

TASK I

Project I.4

METAL CATALYST DISPERSION AND COAL MODEL COMPOUND STUDIES

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Working in collaboration with Professor Larry L. Anderson, a microscopic investigation was carried out of the dispersion of iron and molybdenum catalysts in hydrotreated Blind Canyon, Wyodak and Pittsburgh #8 coals. Incipient wetness and ultrasonication were compared as the means of impregnating the coal particles before hydrotreatment. Dispersion of catalysts in the coal particles was determined before and after hydrotreatment by electron probe microanalysis (EPMA). In the case of demineralized Blind Canyon coal it was possible to quantitate the iron present in impregnated coal particles by using the mineral marcasite as the iron standard in the EPMA experiments. A concentration of approximately 0.14 wt% iron was found in the demineralized Blind Canyon coal after hydrotreatment.

Some of the results obtained in the catalytic hydrotreatment of demineralized Blind Canyon coal are shown in Table I.2.1. Demineralization was carried out under nitrogen using warm (about 60°C) solutions of concentrated hydrochloric acid followed by concentrated HF and then concentrated HCl. In the case of bimetallic catalysts impregnation was sequential from aqueous solutions first using ammonium tetrathiomolybdate followed by iron(III) chloride hexahydrate or nickel(II) nitrate hexahydrate. Samples were hydrotreated in a shaken tubing bomb reactor for one hour at 350°C and 2000 psig of H₂ (hot). Hydrotreated samples were then Soxhlet extracted with tetrahydrofuran (THF) to determine amounts of solubles produced.

We found that bimetallic catalysts were more efficient than either metal alone in producing THF solubles. We also observed that even when loading with Fe/Ni promoters is substantially decreased, significant amounts of THF solubles are still found. In all cases the metals located on the outside of the coal particles before hydrotreatment were found (by EPMA) to have migrated to the interior of the particles during hydrotreatment. Iron was more uniformly dispersed through the interior of the coal particles after hydrotreatment than either Ni or Mo. These latter metals are observed (by EPMA) to clump somewhat inside the coal particles.

In a comparison of yields of THF solubles obtained from Blind Canyon, Wyodak and Pittsburgh #8 coals it was found that the best yield was obtained from the subbituminous Wyodak coal. A rationale for this result was proposed based on the correlation of coal rank and carbon content with the porosity of the coal structure.¹ These results were presented at the symposium on "Structure and Reactivity of Coals, Tar Sands and Oil Shale" at the San Francisco American Chemical Society meeting, April 5-10, 1992 and will be published in Fuel Processing Technology.²

Early in the contract year it was determined that hydrotreatment of a mixture of coal and waste rubber tires potentially has significant advantages over hydrotreatment of coal alone. The rationale for such a program has been described succinctly by Farcasiu.³ A number of waste rubber tires were collected and stored in our laboratory.

In order to obtain small rubber particles, to carry out rubber tire experiments, rubber samples were initially chopped by hand with razor blades to produce fine particles. We subsequently found that an SH-5 standard Dura-Cut (1/4 shank) carbide tipped bit from Ultra Tool International (Huntington Beach, California) in an electric hand drill produces fine rubber particles in shorter periods of time.

The ground rubber tire samples were placed in 1.4 cm I.D. glass tubes. The glass

tubes were then sealed and placed in a muffle furnace for 1 to 2 hours at 400°C. The tubes were then cooled and opened. Oils soluble in methylene chloride were extracted. Samples of the original tires, the oils produced and the residue were sent out for elemental analyses. The results are shown in Table I.2.2.

Oils extracted from the rubber tire samples were analyzed with a Nicolet FT-IR spectrometer. Infrared spectra for the oils indicated that the tires are very much alike in their functional group makeup. Oils extracted from samples made up of only sidewall material from the tires contain a weak stretch at 2300 wavenumbers which suggests the presence of either a $C \equiv C$ or a $C \equiv N$ stretch that is not seen for samples taken from the tread portion of the tire.

Proton NMR measurements (see Table I.2.3), made on a Varian XL-300 spectrometer, indicate that the tire oils extracted contain a higher percentage of aliphatic protons than of aromatic protons. No measurements were made on the sidewall samples.

The glass tubes cannot withstand high gas pressures. A large percentage of the tubes ruptured during the heating process. Sample tubes also ruptured frequently after reaction when they were opened at room temperature spraying out sample. These high pressures are not observable with pure coal samples but are seen only upon the addition of rubber tire particles or waste polymers. This suggests that oils in the rubber tire are responsible for the gas produced. The glass tube experiments were eventually discontinued in favor of less convenient but safer experiments carried out in metal tubing bombs. The tubing bomb is mounted horizontally and shaken in a heated sand bath. In addition to greater safety, tubing bombs have the advantage of permitting the addition of hydrogen gas (that is not possible in our glass tube experiments.)

Samples of rubber tires and coal have been prepared with and without catalyst, hydrotreated and analyzed for THF soluble products. Amounts of each reactant have been

varied and two catalyst impregnation techniques have been implemented in seeking to maximize the recoverable THF soluble products from a combination of coal and waste rubber tire reactants. Each tubing bomb experiment was carried out at 1000 psi H₂ (cold) and 350° C for one hour. The results in Table I.2.4 show that the addition of ground rubber tires to coal enhances the amounts of THF solubles recovered compared to coal samples prepared with no waste rubber tire particles added. A further increase of THF soluble products is seen to arise from the addition of catalyst, particularly when using the incipient wetness technique to impregnate the sample with catalyst.

EPMA experiments are being carried out to determine what effect the rubber tire particles have on the dispersion of catalyst in the coal particles. At the request of M.M. Taghiei (University of Kentucky) we also did some EPMA experiments that demonstrated that an ion exchange process (iron substituting for calcium) can be used effectively to impregnate coal.

References

1. Derbyshire, F., "Vitrinite structure: Alterations with rank and processing," Fuel 1991, 70, 276-284.
2. Sommerfeld, D.A.; Jaturapitpornsakul, J.; Anderson, L.L.; Eyring, E.M., "Microscopic studies on the dispersion of iron/molybdenum bimetallic catalysts in hydrotreated Blind Canyon, Wyodak, and Pittsburgh #8 coals," Fuel Processing Technology 1993, in press.
3. Farcasiu, M., "Another use for old tires: Coprocess them with coal to make liquid fuels," Chemtech 1993, 23, 22-24.

Table I.2.1. Catalytic hydrotreatment of demineralized Blind Canyon coal			
Catalyst ^a	Impregnation ^b	THF ^c	
		Sol.	Insol.
0.05% Mo	U	40	52
0.05% Mo	I	42	52
1% Fe + 0.05% Mo	I	55	41
0.01% Fe + 0.05% Mo	I	50	43
1% Ni + 0.05% Mo	I	50	46
0.01% Ni + 0.05% Mo	I	52	45

^aCatalyst loadings are given in wt%.

^bImpregnation: U = ultrasound, I = incipient wetness.

^cYields are given as % m.a.f. coal.

Table I.2.2. Waste Rubber Tire Elemental Analyses ^a				
entry	tire	carbon%	hydrogen%	sulfur%
1	LRR	85.3	7.0	2.3
	oil	89.4	8.2	1.7
	residue	87.6	1.3	2.8
2	Michelin XA4	86.7	6.9	2.1
	oil	89.8	8.0	1.6
	residue	91.3	1.5	2.1
3	Radial 155SR12	86.3	7.2	2.2
	oil	-	-	-
	residue	89.0	1.4	2.6
4	Michelin XZX	87.2	6.9	2.2
	oil	88.4	9.9	1.3
	residue	89.4	0.9	2.7
5	EMPCO	87.4	6.7	1.7
	oil	89.0	9.1	1.2
	residue	89.6	0.9	2.4
6	B.F.Goodrich	76.6	6.6	1.7
	GT-200	88.5	10.0	1.1
	oil	75.2	0.9	2.6
	residue			
7	LRR ^b	-	-	-
	oil	-	-	-
	residue	85.5	1.1	4.2

a reaction conditions: 1 g of powdered tire in sealed glass tube, heated for two hours at 400°C, extracted with 25 ml of methylene chloride, solvent then removed with rotary evaporator.

b 1 gram sample of powdered tire reacted with 1% by weight of ammonium tetrathiomolybdate.

Table I.2.3. Proton NMR Analyses^a of Waste Rubber Tire Samples

entry	tire	oil(mg)	aromatic/ aliphatic ^b	solid residue(mg)
1	LRR	244	30/70	460
2	Michelin XA4	275	36/64	466
3	Radial 155SR12	255	32/68	459
4	Michelin XZX	493	17/83	408
5	EMPCO	361	21/79	366
6	B.F. Goodrich GT-200	450	15/85	395
7 ^c	LRR	397	23/77	396

a reaction conditions: 1 g of powdered tire in sealed glass tube; heated for two hours at 400°C; extracted with 25 mL of methylene chloride; solvent then removed with rotary evaporator.

b relative NMR peak areas for aromatic and aliphatic protons in the oil

c sample included 1% by weight ammonium tetrathiomolybdate

Table I.2.4. Results of Reacting DECS-17 Coal with Waste Rubber Tires (WRT)

Coal %	WRT%	Catalyst	Yield of THF Solubles ^c
100	0	0	0.387 g
60	40	0	0.558 g
50	50	.01 g H ₂ O impreg. ^a	0.651 g
60	40	.01 g H ₂ O impreg. ^a	0.797 g
50	50	.01 g added dry ^a	0.551 g
60	40	.01 g H ₂ O impreg. ^b	0.602 g

^a Ammonium Tetrathiomolybdate

^b Wender's Sulfated Iron Oxide

^c Based on 1 gram of sample before hydrotreatment

TASK I

Project I.5

NOVEL TEST REACTORS FOR COAL LIQUEFACTION

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OBJECTIVE

The main objective of this project over the past year was the development and characterization of a semi-batch reactor with vapor flow-through and vertical agitation, and the use of this reactor to assess catalysts for coal liquefaction. Hydrogen was used as the vapor stream purge gas. An advantage of the continuous-flow semi-batch liquefaction reactor over a batch liquefaction reactor is that light liquefaction products produced in the former can be removed by the flowing H₂ from the reactor, thus preventing further cracking and condensation. The reactor is dynamically balanced so that vertical agitation at up to 500 rpm is possible. Temperatures up to 450°C are attainable by means of a fluidized, constant-temperature sand bath.

RESULTS

1. Initial Testing

The semi-batch liquefaction reactor system was initially built with some mechanical modifications such as the use of larger capacity mass flow meters and spring coil inlet/outlet tubing. Test runs were then carried out to study the effect of purge gas flow velocity. Ideally, the gas flow should sweep out light products of liquefaction but retain tetralin (the solvent) in the reactor. A mixture of tetralin (87 wt%) and iso-octane (13 wt%, b.p. = 100°C) was used to simulate the reactor contents during coal liquefaction. The test runs were made at 400°C, 1000 scc/min of nitrogen and hydrogen at 300 rpm (300 psig N₂ and 500 psig H₂ pressure, typical conditions for coal liquefaction). The results in Figure 1 show that most of the solvent is swept out of the reactor in 6 minutes (normal liquefaction runs take 30 to 60 minutes), indicating the solvent loss is far too severe. Tetralin, therefore, can not be retained

in the reactor during the entire liquefaction period. This problem resulted from the high reaction temperature and high gas velocity. Since high gas velocity is necessary for sweeping out the light products and the reaction temperature must be kept around 400°C, it was decided that a pre-reactor tetralin saturator was needed to compensate for the tetralin loss from the reactor.

2. Test of the Reactor with a Tetralin Saturator

A stainless steel saturator, with a volume of 230 ml, a jacket heater and an internal thermocouple was installed upstream of the preheater coil. A product- (and solvent-) trap of the same size as the saturator was installed downstream of the reactor. About 190 ml of tetralin was loaded into the saturator before the test runs. The test conditions were the same as those described earlier but the run time was kept to 30 minutes. The test results at a residence time (τ) of 0.9 min are shown in Figure 2. The objective of the test was to maintain 10 ml of tetralin in the reactor for the duration of the liquefaction run (30 min). As indicated by the data, this objective was not achieved. Although a large amount of tetralin passed through the reactor to the collector (162 g at the saturator temperature of 400°C), the amount retained in the reactor is small (1.4 g at the saturator temperature of 400°C). The small tetralin level in the reactor suggested that the feed H₂ from the saturator to the reactor was not fully saturated. It may also have resulted from the expansion of the reactor contents when the reactor temperature is suddenly increased, and the subsequent high linear velocity in the effluent. These combined effects entrained the tetralin out of the reactor. Therefore some modification of the reactor itself was necessary.

3. Test of the Reactor After Reactor Modification

The original coaxial inlet/outlet in the center of the reactor was replaced by a separate, small-diameter (1/4") inlet at one end and a larger-diameter (1/2") outlet at the center of the reactor (see Figure 3). Thus the minimal cross-sectional area for the outlet stream increased by greater than an order of magnitude, from 0.011 in² to 0.126 in². The linear velocity in the outlet tube, therefore, decreased to less than 9% of the original value. The test results shown in Figure 4 (the circles), together with the data in Figure 2 as a comparison, indicated that the objective of maintaining 10 ml tetralin in the reactor can be reached by adjusting the saturator

temperature to below 300°C. This also suggested that the tetralin entrainment occurs only in the reactor outlet tube, therefore an increase of the outlet tube diameter reduces the tetralin entrainment from the reactor. Since the vapor pressure of tetralin is small at temperatures below 300°C, the results also suggested that the use of the pre-saturator is not necessary for the modified reactor. Data shown in Figure 5, as circles, indicate that as long as the H₂ velocity is less than 780 scc/min ($\tau = 1.2$ min), the saturator is not needed and that 94% of the tetralin initially loaded can be retained in the reactor for a 30-minute experiment. However, for the H₂ flow of greater than 1000 scc/min loss of tetralin is significant.

In order to reduce H₂ residence time further, test runs were also made with the addition of stainless steel (SS) beads into the reactor to reduce the reactor volume. For the same H₂ velocity, the reduced reactor volume gives a shorter gas residence time while maintaining the lower linear velocity in the outlet tube, which in turn enhances the amount of tetralin retained in the reactor. Runs with addition of 149 and 187 g of SS beads showed (square and triangles in Figure 5, respectively) that a residence time as small as 0.5 minute can be reached at a H₂ flow rate of 1000 scc/min with only about 14% loss of tetralin after 30 minutes.

At this stage, the modified reactor system (Figure 6) is capable of handling high H₂ flow rates (1000 scc/min, for example) to give short gas residence times (0.5 min for 1000 scc/min gas flow, 400°C and 500 psig pressure) with minimal loss of tetralin. The results obtained in the semi-batch reactor, therefore, can be compared with those obtained from a batch reactor at the same reactor conditions. The study of the effect of gas flow on coal conversion, oil and gas yield now becomes possible.

4. Coal Liquefaction Experiments

Uncatalyzed coal liquefaction experiments were carried out using DECS-6 coal in the modified reactor. The reactor conditions are 400°C, 500 psig H₂ (hot), 1000-1240 scc H₂/min, 300 rpm agitation, and 30 minute reaction time. The coal-to-tetralin ratio was 4 g/7ml. The results for these tests are shown in Figure 7 and compared with the batch data obtained at the same conditions but with no H₂ flow. It is seen that the increase of H₂ flow decreases the total conversion of coal but does not alter the yield to oil and gas. In other words, fewer asphaltenes are produced. The decrease in total conversion with the H₂ flow may be partially caused by the loss of tetralin. As discussed earlier, about 14% of the tetralin is swept out of

the reactor during a 30 minute run at these conditions. Prior results have shown that the effect of tetralin is mainly to increase the asphaltene yield for this coal under the same conditions. An additional reason for this finding may be due to a non-ideal flow pattern of hydrogen gas through the reactor. It was noted that upon completion of the reaction, the reactor region closest to the hydrogen gas inlet was dry of tetralin. Without the high concentration of hydrogen donor in this region, recombination reactions could be favored. Further work on the potential of non-ideal gas flow is on-going.

The insensitivity of the oil + gas yield to the H₂ flow is unexpected. If the main effect of the flowing H₂ is to eliminate retrogressive reactions of the light products, an increase in the oil+gas yield should be observed for the semi-batch operation. The results indicate that the reduction of the retrogressive reactions by the flowing H₂ is insignificant. However, it is also possible that the H₂ does not play a major role in the production of oils. Experiments made using N₂ instead of H₂ at the same conditions suggest that this hypothesis may be true (see Table 1), at least for uncatalyzed liquefaction at 400°C. Compared to the H₂ atmosphere, N₂ decreases the total conversion but the oil+gas yield remains relatively constant for both the batch and flow-through runs.

Table 1.
Effect of Gas Type on Coal Liquefaction
(400°C, 500 psig, 300 rpm, 30 min, coal/tetralin-4g/7ml)

flow, scc/min	0		996		996	
Gas type	H ₂	N ₂	H ₂	N ₂	H ₂	N ₂
Conv., %	72	29	53	26		
O+G, %	20	19	16	18		

5. Gas Analysis

As shown in Figure 6, the reactor system has an on-line GC with a sampling valve. A small amount of the reactor effluent can be injected to the GC by switching the sampling valve. A chromatogram obtained at an analysis rate of 1 injection per minute is shown in

Figure 8. The reaction was quenched at 30 minutes but injections continued to show some products in the gas phase up to 15 minutes after reaction termination. The slight zigzag in peak height resulted from a slight volume difference between the two sample loops used for injection. By knowing the areas of the peaks, volume of the sample loops, pressure, temperature and the effluent flow rate, the total amount of gas produced can be determined. The chromatogram indicates that at 400°C most of the gas fraction of the products is produced during the early reaction period which may correspond to initial pyrolysis of the coal.

6. Residence Time Distribution Studies

Another useful and interesting aspect of this project was an attempt to obtain the residence time distribution (RTD) for the flow-through reactor. When applied to reaction conversion data, the RTD aids in the quantification of kinetic information. The ultimate purpose is to gain an insight into the actual flow patterns occurring in the reactor and into the kinetics of the liquefaction reaction. It is hoped that this will suggest means of improving the conversion to the desired products.

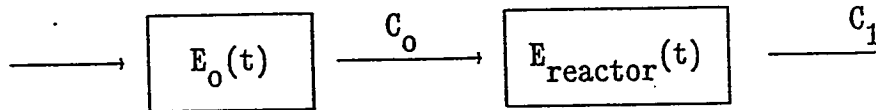
Experimental Procedure

A step change is introduced at the inlet of the system by switching the purge gas flow from hydrogen to helium, using a three-way valve. The response is measured separately at the inlet and the outlet of the reactor, so that the RTD for the reactor in isolation can be calculated. To measure and record the response with time, a thermal conductivity detector on a gas chromatograph is employed. Since the flow rate of the purge stream is much beyond

beyond the capacity of the GC, a gas sampling valve is incorporated in the line before the GC. This valve has two sample loops of equal volumes. By switching the valve position at equal intervals of time, a gas sample from an alternate loop is swept into the GC by the carrier gas. Thus the concentration of the outlet stream is sampled at regular intervals. The recording gives the concentration-time profile for the tracer (He), from which the so-called F curve and consequently the E curves (the RTD for the reactor) are determined.

Model Development

The reactor system is modeled as two units in series: an ideal plug-flow reactor (E_0) which is essentially a dead time and an ideal mixed reactor (E_{reactor}). The E curve, i.e., the RTD for the reactor, is calculated using the following relation for the scheme shown below.



Here $C_1 = C_{\text{in}} * E_0 * E_{\text{reactor}}$ where '*' is the convolution integral:

$$C_{\text{in}} * E_0 \triangleq \int_0^t C_{\text{in}}(t-t') E_0(t') dt'$$

This can be rearranged to give E_{reactor} as shown:

$$E_{\text{reactor}} = \frac{\frac{d}{dt} (F_1(t))}{F_0(t)} \quad \text{where, } F_0(t) = \frac{C_0(t)}{C_{\text{in}}(t)}, \quad F_1(t) = \frac{C_1(t)}{C_{\text{in}}(t)}$$

Here C_{in} represents the step change introduced, C_0 and C_1 are measured at locations

immediately before and after the reactor respectively. Thus the reactor can be modelled as a two-parameter combination of ideal reactor behavior.

PLANNED FUTURE WORK

Thus far, preliminary RTD experiments indicate that the data are sufficiently accurate to obtain model parameters for the residence-time distribution model. In essence, this model accounts for nonidealities in the flow patterns of the reactor system. These nonidealities are superimposed on any actual kinetic data taken on this apparatus for actual liquefaction runs. Thus it is planned to sample the product gas in the outlet stream during the course of a liquefaction run, so as to obtain the time dependence of conversion to gaseous products. Using these data in conjunction with the RTD data, we will attempt to obtain the actual kinetics of the evolution of gas products in the liquefaction reaction.

400°C, 1000 cc/min of gas flow, 300 rpm
Solvent: 87% of tetralin and 13% of iso-octane

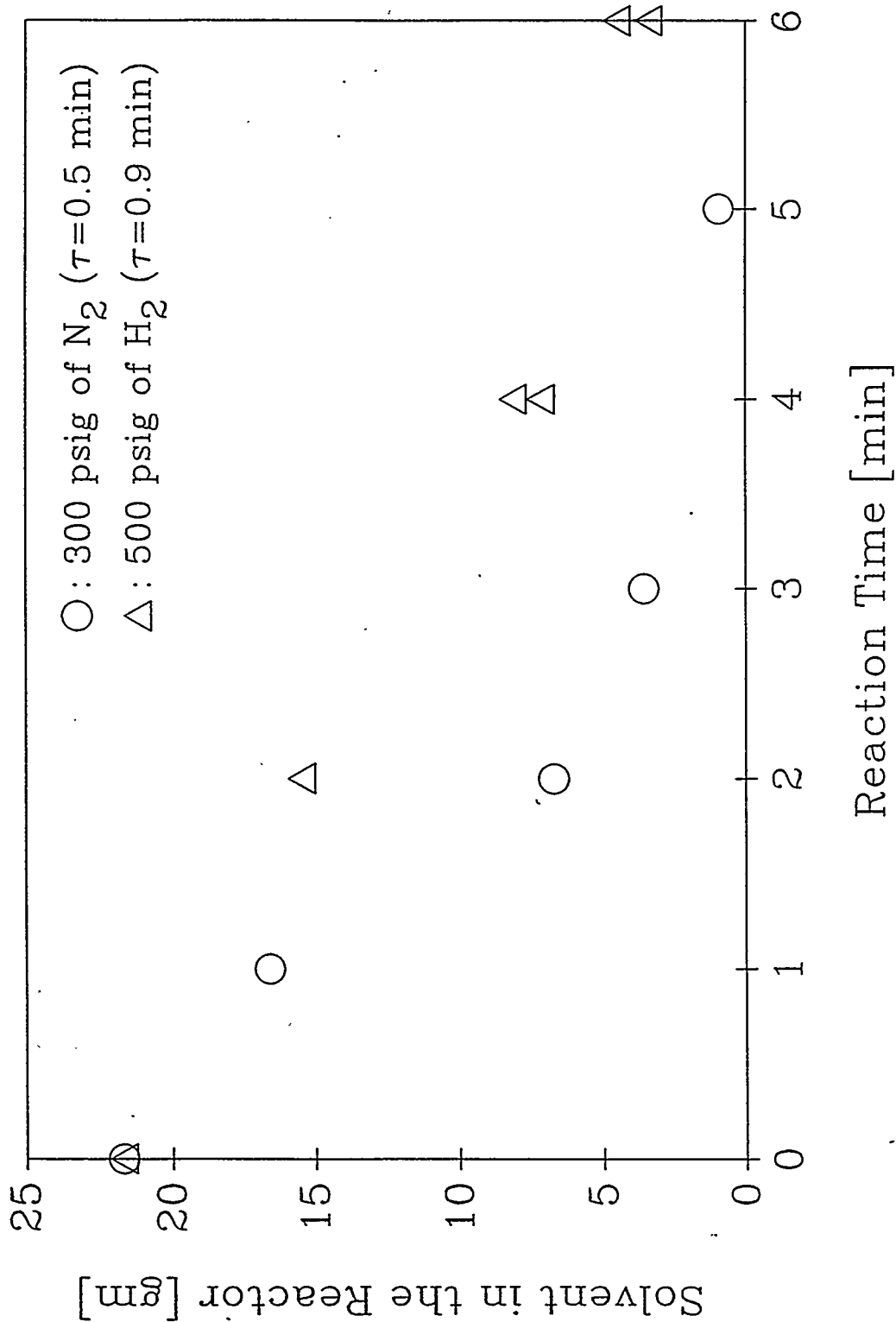
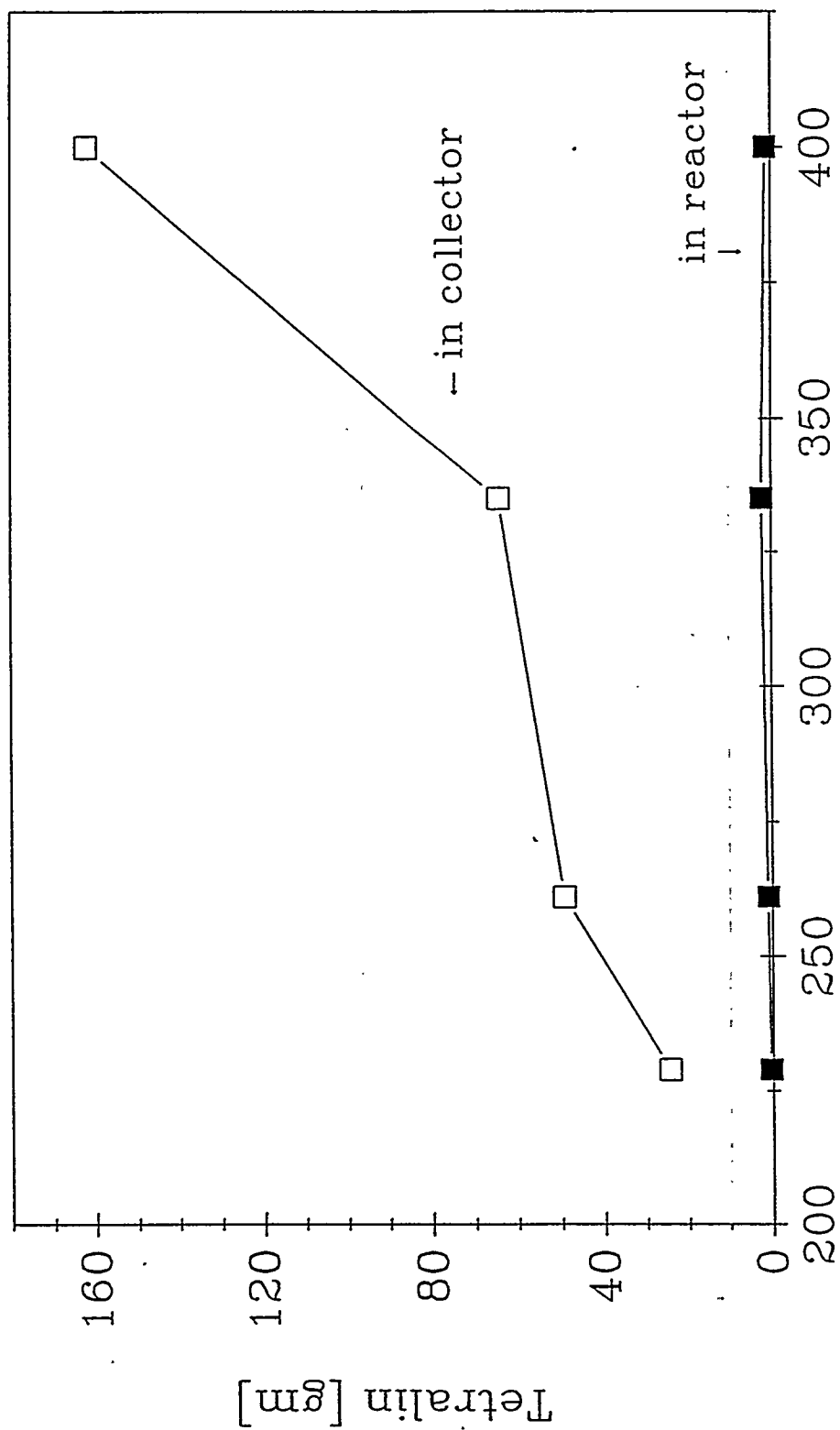


FIGURE 1. Results of solvent removal from the flow-through liquefaction reactor for a gas purge of 1000 scc/min at two different pressures with N₂ and H₂.

Reactor: 400°C, 500 psig, 1000 cc/min of H₂, 30 min
(Initial teralin loading in reactor = 20 ml)



Temperature of the Saturator [C]

FIGURE 2. Results of solvent loss with tetralin-saturated H₂ gas purge.

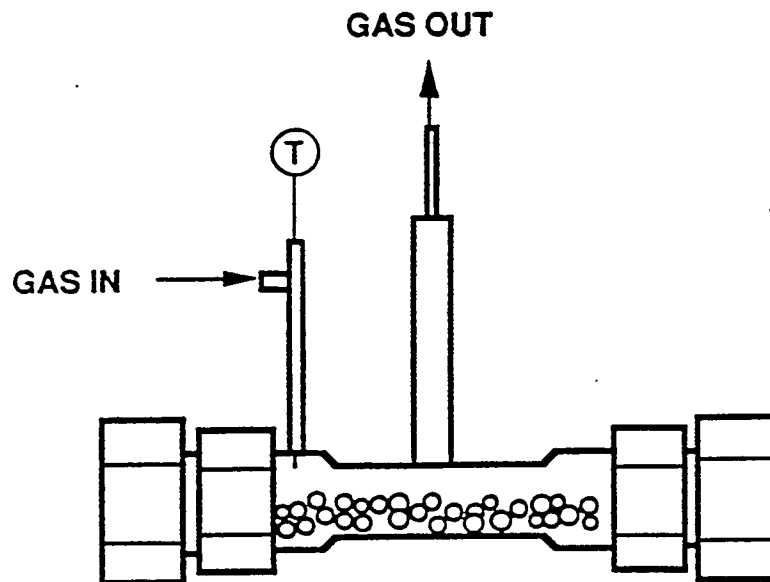
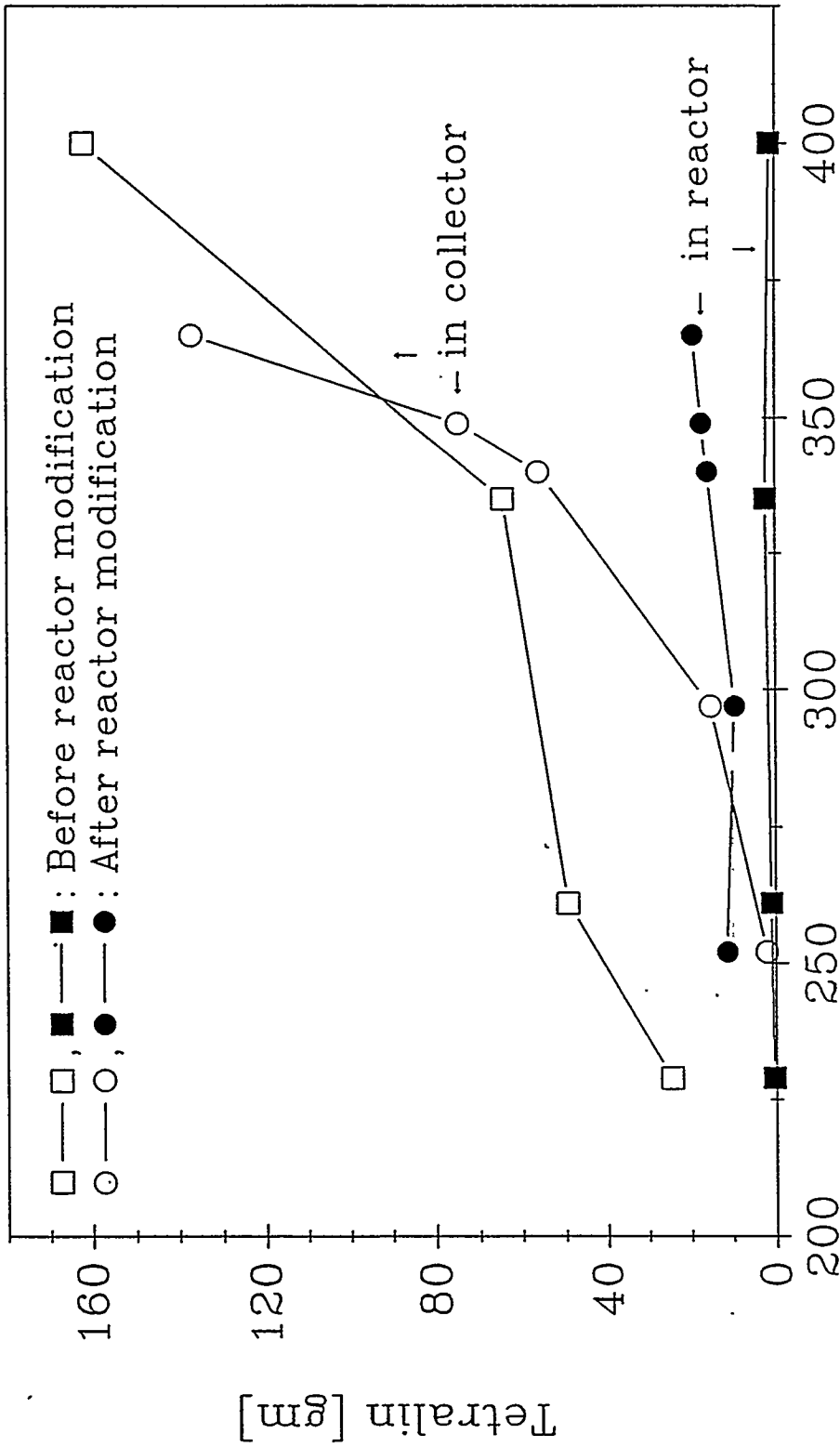


FIGURE 3. Schematic representation of modified flow-through liquefaction reactor.

Reactor: 400°C, 500 psig, 1000 cc/min of H₂, 30 min
 (Initial teralin loading in reactor = 20 gm)



Temperature of the Saturator [C]

FIGURE 4. Results of tests showing solvent-retention in the flow-through reactor before and after reactor modification.

400°C, 500 psig, 300 rpm, 30 min
 (without the saturator, initial tetralin loading = 9.4 gm)

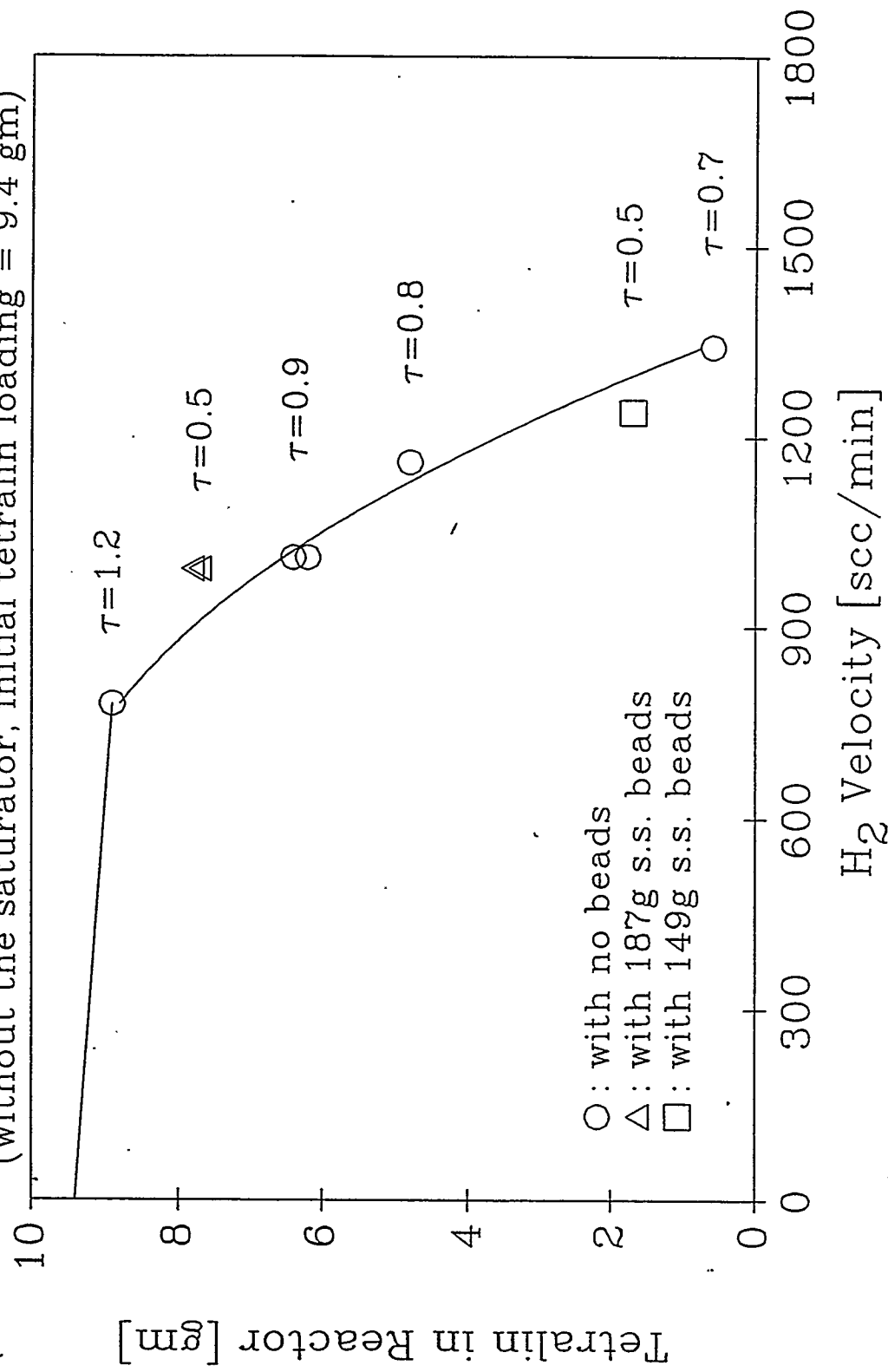


FIGURE 5. Relationship of tetralin retention in the flow-through liquefaction reactor as a function of hydrogen gas velocity.

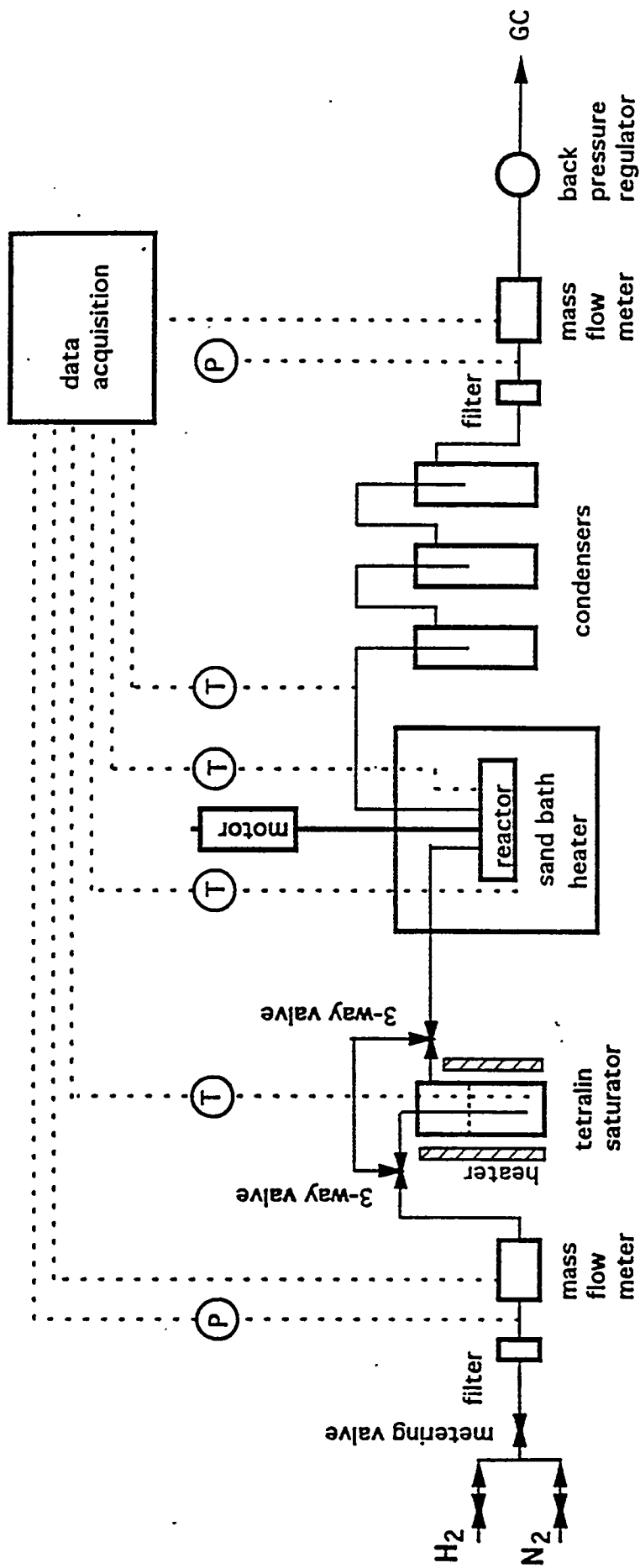


FIGURE 6. Schematic Diagram of Hydrogen-Purged, Semi-Batch Liquefaction Reactor

DECS-6, 400°C, 500 psig (hot), 300 rpm, 30 min
(coal=4 g, tetralin=7 ml)

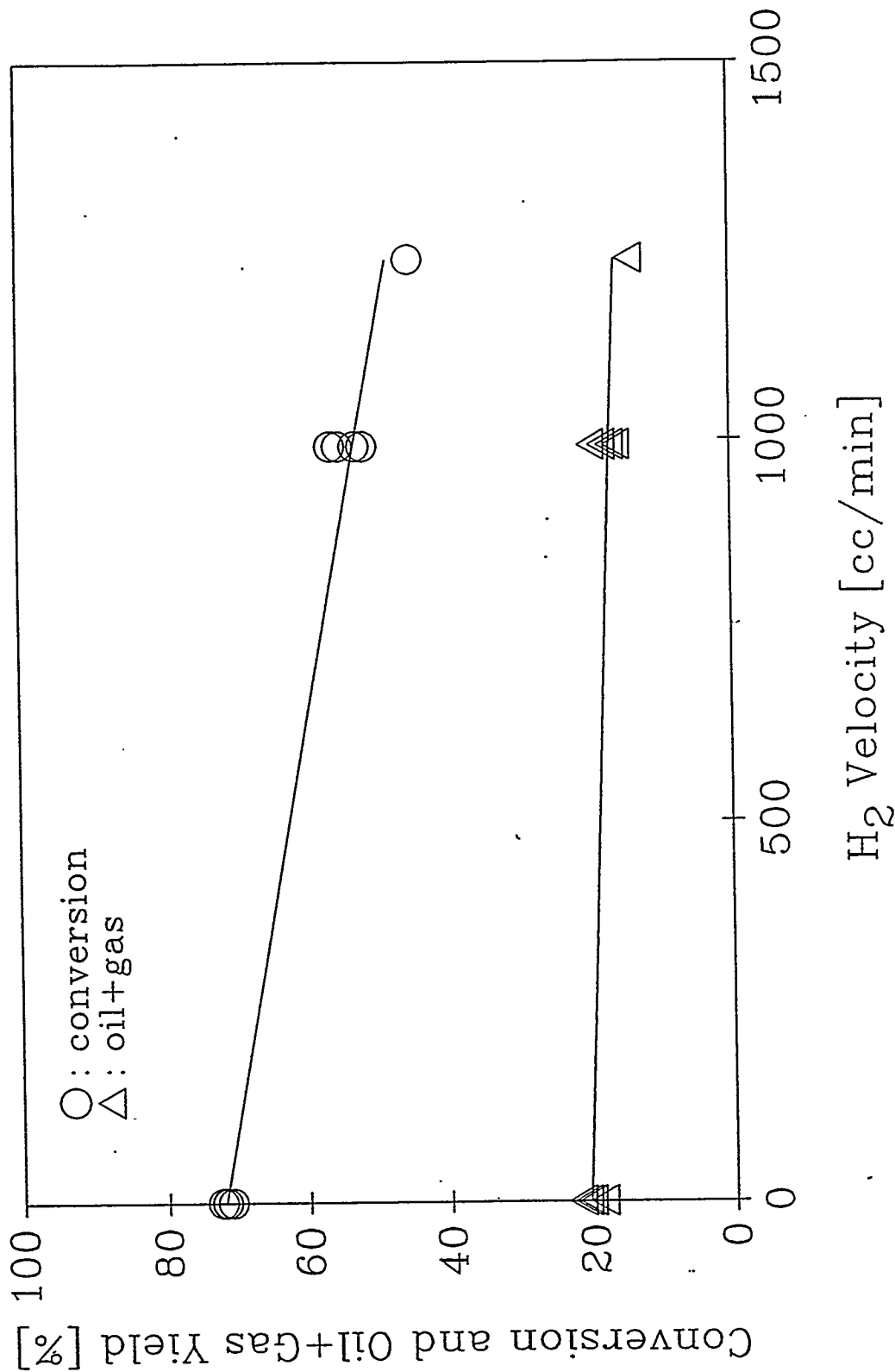


FIGURE 7. Total conversion and oil-and-gas yield for coal liquefaction with and without hydrogen gas purge.

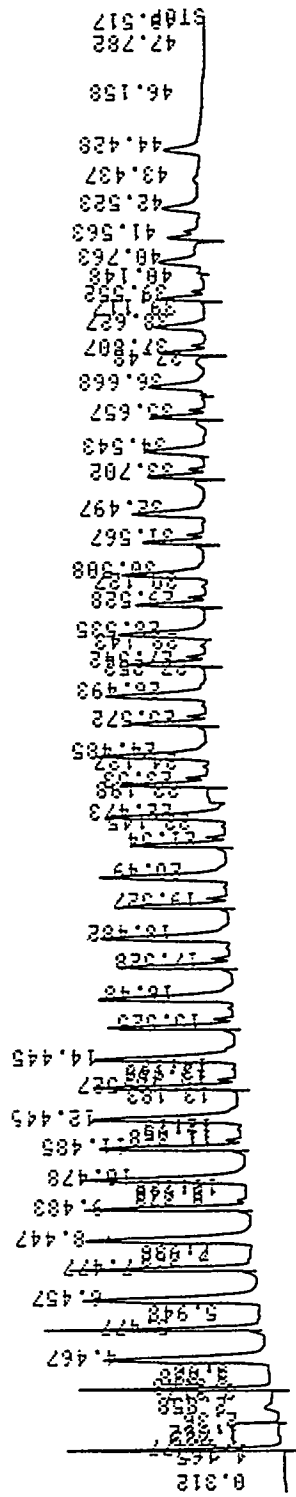


FIGURE 8. Example chromatogram for on-line product gas analysis during coal liquefaction in the modified, flow-through reactor.

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START