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COAL CONVERSION PROCESSES

Quarterly Report for the Period December 13, 1983—March 12, 1984

By
James T. Cobb, Jr.
Paul Biloen
Gerald D. Holder
George E. Klinzing
John W. Tierney

May 1984

Work Performed Under Contract No. FG22-83PC61256

University of Pittsburgh
Pittsburgh, Pennsylvania

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I. ABSTRACT

Experimental work is continuing on four separate projects related to coal conversion processes.

The direct digital control of exothermic multiphase reactions is being studied in an experimental adiabatic flow reactor. The existence of two stable steady states for the Fischer-Tropsch reaction network at the same temperature and feed condition has been verified and quantified.

Various absorbents for SO_2 and NO_X are being studied. The absorption of NO_2 by methanol and N-cyclohexyl-2-pyrrolidone has been extensively examined. Preliminary data has been obtained with triethylene-tetraamine. Hindered amines will be studied next. Procedures for the preparation of liquid membranes have been tested and the incorporation of hindered amines in them will now be examined.

Isotopic switching is being used to study the way in which promoters affect supported metal catalysts. With improved resolution from the mass spectrometer, early quantitative results give indications of three different surface species and of non-statistical ingrowth of ^{13}C into the product molecules.

A program for the study of the extraction of coal and oil shale using supercritical fluids is being carried out. The effect of the presence of piperidine on the amount of toluene solubles produced by supercritical extraction of coal with toluene/piperidine mixture has been determined. A new kinetic model for the extraction/liquefaction of coal by supercritical toluene and THF has been developed and proven satisfactory. Bruceton coal and Hi Na lignite have been extracted with supercritical water.

II. INTRODUCTION

Work continues on four subjects of importance in coal conversion:

- thermal behavior of slurry reactors for indirect coal liquefaction
- use of chromatographic techniques to explore absorbers for SO_2 and NO_X
- support and promoter effects on composite CO/H_2 conversion catalysts
- extraction and conversion of coal and oil shale using supercritical fluids.

This quarterly report has been prepared by Professors Paul Biloen (Section V), Gerald D. Holder (Section VI), George E. Klinzing (Section IV) and John W. Tierney (Section III). The overall project is coordinated by Professor James T. Cobb, Jr.

III. THERMAL BEHAVIOR OF SLURRY REACTORS USED FOR INDIRECT COAL LIQUEFACTION (TASK 1)

A knowledge of thermal effects is important in the design and control of reactors for indirect coal liquefaction. The reactions are exothermic, and at high conversions the removal of substantial quantities of heat are required. A slurry reactor is a promising candidate for carrying out these reactions because of the good heat transfer between the liquid and gas phases and between the catalyst and the fluids. A slurry reactor especially equipped to measure heat evolution has been built in the Chemical and Petroleum Engineering Department, and it is being used in this work.

In the last quarterly progress report it was indicated that Fischer-Trospch experiments made using a ruthenium catalyst seemed to indicate that there were two stable steady states for the reaction at the same temperature and the same feed conditions. We have since verified this and are in the process of preparing a paper for publication which will describe the results in detail. Some typical results are shown in Table 1 and plotted in Figures 1 and 2. The feed flow rates, feed composition, pressure, and other experimental conditions are the same. Of particular interest in Table 1 are the heat removal requirement (cal/hr-gm catalyst) and the methane produced (mol/hr-gm catalyst). It is evident that at the same or very similar temperatures, the methane formation and heat generation are different. This can be seen quite clearly in Figures 1 and 2. Then the reactor is started up, it follows the lower curve in every case as the temperature is increased. At about 560 K the rate of heat generation increases rapidly, and the methane production increases, moving to the upper curve. Subsequent cooling of the reactor follows the upper curve.

These results substantiate the proposition that control of indirect liquefaction using a slurry reactor is an important design problem and underscores the importance of obtaining good experimental measurements for the reaction under consideration.

During the next quarter, we will continue to explore the reactor behavior as a function of system parameters.

IV. USE OF CHROMATOGRAPHIC TECHNIQUES TO EXPLORE ABSORBERS FOR SO_2 AND NO_X (TASK 2)

A. Activity Coefficients

Several organic compounds such as methanol, triethylene-tetraamine and N-cyclohexyl-2-pyrrolidone have been studied this quarter in our laboratory for their ability to absorb NO_2.

For the purpose of establishing a reliable base of operation with the gas chromatograph technique, methanol was used to reproduce the data of Mohamed [1]. The activity coefficient at infinite dilution of a NO_2 in methanol was found to be 12.8 at 26°C. This result is compared with Mohamed's findings for 28°C in Figure 3. Good agreement is seen.

When testing N-cyclohexyl-2-pyrrolidone for NO_2 absorption ability, it was found that there is some absoroption of NO_2 (about 10% wt of what is injected) at conditions of 25°C with carrier gas (He) flow rate 5 cc/min. However, the activity coefficient at infinite dilution could not be calculated because the retention times for air and NO_2 were identical and not separable at the conditions tested.

Further study of this solvent is to be continued. Work will focus on exploring varying operating temperatures, amounts of solvent injected and the carrier gas flow rates.

Triethylene-tetraamine was the third organic solvent tested for the absorption of NO_2. Initial tests proved no absorption; however, more experiments need to be performed to establish this finding absolutely.

A series of hindered amines such as N_1N-Dipropylacetamide, $N_1N_1N_1N^1$-Tetraethyl ethylenediamine, N-Nitrosodiethylamine and N-Nitrosodipropylamine will be studied in the coming quarter. The acid gases SO_2, NO, and NO_2 will be used to establish absorption capacities.

B. Liquid Membranes

Besides the study of the solubility of SO_2, NO_2, and NO in various organic compounds, the use of liquid membranes for the study of acid gas removal will be researched. A typical procedure for making model liquid membranes is as follows:

Procedure for making model liquid membranes

I. Emulsion Formation

1. Reagents:
   a. Heavy Mineral Oil (not light) or Exxon's S-100-N
   b. ICI America-Span-80 - stabilizer
   c. 10 wt % HCl or H_2SO_4
   d. 10 wt % NaOH
2. Using turbine impeller of 1500 RPM add four grams SPAN-80 to 200 cc mineral oil, allow to mix for ten minutes.
3. At ten minutes add 100 cc of 10 wt % NaOH.
4. Allow to mix for 20 minutes.
5. At the end an emulsion must be organic continuous.

II. Contacting

1. Add phenolphehalein to 10 % wt HCl.
2. Switch to marine impeller.
3. In a plastic beaker add 100 cc acid to 200 cc emulsion.
4. Start agitation at 500 RPM.
5. Work up to higher mixing rate until phenolphthalein turns color. The acid/base components in this system are used only to serve as

a demonstration that the liquid membrane formed are carrying out the transfer of species across the membrane. See Figure 4 for a diagram of the process.

It is anticipated that the hindered amine can be incorporated into the oil. The amine can serve as the transporter of the absorbed acid gas from the continuous phase into the interior of the liquid membrane. If the process is carried out in an aqueous continuous phase, an enhancer may be added to the water to facilitate absorption of the acid gas in this phase from the gases bubbled through the emulsion mixture. The liquid membrane can then transport the absorbed gas to the interior aqueous phase which can be caustic to increase the acid gas removal process. Figure 5 shows this operation.

At present the equipment for carrying out the membrane formation has been assembled and model membranes have been made. The hext quarter will explore the use of hindered amines in the membrane formation.

Other materials which have possible potentials as transporters in liquid membranes are EDTA and $FeCl_3$ solutions. Di-2-ethyl-hexyl phosphoric acid may serve as an active transport agent such that the acid gas dissolved may be transported across the liquid membrane against its concentration gradient.

Another avenue to explore in future work is to use a dialyzer of rigid membranes. Physically the dialyzer is similar to a shell and tube heat exchanger arrangement. The dialyzer made of porous membranes in a tubular form can be soaked in an acid gas absorber such as a hindered amine. After draining the amine, a gas containing the SO_2 and NO_X can be passed through the tube side of the exchanger. The gas is absorbed by the membrane and transmitted to the shell side where a caustic solution reacts and carries away the absorbed gas.

V. SUPPORT AND PROMOTER EFFECTS ON COMPOSITE CO/H_2 CONVERSION CATALYSTS (TASK 3)

The objective and methodology of this study are:

- objective: to determine whether promotors (such as ThO_2 in case of cobalt) merely affect extrinsic properties (i.e., surface area) or change intrinsic catalytic properties (i.e., density of active sites, absolute rate constants).
- methodology: switching abruptly the isotopic constitution of the feed to working catalysts, and monitoring the rate of ingrowth of the "new" isotope into products.

We have successfully conducted experiments with unpromoted ruthenium (Figure 6) and cobalt (Figure 7).

By working with deuterium (see the preceding quarterly report) and increasing the electron impact energy of our mass spectrometer to 30 ev, we now have sufficient resolution to follow the stepwise ingrowth of ^{13}C into the C_3 and C_4 Fischer-Tropsch products (Figures 6 and 7).

The quantitative analysis of these data currently is in progress. From preliminary results we are already able to formulate some preliminary conclusions:

- in addition to a CO_{ad} reservoir, there are distinquishable reservoirs of C_1-ad and C_3-ad surface species.
- the rate of C-C bond formation is measurable. It varies from ~ 2s (Ru) to ~ 6s (Co).
- the ^{13}C is not statistically distributed in the C_3 and C_4 products.

Before turning to promoted catalysts, we will first analyse further the currently obtained data, which contain novel and unexpected features (especially the third of the preliminary conclusions just stated).

VI. EXTRACTION AND CONVERSION OF COAL AND OIL SHALE USING SUPERCRITICAL FLUIDS (TASK 4)

A program for the study of supercritical fluids for extraction of coal and oil shale is being carried out. Emphasis is placed on developing a fundamental understanding of supercritical phase behavior as applied to coal conversion and for coal liquid deashing [2]. Initial experiments which have used supercritical water to convert coal to gases, liquids and THF soluble products at supercritical temperatures have produced high conversion with brown coal (75%) and with bituminous coal (58%). Results obtained to date have shown coal rank, coal type, extraction (reaction) time, extraction temperature and initial density of the supercritical phase are important variables.

It has been hypothesized that when coal is contacted with a supercritical fluid, a portion of the coal dissolves instantaneously. The amount of coal which dissolves depends on the density and the temperature of the supercritical fluid and should increase with an increase in density and temperature of the supercritical fluid. It is further hypothesized that only the part of the coal which is dissolved in the supercritical fluid undergoes liquefaction reactions which results in the formation of oils, asphaltenes, preasphaltenes, gases and char. Consequently, short contact time liquefaction of a bituminous coal in a non-donor solvent like toluene will be studied to determine if these effects actually exist. This report briefly describes the progress made during the period December 13 through March 12.

Progress for Period December 13 through March 12

Experiments were done with toluene and piperidine mixtures at the mixtures' critical temperature and densities. In the analysis of the reaction products, the presence of piperidine in the coal can affect the determination of the amount of toluene solubles, because the piperidine will extract some products which are not toluene soluble. In order to eliminate this effect during extraction by toluene and THF, the slurry (piperidine + toluene + coal + products) was kept in the hood so that the piperidine and toluene could vaporize (This is Extraction Procedure A). Next it was slurried with fresh toluene and extracted with toluene and then with THF. The results are summarized in Table 2.

It was found that the conversion to THF soluble products for fractions of piperidine greater than 50% were negative. It has been reported by Jolley et al. [3] that polymerization of pyridine solubles during extraction of the reaction residues occurs unless an inert atmosphere is present.

An experiment was done with piperidine at 380°C, at the critical density of piperidine and for a reaction time of 30 minutes. The results are given in Table 3. The piperidine was allowed to vaporize and the solid mass extracted with toluene and then with THF. The conversion was found to be negative although the conversion at 15 minutes and 60 minutes under otherwise identical reaction conditions were 53% and 83% respectively. The only difference was in the way products were extracted. In the case with high conversions, the slurry from the reactor was not dried, but rather simply diluted with toluene and filtered through an extraction thimble. (This is Extraction Procedure B).

In order to determine whether removing the piperidine from slurry by evaporation or not made a difference in the results, an experiment was performed with piperidine at 380°C and the critical density of piperidine for a reaction time of eight minutes. The slurry taken from reactor after quenching was divided into four identical parts. Two parts were diluted with toluene and extracted (Procedure B) two parts were dried (Procedure A) and then extracted with toluene. The results are given in Table 3. The percent of the slurry which dissovled in toluene was greater in the first case. This indicates that removal of piperidine by evaporation may cause the reaction products to polymerize and/or the piperidine is extracting some of the toluene insolubles.

Experiments were done at 400°C with toluene as the supercritical fluid and for reaction times from two minutes to 60 minutes. The results are given in Table 4. Different liquefaction models were tried but none successfully modeled the behavior. It was then hypothesized that only a certain fraction of coal dissolved in the supercritical fluid and it is this fraction which undergoes liquefaction in the supercritical fluid.

The model can be given as follows:

$$C \rightarrow C_1 \text{ (dissolved)} + C_2 \text{ (undissolved)}$$

$$C_1 \xrightarrow{K_1} A$$

$$P \xrightarrow{K_2} A$$

$$P \xrightarrow{K_3} \text{char}$$

The lump A includes asphaltenes, oils and gases together.

For a gradientless reactor the model equations are set up as:

$$dC_1/dt = -K_1 * C_1$$

$$dP/dt = -K_2 * P - K_3 * P$$

$$dA/dt = K_1 * C_1 + K_2 * P$$

$$d\ char/dt = K_3 * P$$

$$C = C_1 + C_2 + char = f(P,T)$$

$$C_1/C = K_4$$

$$K_4 = f(P,T)$$

The initial concentration of P and A was obtained from solubility of raw coal in toluene and THF respectively. The differential equations were solved analytically and the kinetic constants were fitted using multi-parameter optimization. The average absolute deviation (AAD) between calculated and experimental values of asphaltenes and preasphaltenes was found to be 1%. The results are given in Table 5. Experiments done previously at higher densities of toluene gave higher conversions under otherwise identical conditions. Higher conversion were also obtained when higher supercritical densities of water were used. An experimental program is being undertaken to quantify their effects by studying short contact time liquefaction kinetics of Bruceton coal in supercritical toluene at different densities and at different temperatures.

An experiment was conducted with Bruceton coal and water at 380°C and at 0.35 g/cc density of supercritical water for a reaction time of 30 minutes. The raw coal solids after filtration and the THFI of those solids have been sent to PETC for microscopic analysis. The results are awaited. The coal injected was of the order of 3g and conversion to gases, liquids and THF soluble products was 33%. The results are given in Table 6.

An experiment was carried out with Hi Na lignite and water at 380°C and at 0.35 g/cc density of supercritical water for a reactor time of 30 minutes. The conversion to gases, liquids, and THF soluble products was 46%. The results are given in Table 6.

Plans for the Next Quarter:

Experiments will be carried out with Bruceton coal and toluene at different stirrer speeds to find out at which stirrer speed the mass-transfer resistances are eliminated.

Experiments will be carried out with Bruceton coal and toluene at reduced densities of 1.0 to 1.5, temperatures of 380°C and 400°C and reactor times of two minutes to ten minutes to study the short contact time liquefaction kinetics.

VII REFERENCES

1. R. Mohamed, M.S. Dissertation, University of Pittsburgh, 1983.

2. G.D. Holder, J. Gopal, and G.V. Deshpande, "The Supercritical Fluids for Reaction and Extraction of Coal and Heavy Oils," Final Report, (Pittsburgh, PA: University of Pittsburgh, Department of Chemical and Petroleum Engineering , for U.S. DOE, September 1983).

3. R.L. Jolley, B.R. Rodgers, B.M. Benjamin, M.L. Poutsma, E.C. Douglas, and D.A. McWhirter, " Studies of the Effect of Selected Hondonor Solvents on Coal Liquefaction Yields," ORNL/TM-3662, September 1983.

VIII. DISTRIBUTION

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TABLE 1

Typical Experimental Results With Supported Ru Catalyst
(Pressure = 1.46 MPa, Stirrer Speed = 2300 rpm, feed CO (%) = 20.71)

Temp (K)	Feed Flow Rate (scc/min)	Non-Condensable Off Gas Flow Rate (scc/min)	CO Conversion (%)	Moles CO consumed/hr gm Catalyst ($x10^3$)	Mole CH_4 produced/hr. gm Catalyst ($x10^3$)	Mole CO_2 Produced/hr. gm Catalyst	Rate of Heat Generation KCal/mol CO Converted	Heat Removal Cal/hr. gm Catalyst
524.0	496.78	333.13	49.84	4.66	1.24	0.90	33.19	154.66
538.0	500.11	263.31	83.31	7.81	4.02	2.25	33.24	259.60
548.0	527.64	264.68	84.42	8.46	5.15	2.41	35.05	296.52
556.0	511.75	233.77	92.39	8.79	5.18	2.77	36.32	319.25
568.0	533.97	208.50	97.80	9.96	7.58	0.946	52.89	527.26
569.0	526.82	243.89	95.69	9.18	8.37	0.85	57.57	528.49
578.0	526.82	231.94	94.80	9.09	8.95	0.916	58.86	535.12
559.0	526.82	235.17	92.56	8.88	8.64	0.901	58.00	515.04
549.0	526.82	249.10	90.92	8.72	8.82	0.774	57.03	497.36
538.0	526.82	260.33	88.29	8.47	8.37	0.75	57.11	483.90
523.0	526.82	279.87	83.98	8.05	7.75	0.06	39.34	316.68

Table 2

Summary of Batch Extraction/Reaction fo Briceton Bituminous Coal Using Supercritical Toluene-Piperidine Mixtures

Run #	39	40	41	42	43	45
Toluene, wt %	94.93	75.00	54.92	34.98	15.50	54.63
Piperidine, wt %	5.07	25.00	45.08	65.02	84.50	45.37
Fluid denisty, kg/m^3	291.90	306.60	294.90	294.50	298.00	296.80
Coal charged x 10^3 kg	37.00	34.70	42.30	38.10	32.10	58.70
Temperature, K	647.60	647.60	647.60	647.60	647.60	647.60
Pressure prior to injection, MPa	7.23	6.87	6.84	6.89	7.08	7.01
Pressure, MPa (solvent + argin)	10.88	9.80	10.13	10.16	10.25	11.38
Reaction time, min.	15.00	15.00	15.00	15.00	15.00	15.00
Stirrer speed, rpm	2500.00	2500.00	2500.00	2500.00	2500.00	2500.00
Solid product, *%	98.16	97.48	106.40	148.02	165.31	-
Toluene insolubles, *%	93.43	97.48	82.23	130.09	144.03	86.99
THF insolubles, *%	87.64	91.69	82.23	111.67	110.39	83.36
Pyridine insolubles, %	86.49	85.30	80.90	98.89	90.92	-

*The products are expressed as % of coal injected.

Table 3

Summary of Batch Extraction/Reaction of Bruceton Bituminous Coal Using Supercritical Piperidine

Run #	47	57	57
Extraction Procedure	A	A	B
Piperidine density, kg/m^3	299.20	304.60	304.60
Coal charged x 10^{-3} kg	51.00	41.30	41.30
Temperature, K	647.60	647.60	647.60
Pressure prior to injection, MPa	7.21	7.38	7.38
Pressure, MPa (solvent + argin)	11.05	11.81	11.81
Reaction time, min.	30.00	8.00	8.00
Stirrer speed, rpm	2500.00	2500.00	2500.00
Toluene insolubles, %	150.90	107.31	52.49
THF insolubles, %	117.87	107.31	52.49
Pyridine insolubles %	82.05	107.31	-

Table 4

Summary of Batch Extraction/Reaction of Bruceton Bituminous Coal Using Supercritical Toluene

Run #	48	49	53	56
Toluene density, kg/m^3	.298	.301	.303	.303
Coal charged x 10^3 kg	39.930	38.890	48.490	39.010
Temperature, K	672.000	672.000	672.000	672.000
Pressure prior to injection, MPa	7.630	7.620	7.800	8.200
Pressure, MPa (solvent + argin)	11.830	11.870	11.940	12.110
Reaction time, min.	60.000	30.000	8.000	2.000
Stirrer speed, rpm	2500.000	2500.000	2500.000	2500.000
Toluene insolubles, %	84.190	85.420	88.610	92.490
THF, insolubles, %	83.280	83.490	88.610	90.820

Table 5

Summary of Batch Extraction/Reaction of Coal/Lignite Using Supercritical Water

Run #	54	57
Solid Substrate	Bruceton Bituminous Coal	Hi Na Lignite
Water density, kg/m^3	351.70	352.30
Coal/Lignite charged $x\ 10^3$ kg	3.10	11.40
Temperature, K	649.80	649.80
Pressure prior to injection, MPa	23.16	22.55
Pressure, MPa (solvent + argin)	24.48	25.46
Reaction time, min.	30.00	30.00
Stirrer speed, rpm	2500.00	2500.00
% Solid product	79.00	59.60
% Gases	1.51	7.70
% Liquids by diff.	19.49	32.70
% THFI	67.20	53.70

Table 6

Toluene-Bruceton coal at 400°C

$K_1 = 0.09868 \text{ sec}^{-1}$
$K_2 = 1.244 \text{ sec}^{-1}$
$K_3 = 2.402 \text{ sec}^{-1}$
$K_4 = 0.195$

Exptl % GOA	Predicted % GOA	Exptl % Preasphaltenes	Predicted % Preasphaltenes	Reaction time, min.
7.51	7.51	1.67	.06	2.00
11.39	11.39	0	0	2.00
17.07	13.77	2.58	0	8.00
14.58	15.49	1.93	0	30.00
15.81	15.81	0.91	0	60.00

% GOA = 100 - % Toluene Insolubles

% Preasphaltenes = % Toluene Insoluble - % THF Insolubles

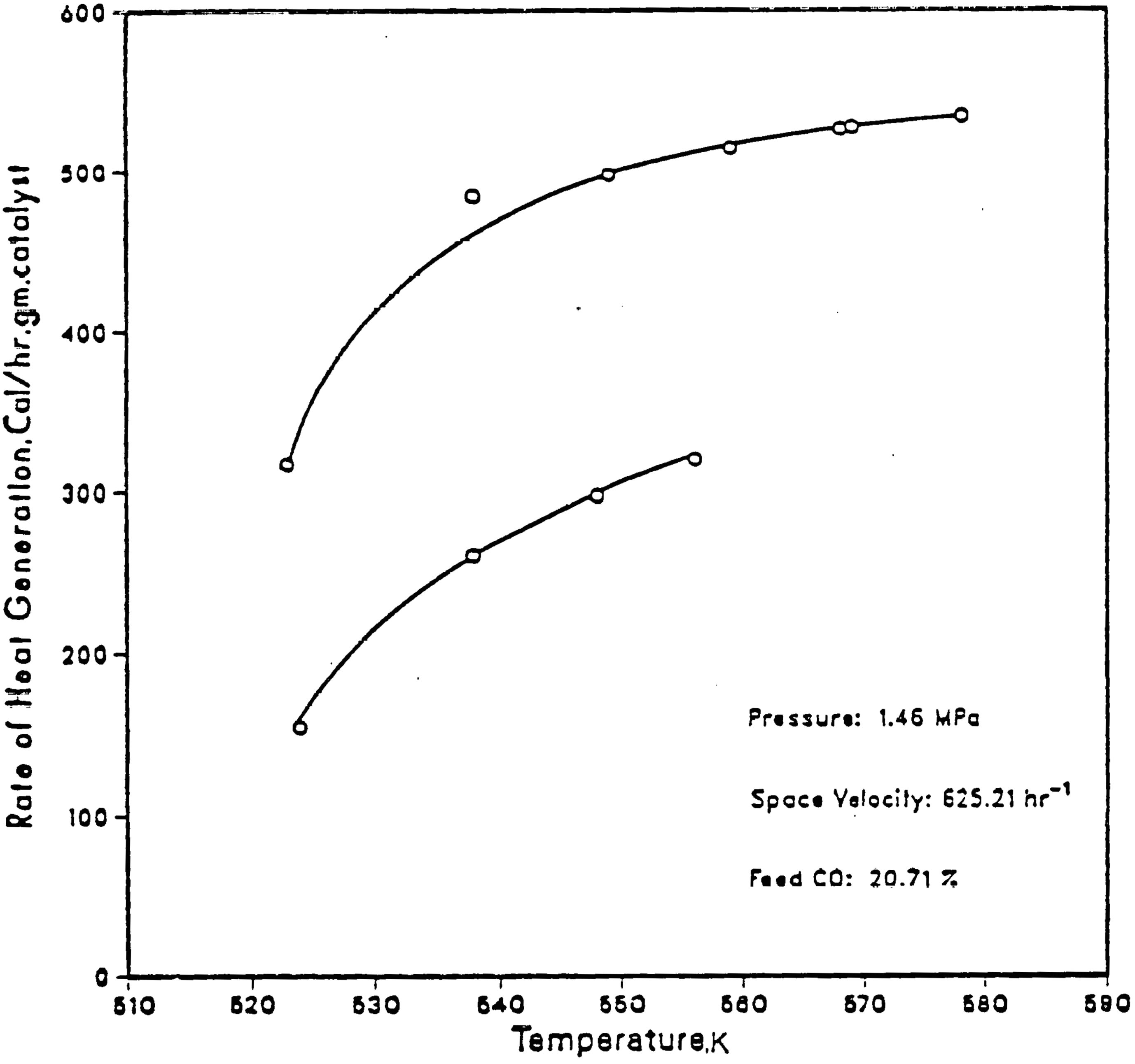


Figure 1. Variation of rate of heat generation with temperature using a ruthenium catalyst.

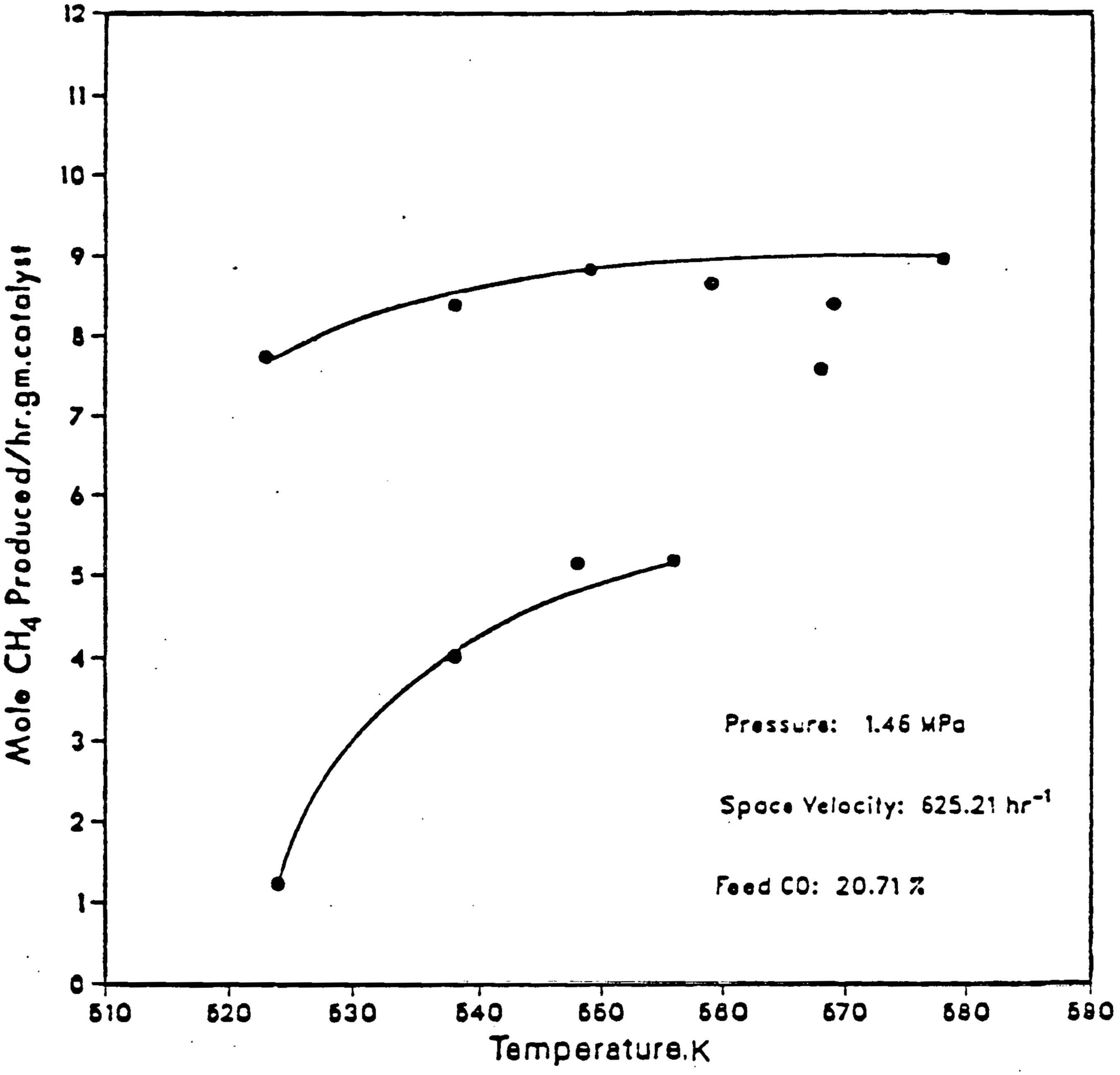


Figure 2. Methane production versus temperature for slurry reactor using ruthenium catalyst.

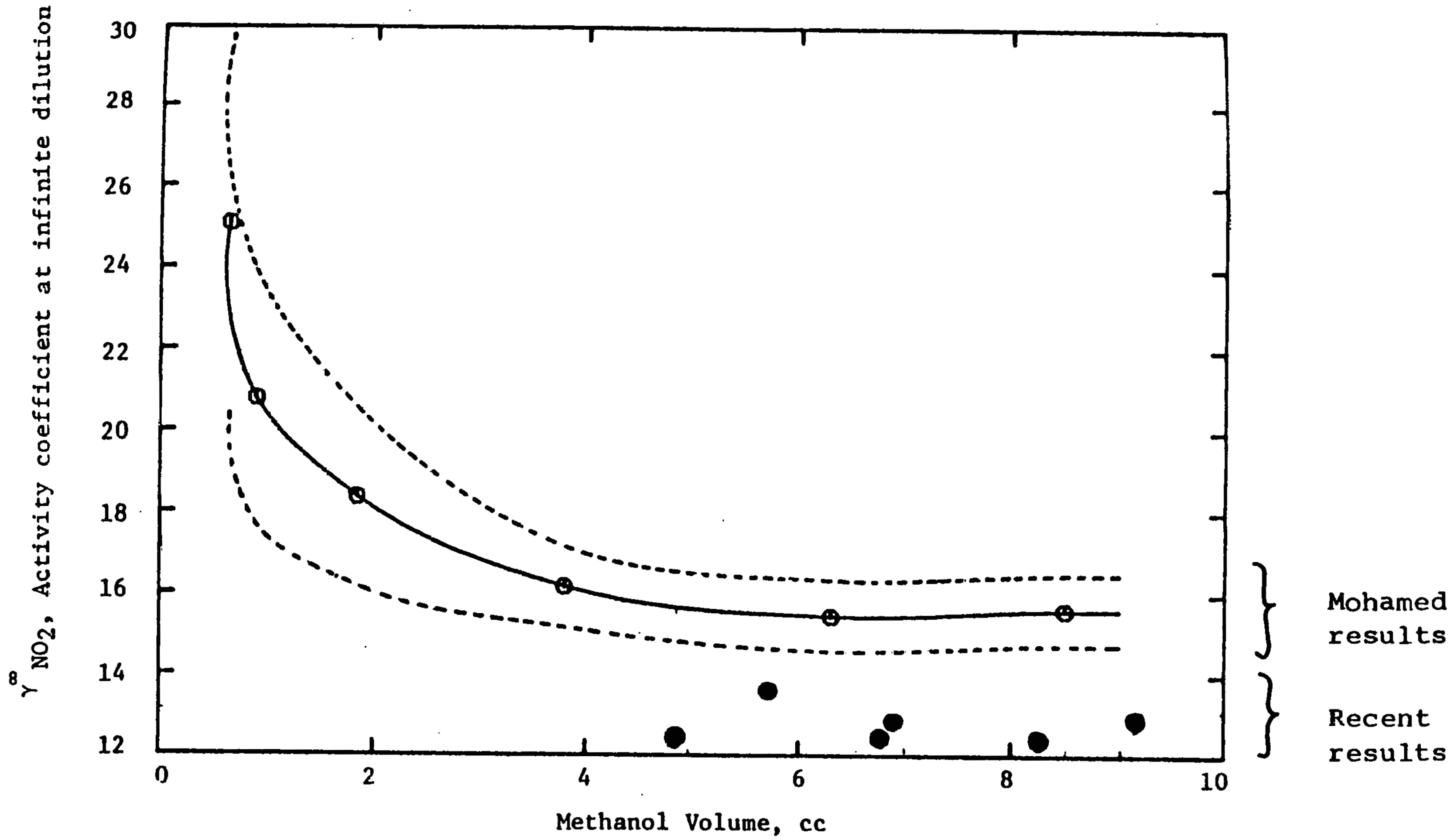
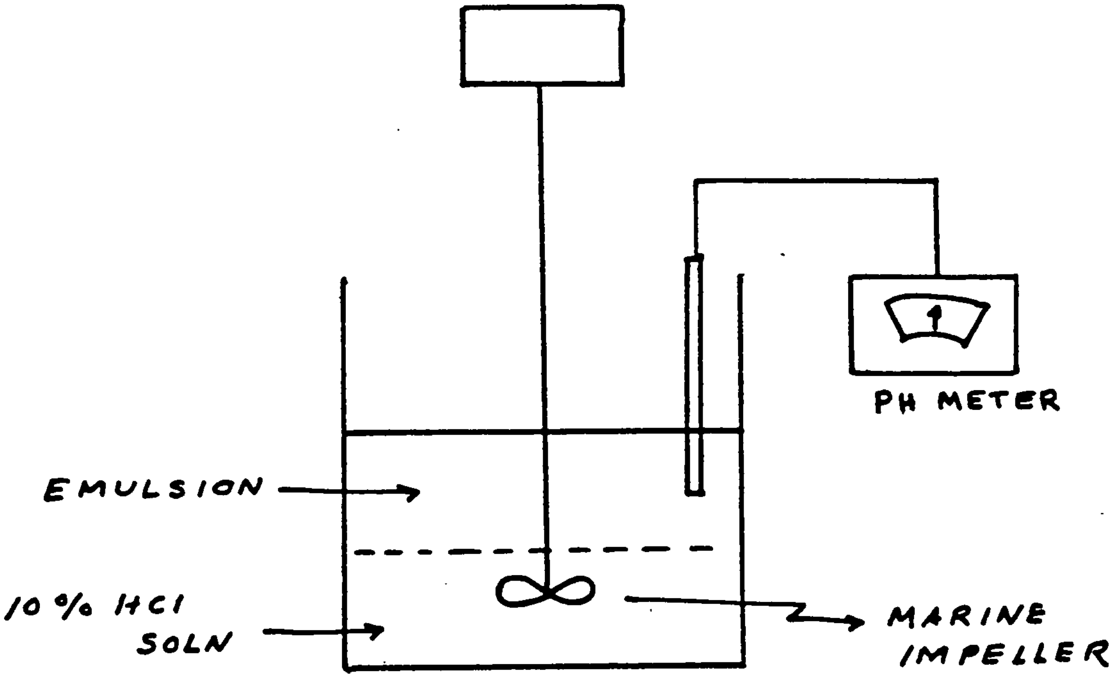


Figure 3: Absorption of NO_2 by methanol.

⊙ Mohamed results

Recent results



PRIOR TO CONTACTING OPERATION

Figure 4: Equipment for preparation of liquid membrane.

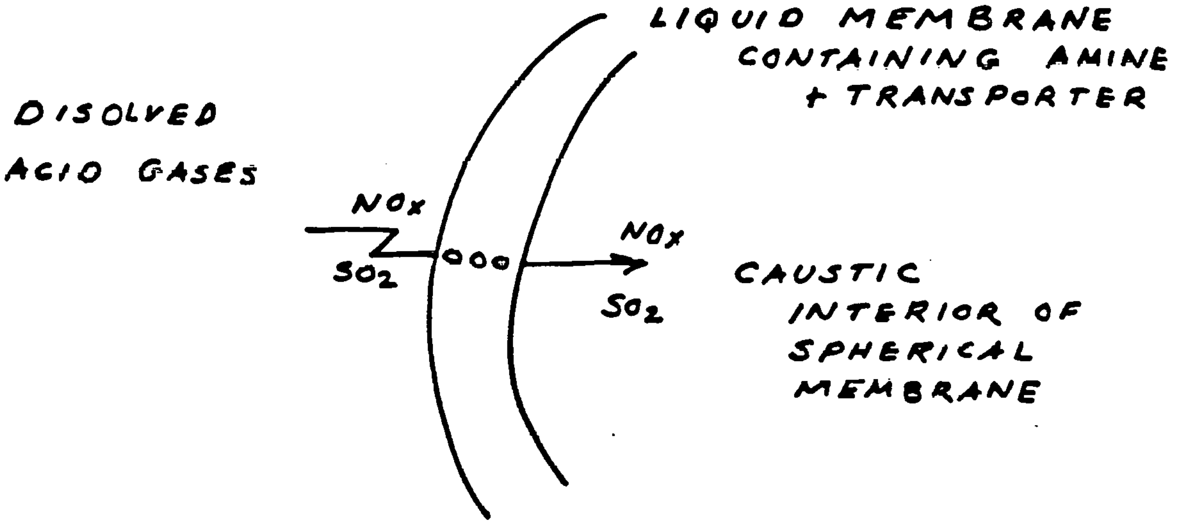


Figure 5: Membrane Mechanism

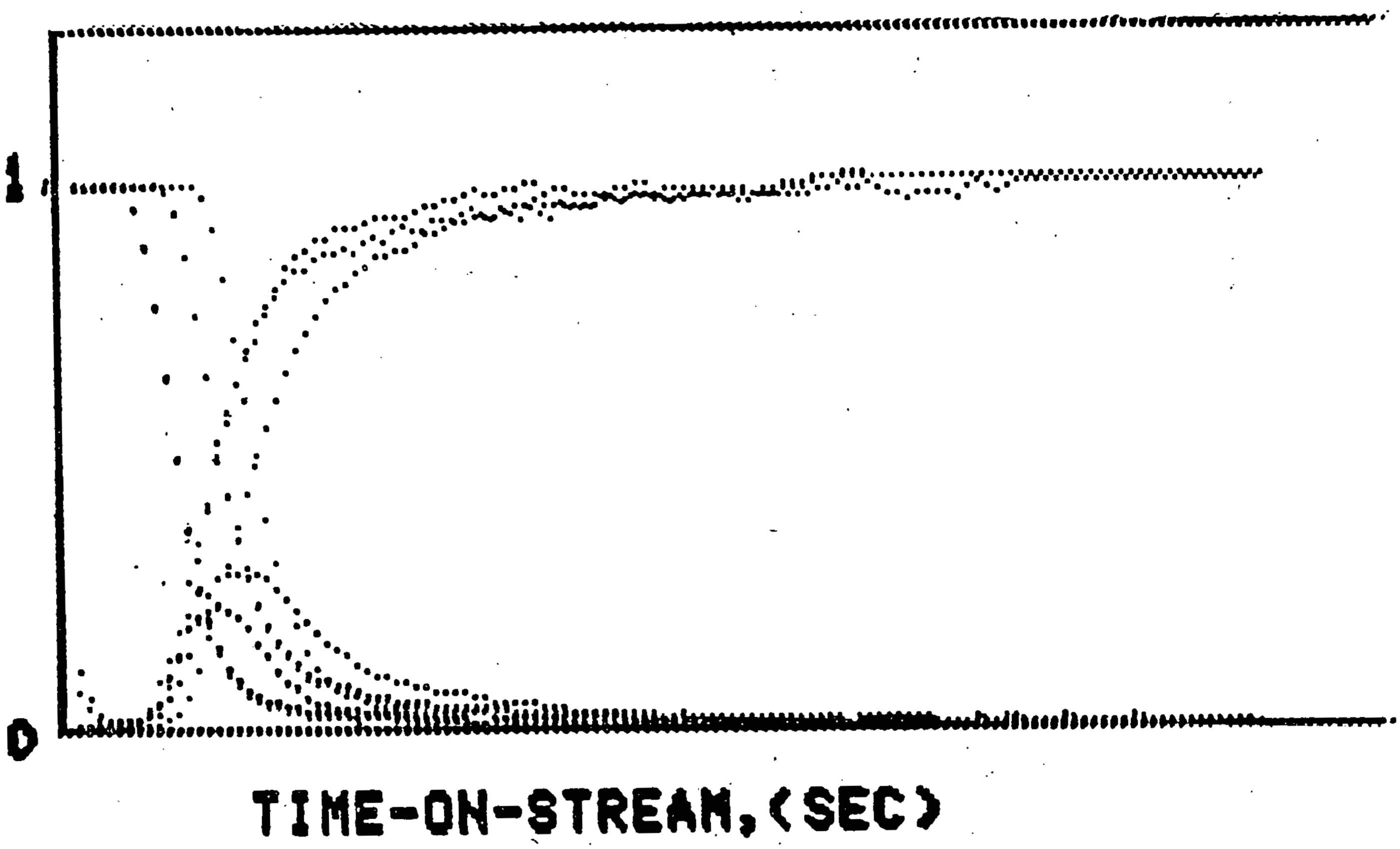


Figure 6: Isotopic switching with unpromoted ruthenium.

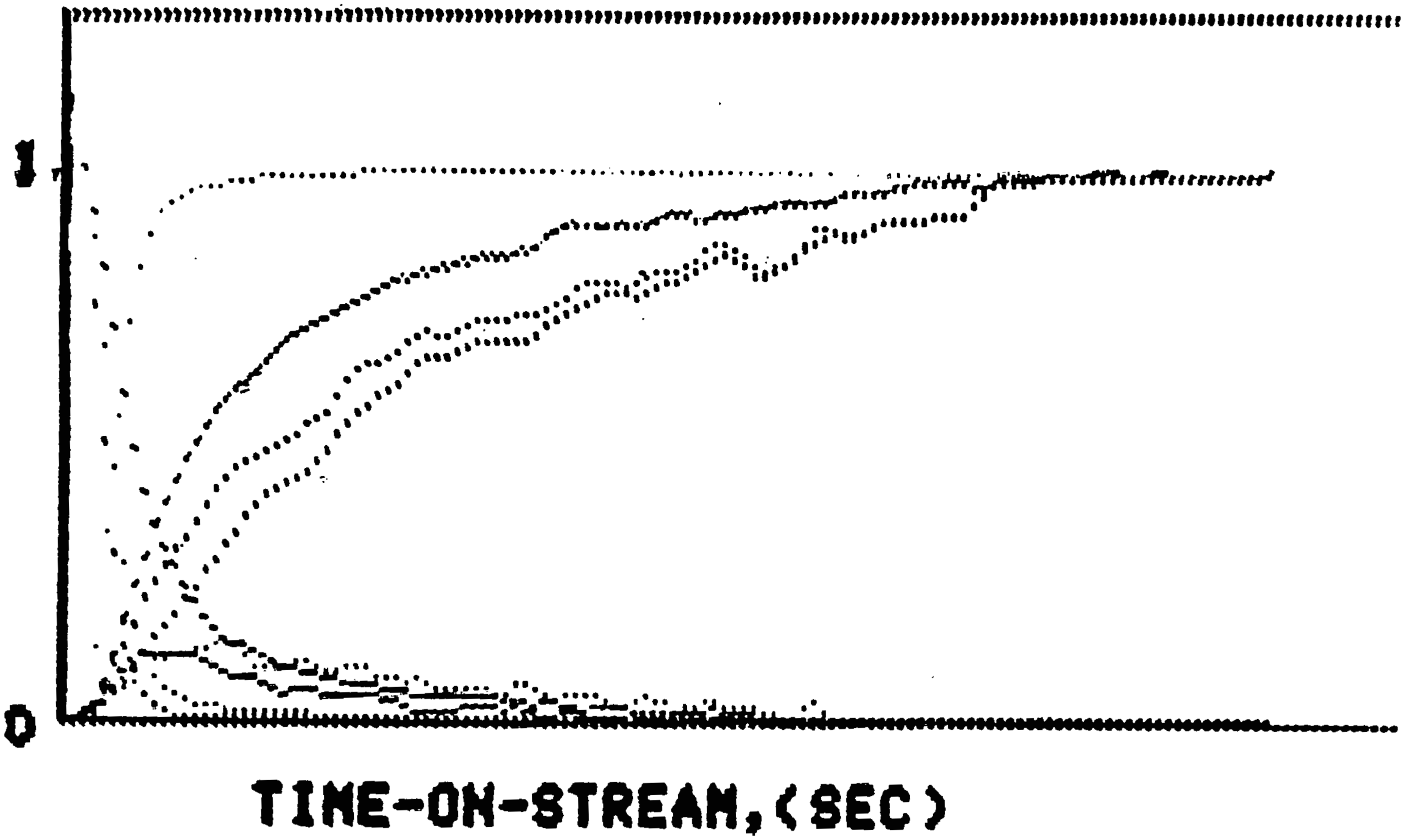


Figure 7 Isotopic switching with cobalt.

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