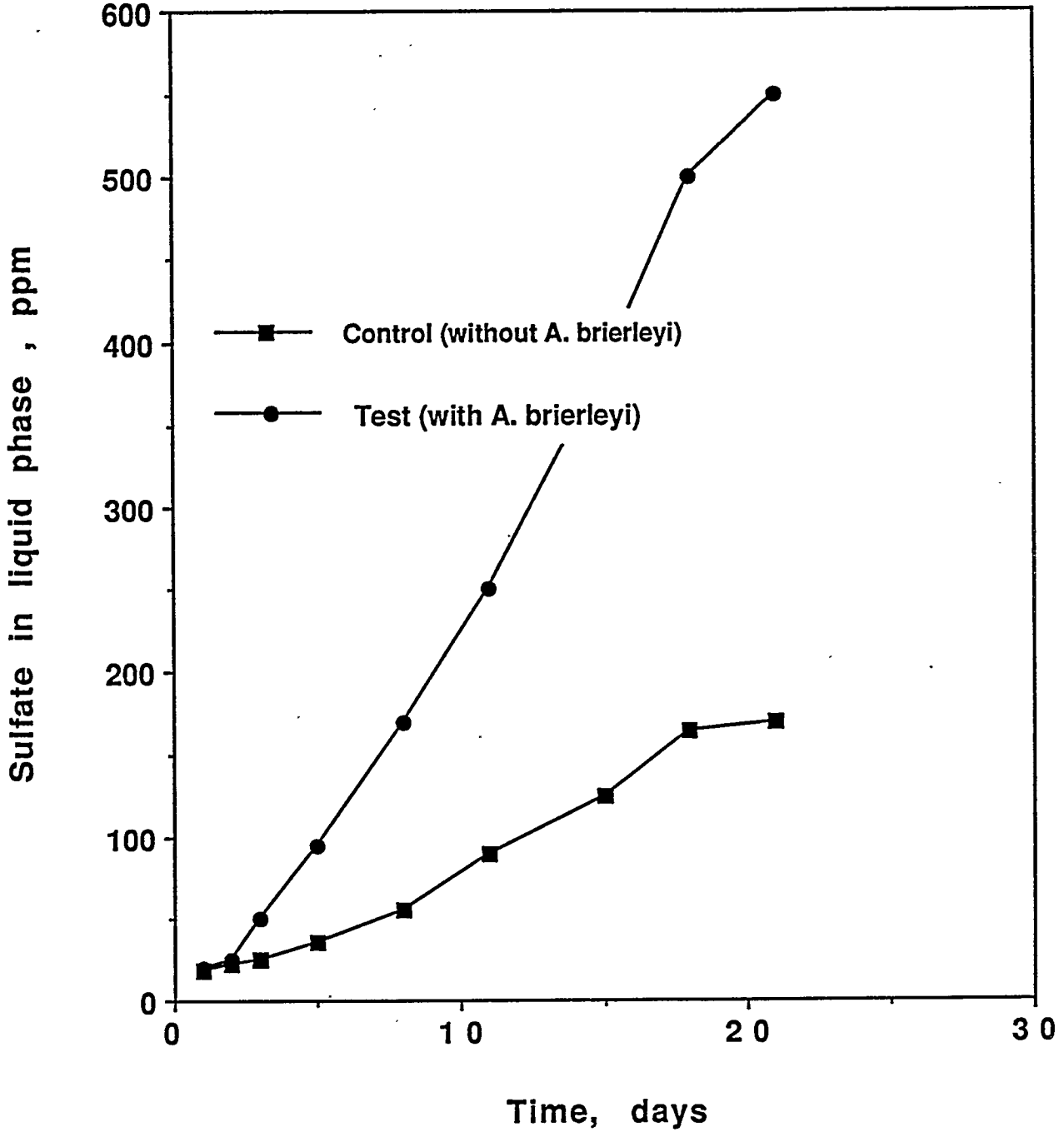


Figure 14. Variation of Liquid Phase Iron Released from DECS #17 Coal (plus 2500 ppm pyrite) When Treated with A. brierleyi with an Initial pH of 2.5 at 68°C Incubated in Flasks Kept on a Rotary Shaker