1977

The Liquid Phase Conversion of Carbon Dioxide to Hydrocarbons Over Ruthenium Catalyst Systems

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THE LIQUID PHASE CONVERSION OF CARBON DIOXIDE TO HYDROCARBONS OVER RUTHENIUM CATALYST SYSTEMS

BY

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B.S., Teacher Training University, 1973

RESEARCH REPORT

Submitted in partial fulfillment of the requirements
for the degree of Master of Science: Industrial Chemistry
in the Graduate Studies Program of the College of Natural Sciences
of Florida Technological University

Orlando, Florida
1977

ABSTRACT

The purpose of this research project was to evaluate the feasibility of producing hydrocarbons by liquid phase hydrogenation of carbon dioxide. Initial studies dealt with the evaluation of ruthenium (III) chloride over a wide range of reaction conditions. High conversions were observed and were found to vary with catalyst concentration, temperature and time. Conversion of carbon dioxide reached 73% after twenty-four hours at a catalyst concentration of 0.75 g/mole of CO_2 feed. The hydrogen to carbon dioxide ratio was found to have a significant effect on product distribution and amount of methane produced. For example, low ratios of H_2/CO_2 gave large amounts of high molecular weight hydrocarbons, while relatively more methane was formed at high H_2/CO_2 ratios.

An attempt was made to determine whether the reaction was taking place in the gas phase or the liquid phase or both. A number of solutions were tested, with sodium hydroxide solutions exhibiting the best results. Since the carbon dioxide feed gas dissolves in this solution immediately to form carbonate species, it is assumed that

the hydrogenation reaction takes place through a carbonate species in solution. This mechanism is supported by the observation that the carbonate molarity in solution strongly affected the conversion. The conversion of carbon dioxide over different molarities of sodium hydroxide was observed to exhibit a maximum at the concentration of sodium hydroxide, which gives the maximum $NaHCO_3$ concentration.

Sodium carbonate and sodium bicarbonate solutions were also tested as starting reagents in the hydrogenation reaction. Conversion was found to be 10.68% for sodium carbonate and 15.88% for sodium bicarbonate, compared with 19% conversion of carbon dioxide under the same reaction conditions. These data suggest that the major part of the hydrogenation reaction takes place through a HCO_3^- species in solution.

The rate of hydrogenation of sodium bicarbonate and sodium carbonate were found to be first order in catalyst concentration. A linear relationship was also found to exist between conversion of carbonate species and temperature in the range of 150-300°C.

Three catalyst systems; $RuCl_3$, Ru metal and 1% Ru supported on graphite were tested in the hydrogenation of carbon dioxide over sodium hydroxide solutions. One percent Ru on graphite exhibited the fastest rate at which equilibrium was achieved, with a 76-77% conversion of carbon dioxide to methane, and higher hydrocarbons being observed after 24 hours. The activity of Ru metal catalysts was observed to decrease during the course of the reaction, probably because of the loss of active catalyst sites, due to fusing of the catalyst on the surface of the glass liner.

The rate of reaction between carbon dioxide and hydrogen over $RuCl_3$ in the gas phase was found to be faster than the rate of this reaction in the liquid phase. In the gas phase reaction, equilibrium was achieved after 24 hours, with 89% conversion of carbon dioxide to methand and higher hydrocarbons, compared with 70% conversion in the liquid phase, under the same reaction conditions. One percent Ru supported on graphite exhibited a faster rate of reaction in the gas phase than in the liquid phase. But the rate of the reaction over Ru metal was faster in the liquid phase than in the gas phase. Table I summarizes the comparison between the gas phase and the liquid phase hydrogenation reaction for the three catalytic systems under the same reaction conditions.

TABLE I

Comparison Between Gas Phase and Liquid Phase Hydrogenation Reaction

Catalyst	% Conversion after 24 hours Gas Phase	% Conversion after 24 hours Liquid Phase
$RuCl_3$	89.80%	70.22%
Ru metal	50.49%	63.57%
1% Ru on graphite	85.57%	76.86%

ACKNOWLEDGEMENTS

The author would like to thank Dr. Chris A. Clausen for his guidance and patience in directing this research study.

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INTRODUCTION

Increasing demand for natural gas as a fuel and chemical raw material, coupled with limited gas reserves, has focused considerable interest on utilizing the tremendous coal reserves as a possible source of gaseous fuel. One attractive process is the production of a synthesis gas, containing carbon monoxide and carbon dioxide by the reaction of coal with oxygen and superheated steam, and the subsequent catalytic hydrogenation of the gas to methane and other hydrocarbons.[1]

In the next section, an historical review of research work concerning catalytic conversion of oxides of carbon to hydrocarbons is presented. All of these studies are heterogeneous, with no previous work having been reported on the liquid phase hydrogenation of carbon dioxide to produce methane. As the present study shows, liquid phase reaction of carbon dioxide and hydrogen is possible and a fruitful field of investigation.

Historical Review

Methane was first synthesized in 1896,[2] by passing mistures of carbon monoxide, carbon dioxide and hydrogen over finely divided metals at temperatures below 400°C.

In 1902, Sabatier and Senderens described the synthesis of methane by hydrogenation of carbon monoxide using a Ni catalyst at atmospheric pressure and 250°C.[3] They reported that nickel was an excellent catalyst. Since that time, the most active catalysts have been identified as transition elements with unfilled 3d, 4d, and 5d orbitals: Iron, cobalt, nickel, ruthenium, rhenium, palladium, osmium, indium, and platinum as well as a few elements that can assume these configuration (e.g. silver).

In 1913, a patent application issued to Badische Anilin and Sodafabrik,[4] claims the production of hydrocarbons and oxygenated organic compounds at pressures of 100 atm. and higher over various catalysts. Nickel, cobalt, iron, manganese, chromium, titanium, osmium, cerium, molybdenum, zinc, and palladium are mentioned.

In the early 1920's, Fischer, Tropsch and Dithey[5] compared the methanation activities of various metals at temperatures up to 800°C. The decreasing order of methanation activity was $Ru > Ir > Rh > Ni > Co > Os > Pt > Fe > Mo > Pd > Ag$. Thus, by 1925, all of the metals now considered active for methanation of carbon oxides had been identified. In terms of metals important for methanation, the list could now be shortened to Ru, Ni, Co, Fe, and Mo.[6]

During the period between 1922 and 1923, the first important work by Fischer and Tropsch on catalytic hydrogenation of carbon monoxide was published.[7] Alkalized iron turnings and other catalysts were tested for the water gas reaction at pressures above 100 atm. and temperatures in the region of 400°C. The reaction product was a mixture of oxygenated compounds.

Patents by Pan and Winkler,[8] for exclusive controlled catalytic conversion of carbon monoxide and hydrogen to methanol, was issued in 1923. ZnO, Cr_2O_3 catalyst were used. Also in 1923, Fischer and Tropsch[9] produced the first measureable quantities of hydrocarbons by catalytic reduction of carbon monoxide. The reaction conditions involved recycling carbon monoxide and hydrogen over alkalized iron fillings at 410°C. They were able to vary the ratio of oxygen-containing molecules to pure hydrocarbons, by varying the pressure.

The Fischer-Tropsch normal-pressure synthesis of gasoline was accomplished in 1925 by the use of Fe and Co catalysts prepared by the decomposition of salts (e.g., nitrates) at one atmosphere of pressure and temperatures of 200-250°C.[10,11,12]

A Ni-ThO_2-Kieselguhr precipitation catalyst for normal-pressure synthesis was developed by Fischer and Meyer,[13] in 1931. The following year, a Co-ThO_2-Kieselguhr precipitation catalyst (standard catalyst) was developed by Fischer and Koch.[14] In 1934, Fischer and Pichler[15] began investigations directed towards increasing the fields of useful synthesis products by changing the physical performance of the process. The synthesis was done in steps with intermediate removal of condensables.

In 1936, the first full-scale Co normal-pressure synthesis plant was built in Oberhausen-Holten, Germany.

The medium pressure synthesis of hydrocarbons by reaction between carbon monoxide and hydrogen over Co catalysts at 5-20 atm., and 180-200°C was developed by Fischer and Pichler in 1936.[16,17,18]

A medium pressure synthesis with an Fe catalyst at 5-20 atm. and 180-200°C was developed by Fischer and Pichler in 1937.[19]

A high pressure synthesis of high-melting paraffins using a ruthenium catalyst at 50-100 atm., and temperatures in the region of 100-200°C was developed by Pichler in 1938.[20]

The starting of the first commercial-scale Co medium pressure plant at Oberhausen-Holten, Germany, was accomplished in 1938.

A high-pressure synthesis of branched hydrocarbons (iso-synthesis) in the presence of thorium oxide and other oxide catalysts at 150-200 atm., and temperatures in the region of 400-500°C was developed in 1941.[21-24]

In 1949, a process using carbon monoxide and water as the synthesis gas was developed.[25]

In 1950, a commercial-scale medium-pressure synthesis plant was erected at Brownsville, Texas, for the conversion of Co and H_2 from natural gas over an Fe catalyst in a fixed fluid-bed reactor.

The start-up of a large-scale syntehsis plant in 1955 by South African Coal, Oil, and Gas Corporation, Ltd., at Sasselbury, South Africa, for medium synthesis with Fe catalysts was accomplished in modern fixed-bed reactors (Lurgi-Ruhrchemic) were used in combination with entrained fluidized-bed reactors.

Commercial plants for the production of synthetic liquid fuels from carbon monoxide and hydrogen are listed in Table II.

Economic comparisons of hydrocarbon and chemicals production from synthesis gas (CO, H_2) are difficult because

TABLE II

Commercial Plants for the Production of Synthetic Liquid Fuels[26]

Country	Name of company	Startup, year	Starting material	Normal-pressure synthesis	Medium-pressure synthesis: Double tube	Medium-pressure synthesis: Fixed bed	Medium-pressure synthesis: Fluid bed	Catalyst: Co	Catalyst: Fe	Design capacity, 1000 ton/yr
Germany	Brabag	1936	lignite	x				x		210
Germany	Gewerkschaft Viktor	1936	coke, coke gas	x				x		50
Germany	Ruhrbenzin A.G.	1936	coke	x				x		30
		1938			x					42
Germany	Gewerkschaft Rheinpreussen	1936	coke, coke gas	x				x		75
Germany	Krupp-Treibstoffwerke	1937, 1939	coke	x				x		47
		1939, 1952			x			x	x	13
Germany	Wintershall A.G.	1937, 1939	lignite	x				x		80
Germany	Essener Steinkohle Chemische-werke	1937, 1938	coke, coke gas	x				x		50
France	Harnes	1937	coke	x				x		30
	Société Kuhlmann	1952				x			x	2
Germany	Hoesch-Treibstoffwerke	1939	coke		x			x		60
Germany	Schaffgotsch-Werke	1939	coke, coke gas		x			x		60
Japan	Mike	1940		x				x		40
Japan	Takikawa	1942, 1943	coal	x				x		100
Japan	Rumoi	1939		x				x		50
Japan	Amagasaki	1939		x				x		70
Manchuria	Fushin	1939	coal	x				x		50
U.S.	Hydrocol Co.	1950	natural gas				x		x	360
South Africa	Sasol	1955	coal				x		x	185
South Africa	Sasol	1955	coal			x			x	69

they are complicated by such factors as raw material costs, locations of consumers, utilities, capacity, by-product use, capital charges, staff, and auxiliary costs. In Germany during World War II, the cost of primary synthesis products amounted to 200-280 Reischmark (RM) per metric ton, at a coke price of 20-68 RM/metric ton.[26] Forty-two percent of the costs of the synthesis products was contributed by the cost of raw materials, 30% by production and 28% by capital charges. Today, with the price of a ton of coal almost identical to the price of a ton of crude petroleum, the synthesis of liquid fuels is no longer economically feasible in the Federal Republic of Germany.

The figures which were used as a basis for the economic evaluation of the Brownsville operation are given in Table III.[27] These figures led to an estimated cost of

TABLE III

Economic Evaluation of the Brownsville Operation

Item	Cost (¢)
Natural gas, m^3	0.35
Oxygen (without steam), m^3	0.13
Carbon monoxide and Hydrogen, 1:2 ratio, m^3	0.22
Catalyst, lb.	4.99
Capital charges	15%

\$0.0757 for the preparation of a gallon of gasoline; the cost of preparing a gallon of gasoline from crude petroleum was estimated at \$0.1098.[26]

In 1962, the synthesis of polymethylene from CO and H_2 with activated Ru catalysts, at high pressure, and at temperatures less than 150°C was achieved.[28]

There has been additional progress over the past years in the area of preferred promoters, supports, and preparation conditions, primarily for the purpose of obtaining high selectivities and maintaining catalytic activity. The following list is representative of these studies:

The kinetics of the reaction between carbon monoxide and hydrogen over a reduced nickel catalyst was studied at 1 atmosphere of pressure over a temperature range of 300-350°C.[29] The rate of reaction between the absorbed reactant molecules on the active centers of the catalyst was found to be the rate-controlling step in the synthesis of methane.

Sabastian worked with molybednum sulfide, the only methanation catalyst unaffected by sulfur impurities.[30]

The U.S. Bureau of Mines, in its search for catalysts capable of producing liquid and gaseous fuels, examined the activity of a ruthenium catalyst with carbon monoxide, carbon dioxide and hydrogen feed stocks.[31]

The ruthenium-catalyzed methanation of low concentration of CO and H_2 has been studied at the Institute of Gas Technology in Chicago.[32]

A 0.5% ruthenium on an alumina support, operating at atmospheric pressure in a fixed-bed flow reactor was tested with a 505,1070 and 3450 ppm CO in H_2 reaction mixture, over the temperature range of 150-275°C. The reaction followed pseudo first-order kinetics.[32-33]

As a part of the Bureau of Mines Research on processes for converting coal to liquid and gaseous fuel, the poisoning of iron Fischer-Tropsch catalysts by small concentrations of H_2S in synthesis gas was studied.[34]

The coadsorption and interaction of carbon monoxide and hydrogen on a series of unsupported noble metal catalysts was studied in the temperature range 100-200°C.[35] These workers mentioned that the highly specific behavior of ruthenium in the methanation reaction is probably due to the lower affinity of Co for Ru than for the other noble metals.

The initial rate of reaction of hydrogen and carbon monoxide was measured on supported Ru and Ni catalysts in a differential batch reactor. The initial rate of supported ruthenium was found to be independent of ruthenium particle size for less than 10 to 90Å. Activation energy for nickel at 280°C was observed to be 20 and 29 kcal mole^{-1} for total hydrocarbon and methane formation compared to 17 and 24 kcal mole^{-1} for Ru.[36]

Modeling, simulation, and operation of a Sabatier reactor was reported by Peter J. Lunde.[37]

An empirical expression was determined[38] for the rate of methanation of carbon dioxide with hydrogen from 200°C over a 0.5% ruthenium on alumina catalyst according to the equation:

$$4H_2(g) + CO_2(g) \rightleftharpoons 2H_2O(g) + CH_4(g) + 43 \text{ kcal}$$

The Isosynthesis process with reduciable oxides as catalysts,[39,40] under proper conditions produces saturated branched-chain aliphatic hydrocarbons containing 4 to 8 carbon atoms. In fact, the reason for developing these catalysts was to produce isobutane for high octane gasoline.[41]

The effects of pressure, compositions and temperature on the rates of methane and carbon monoxide formation was determined for the reaction between hydrogen and carbon dioxide over a nickel-kieselguhr catalyst at pressures of 30 atmospheres.[1] The selectivity of the catalyst is affected by thermal deactivation. The rate of methane formation is decreased and the rate of carbon monoxide formation is increased following the exposure of the catalyst to high temperature.

Pichler revealed that CO_2 in the absence of CO is rapidly methanated even at 100°C.[42] The Bureau of Mines work[31] indicated that methanation of CO_2 (in the absence of CO) is faster than that of CO alone.

In addition to the studies indicated in the previous discussion, several other articles on the gas phase hydrogenation of carbon dioxide have been reported. However, no studies have been reported, either in chemical journals or the patent literature, on the liquid phase hydrogenation of carbon dioxide to produce hydrocarbons.

Chemistry and Thermodynamics

The simplest hydrocarbon producing reaction that can occur in the hydrogenation of carbon dioxide is:

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O$$

This reaction is exothermic over the cited range of conditions.[43-45]

TABLE IV

Heat of the Methanation Reaction

(Heat of formation of methane by reaction between carbon dioxide and hydrogen.)

Temperature		H^o
^oC	^oK	kcal
27	300	-39.40
127	400	-40.650
227	500	-41.779
327	600	-42.792
427	700	-43.680
527	800	-44.449
627	900	-45.105
727	1000	-46.653

The high heat release makes it difficult to prevent overheating and deactivation of the catalyst system. It also causes such large temperature rises, that methanation becomes limited due to thermodynamic equilibrium. The heat of reaction is not greatly influenced by changes in temperature (Figure I). Therefore, it is necessary to develop temperature control systems which will permit safe operation of this reaction.

Changes in the free energy and equilibrium constant for this reaction are quite sensitive to temperature (Figures II and III).

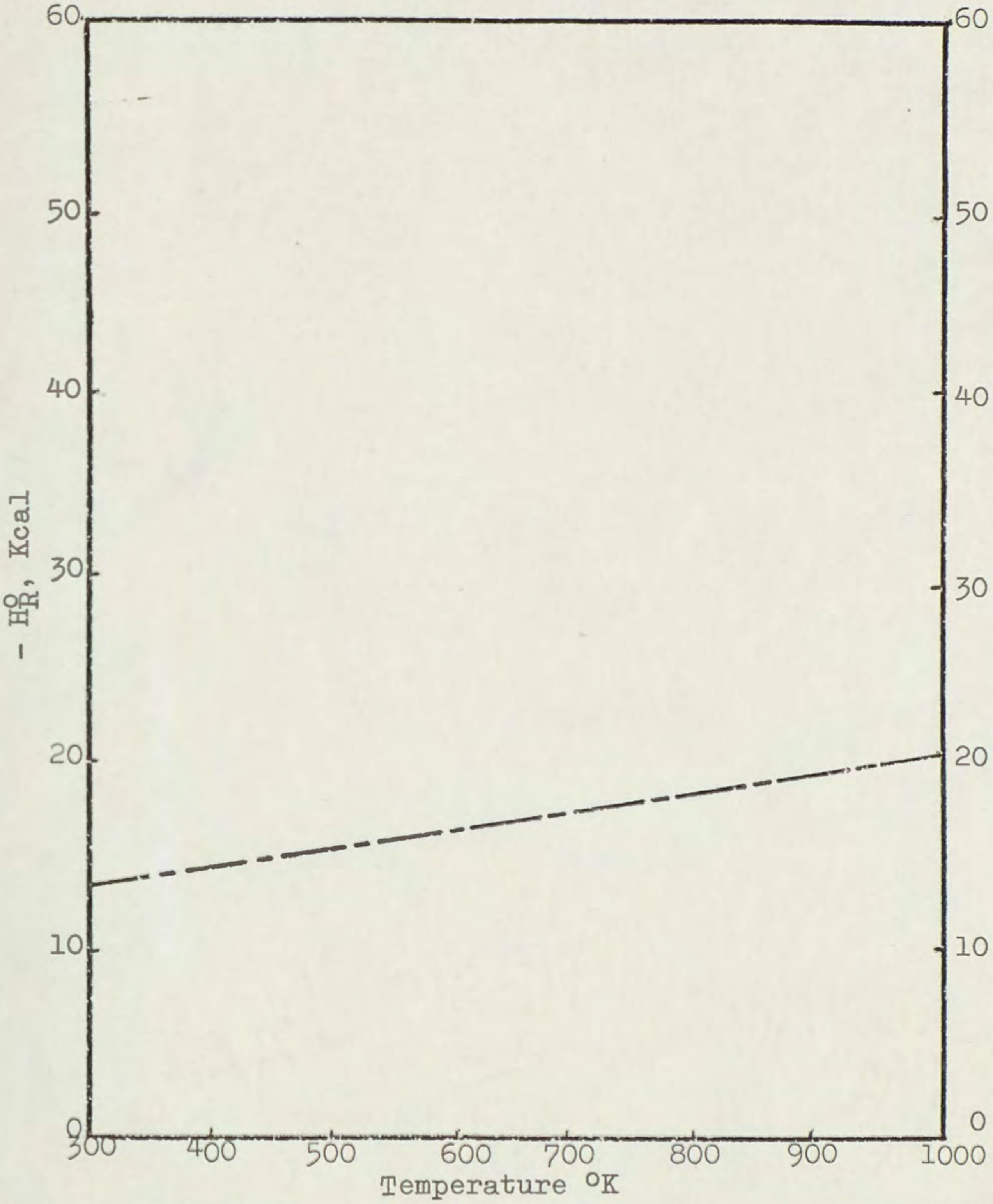


FIGURE I.--Heat of the Methanation Reaction

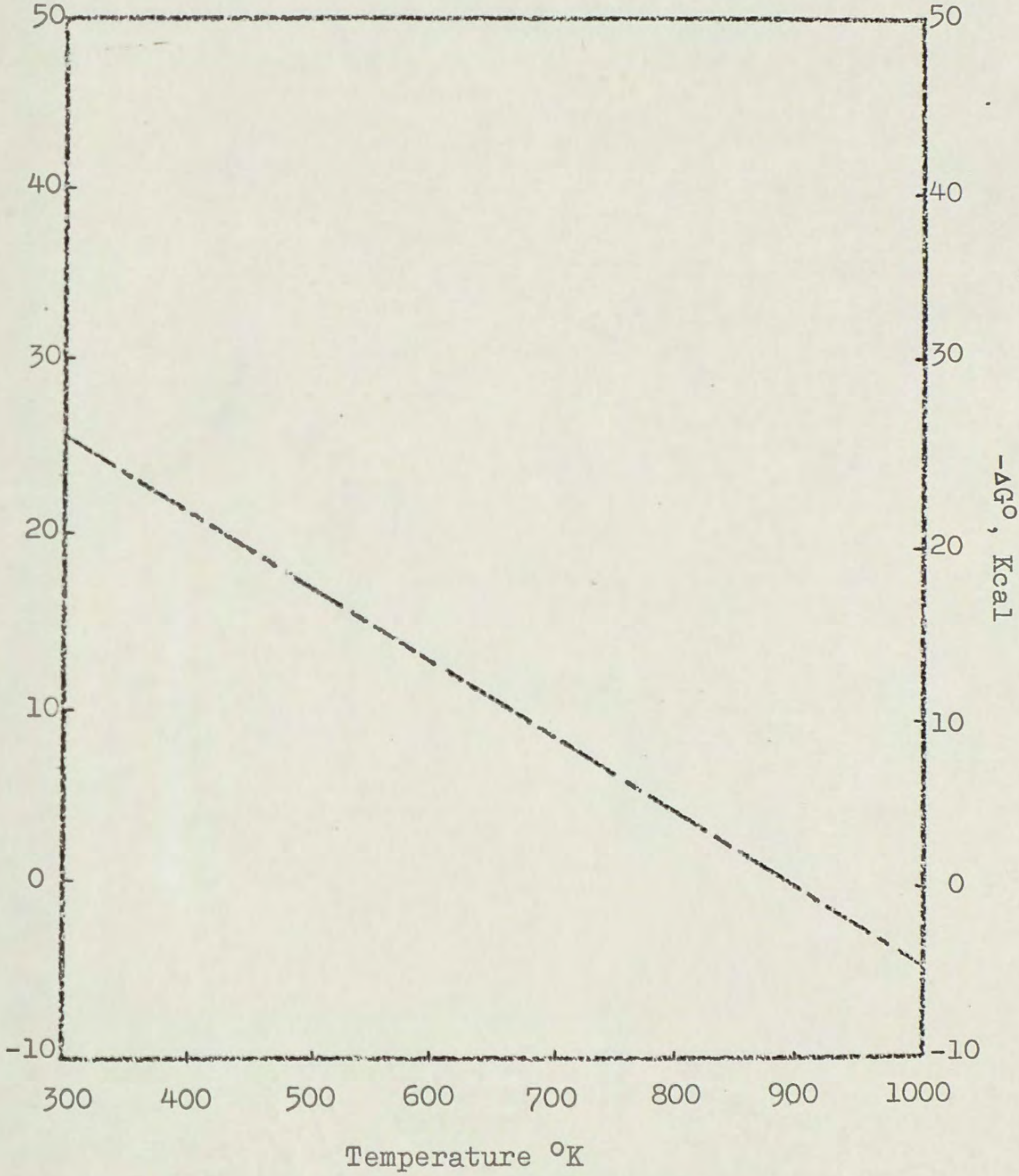


FIGURE II.--Free Energy of Methanation Reaction

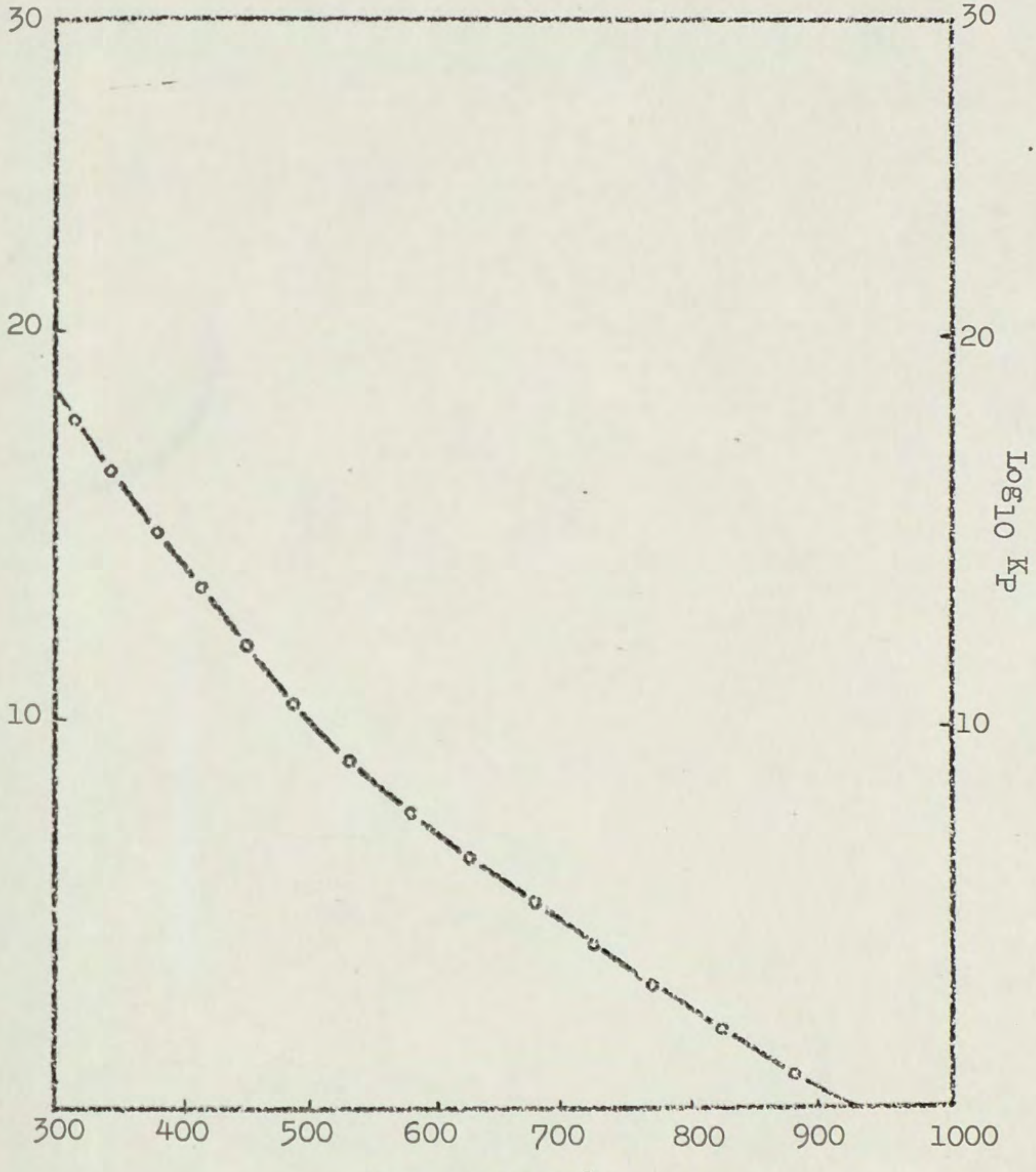


FIGURE III.--Equilibrium Constants of the Methanation Reaction

TABLE V

Free Energy of the Methanation Reaction

Temperature		G
°C	°K	kcal
27	300	-27.007
127	400	-22.769
227	500	-18.168
327	600	-13.347
427	700	- 8.366
527	800	- 3.269
627	900	+ 1.921
727	1000	+ 7.173

Equilibrium constants as a function of temperature were calculated from

$$G = -RT \ln K_p$$

where:

$$\frac{G}{T} = A + BT + C \ln T + \frac{D}{T} + \frac{E}{T^2}$$

with T in °K and the standard state for K_p is one atmosphere.

TABLE VI

Equilibrium Constant for Methanation Reaction

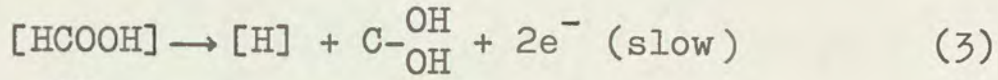
Temperature		log K_p
°C	°K	
27	300	19.724
127	400	12.44
227	500	7.940
327	600	4.861
427	700	2.611
527	800	0.893
627	900	-0.466
727	1000	-1.568

Mechanism

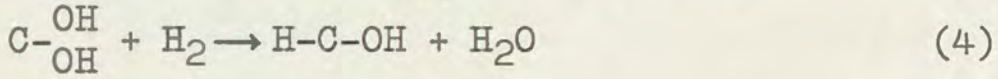
Two schemes for the mechanism of synthesis of methane from carbon dioxide and hydrogen have been proposed.[44] One proposed mechanism suggests that the conversion of CO_2 to CH_4 occurs with the intermediate formation of CO. This view is supported by studies on ruthenium,[46] and iron catalysts.[47] The second proposed mechanism suggests that CO_2 reacts by a pathway not involving intermediate formation of CO.[48] According to a study by Vlasenko and Uzeforeiel,[49] the reduction process is initiated by the activation of hydrogen on the catalyst surface.[44]

$$2[*] + 2e^- + H_2 \longrightarrow 2[H] \qquad (1)$$

$$2[H] + CO_2 \longrightarrow [HCOOH] + [*] \qquad (2)$$



$$[HCOOH] \longrightarrow [H] + C\text{-}\genfrac{}{}{0pt}{}{OH}{OH} + 2e^- \text{ (slow)} \qquad (3)$$



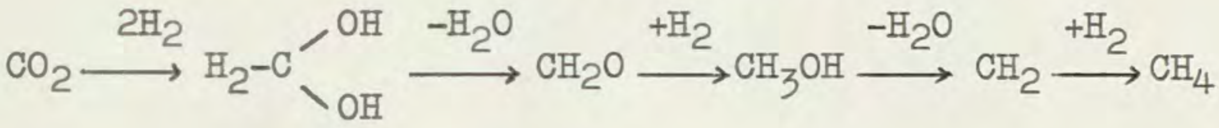
$$C\text{-}\genfrac{}{}{0pt}{}{OH}{OH} + H_2 \longrightarrow H\text{-}C\text{-}OH + H_2O \qquad (4)$$

$$H\text{-}C\text{-}OH + H_2 \longrightarrow CH_2 + H_2O \qquad (5)$$

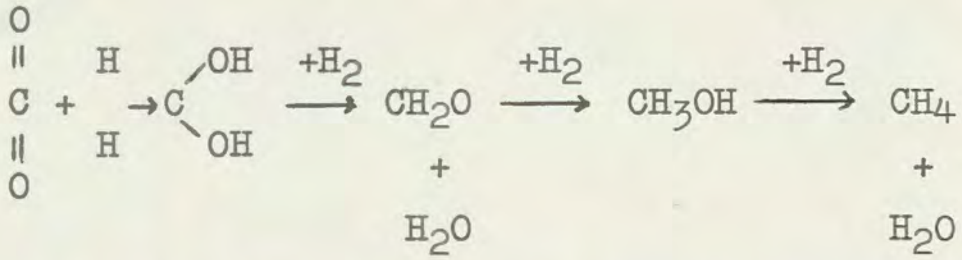
$$CH_2 + H_2 \longrightarrow CH_4 \qquad (6)$$

[*] = active space of catalyst surface area

Another scheme proposed by Medsford[49] is:



and by Pichler:[50]



There are some data which strongly support the proposed idea of no CO formation during the hydrogenation of carbon dioxide.[43] These data are as follows:

a.) In the conversion of carbon dioxide, CH_4 and small quantities of higher hydrocarbons were detected.[50]

b). CO_2 is not hydrogenated in the presence of CO.[6]

c). CO_2 is hydrogenated at lower temperatures than CO. Miller and Steffgen[43] concluded that the mechanism in the hydrogenation of carbon dioxide to methane and higher hydrocarbons is uncertain and is a fruitful field for investigation.

EXPERIMENTAL

Equipment, Material, and Experimental Procedure

The equipment was designed for the study of liquid phase reactions of carbon dioxide and hydrogen over a wide range of operational conditions. Two different size batch reactors were used in this study. One reactor was a Parr Mini Reactor series 4500, with a 400 ml capacity. The larger reactor was a Parr Pressure Reactor with a 920 ml capacity.

The reactor was charged with a solution and catalyst and then the feed gases were introduced into the reactor. All gases were commercial grade and were supplied in commercial cylinders.

The temperature in the reactor was controlled automatically and the time of reaction was recorded by means of an electronic timer.

Reaction was observed to occur immediately upon charging the reactor by a change in the temperature of the reactor. After a definite time for each run, reaction was stopped by cooling down the reactor to room temperature, and analyses were performed on the product gases and liquid.

A total of 61 runs were processed for the purpose of studying the following variables: gas ratio, catalyst concentration, nature of solution, concentration of solution, time to reach equilibrium, etc.

In the following discussions, series 100 runs refer to runs performed in the 400 ml mini reactor, and series 2000 runs refer to those experiments performed in the one liter reactor.

Method of Analysis

A.) Gas Phase

a.) The concentration of methane, ethane and higher hydrocarbons in the product gases, were determined by means of a Perkin-Elmer Model 900 gas chromatograph equipped with a flame ionization detector.

The analysis column consisted of a six foot length by one-eighth inch diameter copper tube, packed with 80-100 mesh por-o-pak.

A temperature program between 80-200°C gave the best analytical results. Initial column temperature was held for three minutes, after which the temperature increased at a rate of 32°C/minute to 200°C. The final temperature was maintained for ten minutes, during which time the remaining compounds eluted. A typical analysis of a product gas mixture is shown in Figure IV.

b.) A Barber Coleman model A 9231 gas chromatograph, equipped with a thermoconductivity detector was utilized to

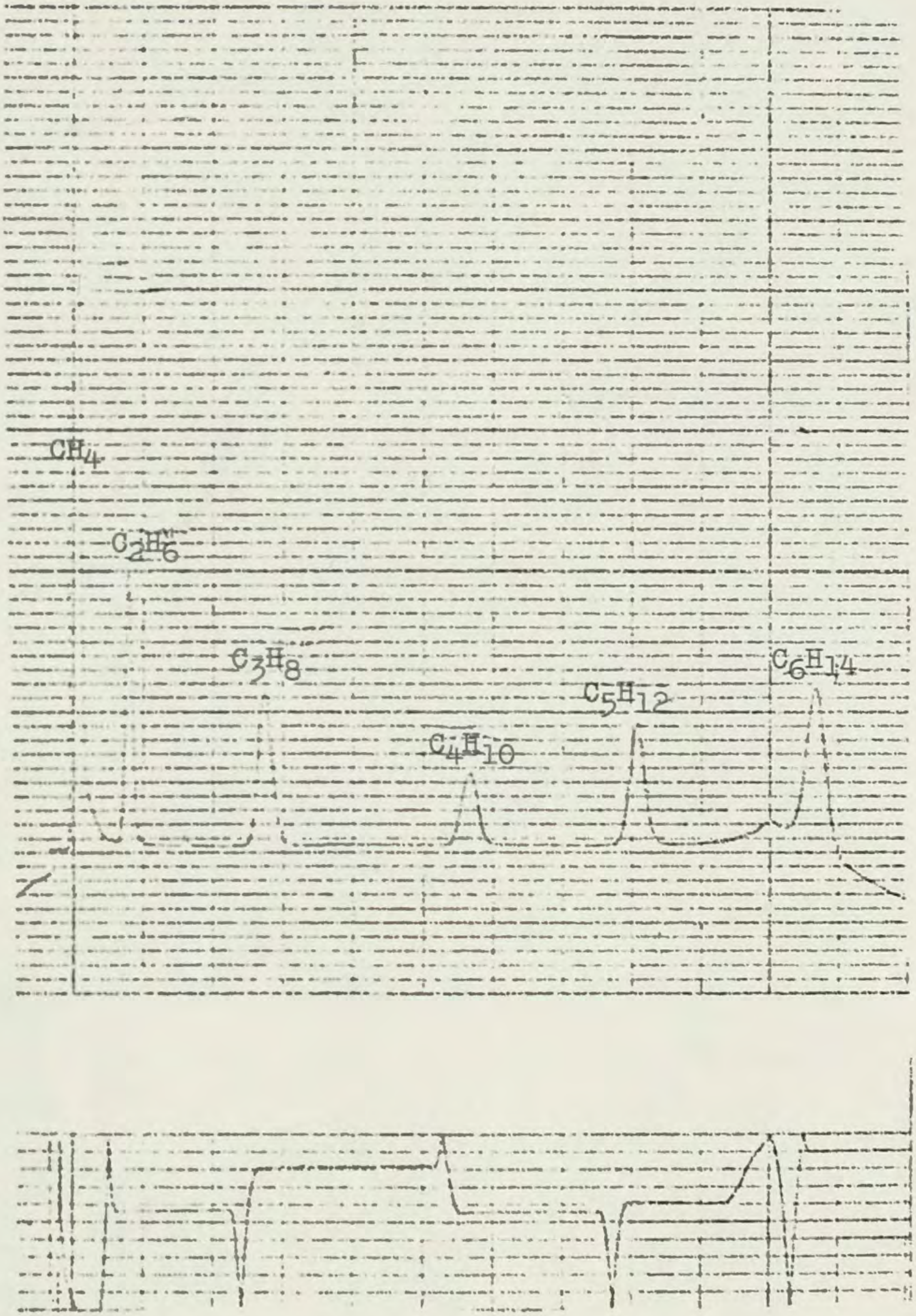


FIGURE IV.--Typical Analysis of a Product Gas Mixture measure carbon dioxide and any other non-hydrocarbon gases in the reaction product. The gases were separated on a carbosive B column isothermally operated at a temperature of 150°C, with a helium carrier gas flow rate of 20 ml/minute.

The thermoconductivity response for hydrogen is very poor, therefore, volume percent of this component in product gases was calculated by subtracting the total volume percent of all hydrocarbons and unreacted carbon dioxide from one hundred.

Since methane could also be analyzed with the carbosiue B-thermoconductivity system, this provided a means for cross-checking the concentration of methane with the results obtained by the flame ionization detector. A typical analysis is shown in Figure V.

Calibration charts, which were prepared by use of standard samples, were used for conversion of chromatograph peak area to molar quantities. The absolute number of moles of each component in the reactor were calculated by means of the ideal gas equation.

B.) Liquid Phase

a.) No hydrocarbon products were detected in the liquid phase.

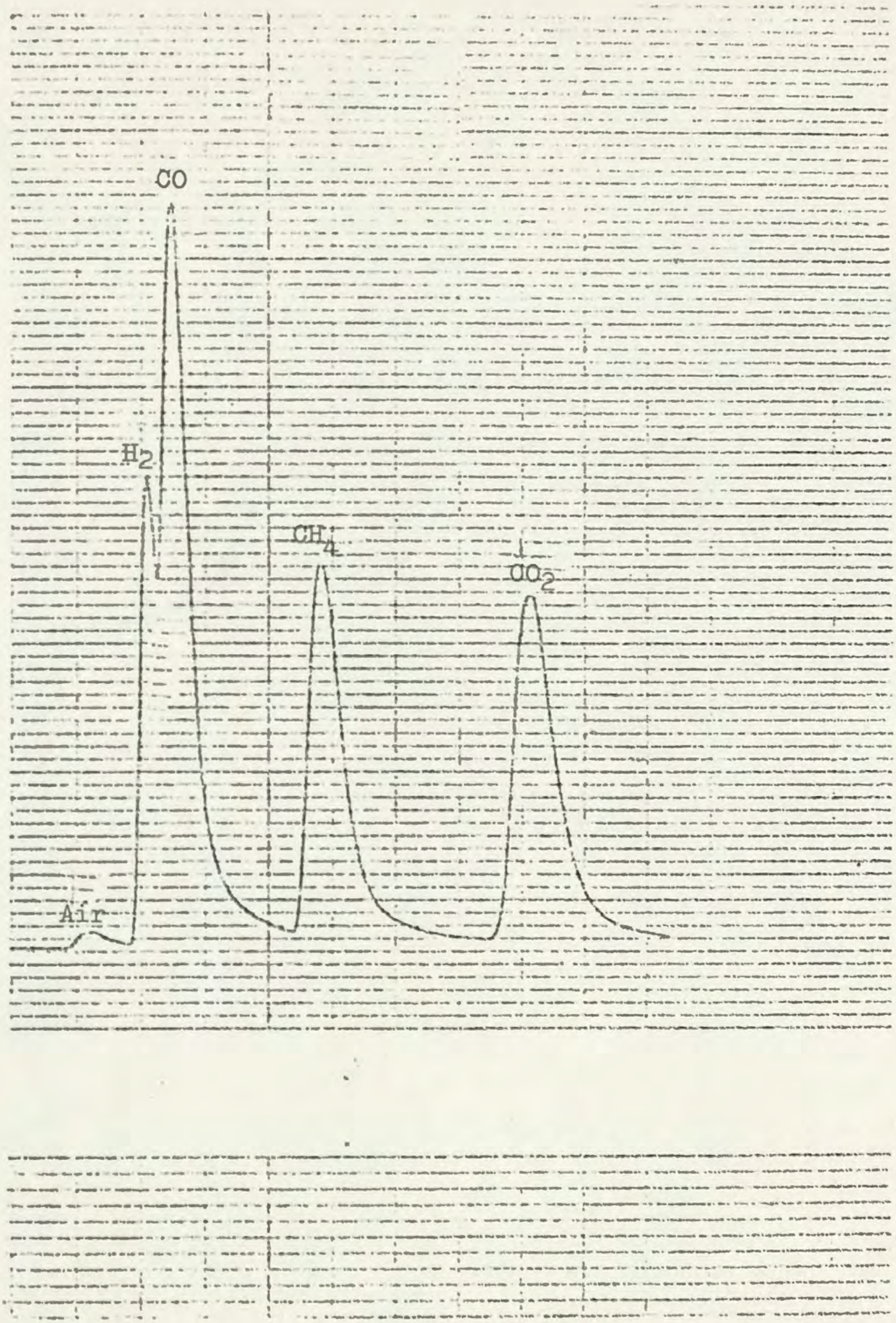


FIGURE V.--Typical Analysis of a Product Gas Mixture b.) To make possible an accounting for the amount of carbon atoms involved in this reaction, a titration procedure was established for the determination of carbonate species formed in solution by the reaction between carbon dioxide and sodium hydroxide. A standardized hydrochloric acid solution was used for the titration with phenolphthalein and bromocresol green indicators used to detect the endpoint.

Material Balance

The following discussion describes a typical material balance for a catalyst test run. The calculation is based upon carbon as a tie element for an eight hour run time with a ruthenium (III) chloride catalyst in a stirred batch reactor with 920 ml capacity. The reactor was initially charged with 400 ml of a 0.15 M sodium hydroxide solution. A 1:4 CO_2/H_2 ratio in the feed gas was accomplished by charging the reactor with 50 psi of carbon dioxide and then with 200 psi of hydrogen gas.

The number of moles of gas phase carbon dioxide in the reactor can be calculated by the ideal gas equation:

$$PV = n_{CO_2}RT$$

$$n_{CO_2} = \frac{PV}{RT}$$

$$n_{CO_2} = \frac{(50\ \text{psi})(920\text{-}400\ \text{ml})}{(1.206\ \frac{\text{psi ml}}{\text{gm mole K}^o})(293^oK)} \times \frac{(1\ 1\ )}{(1000\ \text{ml})}$$

$$n_{CO_2} = 0.07357\ \text{gm mole}$$

During the charging of the reactor some carbon dioxide dissolves in the dosium hydroxide solution to form $HC\bar{O}_3$ and CO_3^{-2} species. Also, some of these species remain in the solution when the reaction reaches completion. Thus, to make possible an accounting for the amount of carbon atoms involved in the reaction a titration procedure was established.

The quantitative and qualitative determination of constituents in a solution containing sodium carbonate, sodium hydrogen carbonate, and sodium hydroxide, alone or admixed can be accomplished by the use of a series of neutralization titrations. No more than two of the three constituents can exist in appreciable amounts, in any solution, because internal reactions will eliminate the third.

The analysis of such mixtures require two titrations with standard acid. An indicator with a transition in the vicinity of pH 8 to 9 is used for one; while an acid range indicator is used for the other. The composition of the solution can be deduced from the relative volumes of acid needed to titrate equal volumes of the sample (See Table VII).

TABLE VII

Volume Relationships in the Analysis of Mixtures Containing Carbonate, Hydrogen Carbonate and Hydroxide Ions

Constituents Present	Relationship between volume of acid needed to reach a phenolphthalein endpoint, Vph, and a bromocresol green end point, V_{bg}
NaOH	$V_{ph} = V_{bg}$
Na_2CO_3	$V_{ph} = 1/2V_{bg}$
$NaHCO_3$	$V_{ph} = 0$
NaOH,Na_2CO_3	$V_{ph} > 1/2V_{bg}$
Na_2CO_3,$NaHCO_3$	$V_{ph} < 1/2V_{bg}$

Experiment # 1--"Determination of carbonate constituents present in the solution before reaction."

A 50.00 ml portion required 32.2 ml of 0.117 N HCl when titrated to a phenolphthalein end point. A second 50.00 ml sample was titrated using bromocresol green as the indicator. The solution was boiled near the second equivalence point in order to remove CO_2. In this example determination exactly 42.88 ml of the HCl was used. Since more than half of this amount was involved in the first titration, $V_{ph} > 1/2V_{bg}$, the solution must have contained some Na_2CO_3 in addition to NaOH. We can now calculate the concentration of Na_2CO_3, where 42.88 - 32.2 = 10.68 ml of HCl used for titration of Na_2CO_3 in mixture. (10.68)(0.117) = 1.2496 number of meq. weight of Na_2CO_3 per ml is $\frac{1.2496}{50}$ = 0.025. The reactor contains 400 ml of solution, therefore the number of meq. weights of Na_2CO_3 in the reactor can be calculated as (0.025)(400) = 10. The number of moles of Na_2CO_3 formed by dissolving CO_2 in the sodium hydroxide solution during the charging of the reactor is: $n_{Na_2CO_3} = (\frac{10}{1000})(\frac{1}{2}) = 0.005$. This number of moles must be considered in calculating the total number of moles of carbon charged to the reactor.

Experiment #2--"Determination of carbonate constituents present in solution after termination of the hydrogenation reaction."

A 50.00 ml portion of liquid required 40.5 ml of HCl when titrated to a bromocresol green endpoint, thus: $V_{ph} < 1/2V_{bg}$. Therefore the constituents present in solution are $\underline{Na_2CO_3}$ and $\underline{NaHCO_3}$. We can now calculate the concentration of the two compounds.

When the phenolphthalein end point was reached, the $CO_3^{=2}$ originally present was converted to HCO_3^-, thus the number of meq. weights of Na_2CO_3 in solution is:

(5.6)(0.117) = 0.655. The titration from the phenolphthalein to the bromocresol green endpoint (4.05 - 5.6 = 39.9 ml) involves both the hydrogen carbonate originally present as well as that formed by titration of the carbonate, thus the number of meq. weights of Na_2CO_3 = (34.9)(0.117) and 4.083 - 0.655 = 3.428 is the number of meq. weights of $NaHCO_3$ in the sample. The normality of the solution can now be calculated as:

$$N_{Na_2CO_3} = \frac{0.655}{50} = 0.0131 \text{ m eq. weight/ml}$$

$$N_{NaHCO_3} = \frac{3.428}{50} = 0.0688 \text{ m eq. weight/ml}$$

Now the number of moles can be calculated for each constituent present in the 400 ml of reactor solution.

(0.0131)(400) = 5.24 m eq. weights of Na_2CO_3 in the reactor

(0.0688)(400) = 27.44 m eq. weights of $NaHCO_3$ in the reactor

$$n' \, Na_2CO_3 = \left(\frac{5.24}{1000}\right)\left(\frac{1}{2}\right) = 0.00262$$

$$n'' \, NaHCO_3 = \left(\frac{27.44}{1000}\right) = 0.0274$$

where ^{n} Na_2CO_3 is the number of moles of Na_2CO_3 and n'' $NaHCO_3$ is the number of moles of $NaHCO_3$ present in the reactor, after termination of the hydrogenation reaction.

Accounting for carbon compounds in the gas phase--The concentration of methane, ethane, and higher hydrocarbons in the product gases was determined by a gas chromatograph equipped with a flame ionization detector. A thermoconductivity detector was utilized for carbon dioxide analysis in the gaseous product mixture. Calibration charts for each gas were used to convert chromatograph chart area to molar quantities (Table VIII).

TABLE VIII

Molar Quantities of Gaseous Products

Compound	(Peak Area)·(Attenuation) F.I.D.	T.C.D.	Mole %
C_1	678,400	-----	17
C_2	10,880	-----	0.112
C_3	2,208	-----	0.0096
C_4	800	-----	0.006
CO_2	-----	800	1.576

The mole fraction of each compound was used to calculate the number of moles of each compound in the reactor by use of the ideal gas equation:

n_1 = number of moles of methane produced

p_1 = partial pressure of methane

p_T = total pressure (125 psi at $0^{o}C$)

V = volume of gas space in the reactor

(720 - 400 = 520 ml)

$$R = 1.206 \frac{(\text{psi})(\text{l})}{(\text{g mole})(^{\circ}\text{K})}$$

$$P_1V = n_1RT$$

$$\frac{P_1V}{P_T} = \frac{n_1RT}{P_T}$$

$$n_1 = \frac{(V)(P_T)}{(R)(T)} \left(\frac{P_1}{P_T}\right)$$

$$\frac{P_1}{P_T} = \frac{\text{vol \%}}{100} = \text{mole fraction}$$

$$n_1 = \frac{(V)(P_T)}{(R)(T)} \times \left(\frac{\text{vol \%}}{100}\right)$$

$$n_1 = \frac{(920\text{-}400 \text{ ml})(125 \text{ psi})}{1.206\left(\frac{\text{psi l}}{\text{g mole }^{\circ}\text{K}}\right)(273^{\circ}\text{K})} \times \left(\frac{17}{100}\right) \left(\frac{1 \text{ l}}{1000 \text{ ml}}\right)$$

n_1 = 0.03356 g mole of methane produced

n_2 = 0.00022 g mole of ethane produced

n_3 = 0.0002 g mole propane produced

n_4 = 0.00001 g mole of n-butane produced

n_{CO_2} = 0.00328 g mole of CO_2 unreacted

Equating the total number of moles of CO_2 charged to the reactor (i.e., the total number of moles of CO_2 in the gas phase plus the number of moles of CO_2 in solution) with the number of moles of CO_2 dissolved in the product solution plus the number of carbon compounds in the product gas gives, input = output:

$$n_{CO_2} + n_{Na_2CO_3} + n_{NaHCO_3} = (n_1 + 2n_2 + 3n_2 + 4n_2 \; ....) + n'_{CO_2} + n'_{Na_2CO_3} + n''_{NaHCO_3}$$

n_{CO_2} = 0.07357 initial number of moles of CO_2

$n_{Na_2CO_3}$ = 0.005 number of moles of Na_2CO_3 formed in the solution during charging the reactor

n_{NaHCO_3} = 20.00 number of moles of $NaHCO_3$ formed in the solution during charging the reactor

n_1 = 0.03356 number of moles of methane produced

n_2 = 0.00022 number of moles of ethane produced

n_3 = 0.00002 number of moles of propane produced

n_4 = 0.00001 number of moles of n-butane produced

n'_{CO_2} = 0.00328 number of moles of carbon dioxide unreacted

$n'_{Na_2CO_3}$ = 0.00262 number of moles of Na_2CO_3 in solution after the reaction

n''_{NaHCO_3} = 0.0274 number of moles of $NaHCO_3$ in solution after the reaction

$$n_{CO_2} + n_{Na_2CO_3} + n_{NaHCO_3} = (n_1 + 2n_2 + 3n_3 + 4n_4) + n'_{CO_2} + n'_{Na_2CO_3} + n''_{NaHCO_3}$$

$$0.07357 + 0.005 = 0.03356 + (2)(0.00022) + (3)(0.00002) + 4(0.00001) + 0.00328 + 0.00262 + 0.0274$$

$$0.07858 = 0.06737$$

86 % carbon accounted for in this example.

Hydrogenation Run Procedure

In the evaluation of $RuCl_3$ in terms of the relationship between conversion and product yield with variations in catalyst concentration, gas ratio, H_2 concentration, nature of the solution, concentration of the solution, time, temperature, etc. the pivot point technique was employed. The evaluation of $RuCl_3$ in terms of operation conditions constituted the first part of the hydrogenation study and is labeled as system (I). In this system, the pivot point technique involved the systematic variation of one operation condition with respect to a set of central reference conditions. The central reference point was chosen to be a 4:1 H_2/CO_2 ratio, which is the stoichiometric ratio for the reaction $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$. After several qualitative reactions, the NaOH solution was chosen as the pivot point reference. A reaction temperature of $150^{\circ}C$ was chosen, based upon the boiling temperature of the solution and preliminary runs. All reaction conditions for this system are summarized in Table IX.

In the second part of this study (System II), comparisons were made between the three catalyst systems: $RuCl_3$, Ru metal, and 1% Ru supported on graphite. Reaction conditions for this study are summarized in Table X.

TABLE IX

Optimum Reaction Conditions for the Hydrogenation Reaction over $RuCl_3$

No.	Series	Catalyst	Catalyst Concentration (g)	Time (hr)	Solution	Molarity of Solution	H_2(psi) Concentration	CO_2(psi) Concentration	Temperature °C
1	2001	$RuCl_3$	0.05	2	NaOH	0.6	200	50	150
2	2002	"	0.1	2	"	0.6	200	50	"
3	2003	"	0.15	2	"	0.6	200	50	"
4	2004	"	0.2	2	"	0.6	200	50	"
5	2005	"	0.25	2	"	0.6	200	50	"
6	2006	"	0.3	2	"	0.6	200	50	"
7	2007	"	0.35	2	"	0.6	200	50	"
8	2008	"	0.5	2	"	0.6	200	50	"
9	2009	"	0.05	2	H_2O	0.6	200	50	"
10	2010	"	0.05	2	HCl	0.6	200	50	"
11	2011	"	0.2	2	NaOH	1.2	200	50	"
12	2012	"	0.2	2	"	0.6	200	50	"
13	2013	"	0.2	2	"	0.3	200	50	"
14	2014	"	0.2	2	"	0.15	200	50	"
15	2015	"	0.2	2	"	0.07	200	50	"
16	2016	"	0.2	2	"	0.03	200	50	"
17	101	"	0.05	2	"	0.6	100	50	"
18	102	"	0.05	2	"	0.6	125	50	"
19	103	"	0.05	2	"	0.6	150	50	"
20	104	"	0.05	2	"	0.6	200	50	"
21	105	"	0.05	2	"	0.6	225	25	"
22	106	"	0.05	2	"	0.6	200	50	"

Continued

TABLE IX (Continued)

No.	Series	Catalyst	Catalyst Concentration (g)	Time (hr)	Solution	Molarity of Solution	H_2(psi) Concentration	CO_2(psi) Concentration	Temperature °C
23	107	$RuCl_3$	0.05	2	NaOH	0.6	150	100	150
24	108	"	0.05	2	"	0.6	100	150	"
25	2017	"	0.5	2	"	0.07	200	50	100
26	2049	"	0.5	2	"	0.07	200	50	150
27	2050	"	0.5	2	"	0.07	200	50	250

TABLE X

Reaction Conditions for Studying the Rate of the Hydrogenation Reaction Over Three Catalytic Systems: $RuCl_3$, Ru metal, and 1% Ru on graphite

No.	Series	Catalyst	Catalyst Concentration(g)	Solution	Molarity of Solution	Gas Ratio	Time (hr)	Temperature °C
28	2018	$RuCl_3$	0.05	NaOH	0.15	4:1	5/6	150
29	2019	"	"	"	"	"	2	"
30	2020	"	"	"	"	"	4	"
31	2021	"	"	"	"	"	8	"
32	2022	"	"	"	"	"	16	"
33	2023	"	"	"	"	"	24	"
34	2024	"	"	"	"	"	48	"
35	2025	Ru metal	0.024	"	"	"	5/6	"
36	2026	"	"	"	"	"	2	"
37	2027	"	"	"	"	"	4	"
38	2028	"	"	"	"	"	8	"
39	2029	"	"	"	"	"	16	"
40	2030	"	"	"	"	"	24	"
41	2031	"	"	"	"	"	48	"
42	2032	1% Ru gr.	"	"	"	"	5.6	"
43	2033	"	"	"	"	"	2	"
44	2034	"	"	"	"	"	4	"
45	2035	"	"	"	"	"	8	"
46	2036	"	"	"	"	"	16	"
47	2037	"	"	"	"	"	24	"
48	2038	"	"	"	"	"	48	"

In the third part of this study (System III), sodium carbonate or sodium bicarbonate solutions and hydrogen gas were used as the starting material for hydrocarbon production. Table XI contains the reaction conditions for this system.

And finally in Table XII, the reaction conditions for gas phase hydrogenation of carbon dioxide over three catalyst systems--$RuCl_3$, Ru metal, and 1% on graphite--are tabulated. Comparisons between the rate of the reaction in the gas phase and liquid phase were made possible from data obtained in this part of the study (System IV).

TABLE XI

Reaction Conditions for the Production of Hydrocarbons Using Carbonate and Bicarbonate as the Starting Material

No.	Series	Catalyst	Catalyst Concentration (g)	Time (hr)	Solution	Molarity of Solution	H_2 Cencentration	N_2 (psi)	Temperature °C
50	2040	$RuCl_3$	0.05	2	Na_2CO_3	0.184	200	50	150
51	2041	"	0.2	"	"	"	"	"	150
52	2042	"	0.3	"	"	"	"	"	150
53	2043	"	0.2	"	"	"	"	"	350
54	2044	"	0.05	"	"	"	"	"	150
55	2045	"	0.2	"	$HaHCO_3$	"	"	"	150
56	2046	"	0.3	"	"	"	"	"	150
57	2047	"	0.3	"	"	0.368	"	"	150
58	2048	"	0.3	"	"	0.736	"	"	150

TABLE XII

Reaction Conditions for the Study of the Gas Phase Hydrogenation of Carbon Dioxide

No.	Series	Catalyst	Catalyst Concentration (g)	Time (hr)	Solution	H_2(psi)	CO_2(psi)	Temperature °C
59	2051	$RuCl_3$	0.05	24	-----	200	50	150
60	2052	Ru Metal	0.05	24	-----	200	50	150
61	2053	1% Ru on graphite	0.05	24	-----	200	50	150

RESULTS AND DISCUSSION

System I: Optimization of the liquid phase hydrogenation of carbon dioxide in the presence of a ruthenium (III) chloride catalyst.

This phase of the study dealt with the relationship between conversion and product yield as a function of catalyst concentration, nature of the solution, concentration of the solution, temperature, and other operational conditions.

A.) Catalyst Concentration: The influence of catalyst concentration is represented in Table XIII.

TABLE XIII

Carbon Dioxide Conversion and Product Yields as a Function of Catalyst Concentration

No.*	Series**	Catalyst Concentration(grams)	C_1	C_2	C_3	C_4	% Conversion after 2 hours
1	2001	0.05	99.99	trace	---	---	1.8
2	2002	0.1	99.99	trace	---	---	3.8
3	2003	0.15	99.89	0.11	trace	---	8.1
4	2004	0.2	99.93	0.07	trace	---	13.7
5	2005	0.25	99.9	0.1	trace	---	19.2
6	2006	0.3	99.89	0.11	trace	---	22.7
7	2007	0.35	99.87	0.13	trace	---	28.1
8	2008	0.5	99.8	0.12	0.08	---	46.4

* and **--Additional information about operational conditions is given in Tables IX, X, XI, and XII under the same run number and series.

Figure VI indicates that at a fixed time, the rate of liquid phase hydrogenation of carbon dioxide over ruthenium (III) chloride is first order in catalyst concentration.

B.) Nature of the Solution

TABLE XIV

Carbon Dioxide Conversion and Product Yields as a Function of the Nature of the Solution

No.	Series	Solution	% Yields C_1	% Yields C_2	% Yields C_3	% Conversion
1	2001	NaOh	99.99	trace	---	1.81
9	2009	H_2O	94.33	4.15	1.51	0.36
10	2010	HCl	99.99	trace	---	0.04

Sodium hydroxide solutions were observed to give the greatest conversion. This observation is probably due to the fact that the solubilities of the carbon dioxide feed gas in the sodium hydroxide solution is high, compared with acidic or pure H_2O solutions. The inability of acidic or neutral solutions to solubilize large amounts of carbon dioxide may be the main reason for the observed lowering of the conversion of this reaction by a factor of 45 for acidic solution and by a factor of 5 for neutral solution.

Carbonates and bicarbonates are formed during the solubilization of carbon dioxide in sodium hydroxide

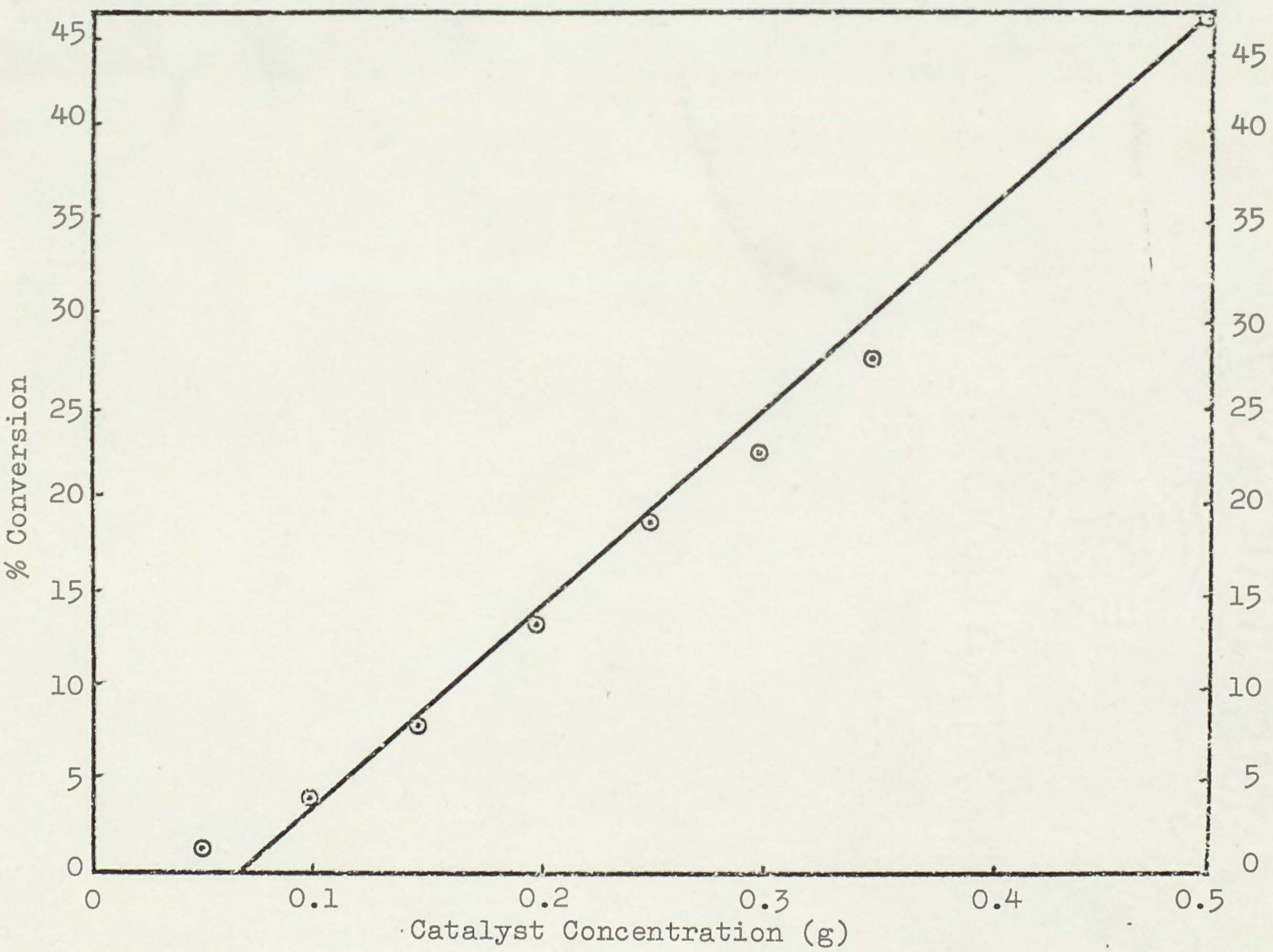


FIGURE VI.--CO_2 Conversion as a Function of Ruthenium (III) Chloride Catalyst solution, thus the large conversion of carbon dioxide in those solutions suggests that the hydrogenation involves a carbonate species in solution.

C.) Concentration of Sodium Hydroxide Solutions

Conversion and yields of products as a function of the molarity of the sodium hydroxide solution for the reaction of carbon dioxide and hydrogen over Ru(III) chloride are represented in Table XV. The data were obtained at a reaction time of two hours.

TABLE XV

CO_2 Conversion and Yields as a Function of Molarity of Sodium Hydroxide Solution

			% Yields					%
No.	Series	NaOH-M	C_1	C_2	C_3	C_4	C_5	Conversion
11	2011	1.2	99.99	0.01	---	---	---	1.6
12	2012	0.6	99.9	0.1	trace	---	---	18.9
13	2013	0.3	99.5	0.47	0.02	0.01	---	29.5
14	2014	0.15	98.5	1.3	0.1	0.1	---	35.5
15	2015	0.07	98.3	1.5	0.1	0.1	trace	33.0
16	2016	0.03	98.7	1.2	0.1	0.1	trace	27.3

In the range of 0.03-1.2 molar sodium hydroxide solution, conversion reaches a maximum of 35.5% (Figure VII). When the molarity of NaOH is at the maximum point, the

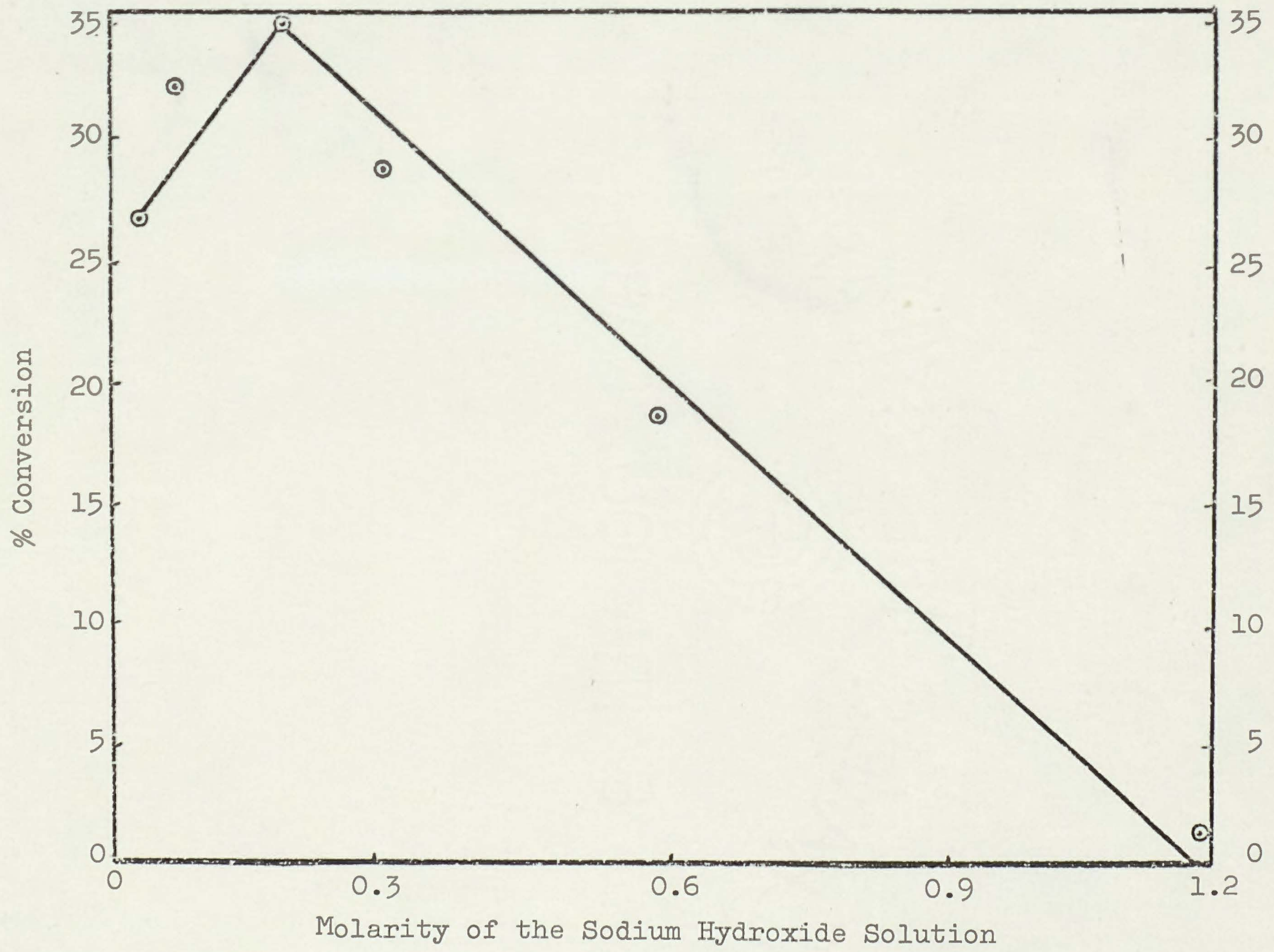


FIGURE VII.--CO_2 Conversion as a Function of the Molarity of NaOH Solution number of moles of sodium hydroxide is approximately equal to the number of moles of carbon dioxide charges. Thus, the formation of $NaHCO_3$ species at this point should be at a maximum. When the number of $NaHCO_3$ species in the solution decreases due to a decrease in the molarity of sodium hydroxide solution, conversion drops. Increasing the molarity of sodium hydroxide is not favorable due to the formation of Na_2CO_3 species.

The molarity of the sodium hydroxide solution also seems to have an effect on the product distribution. High molarities are favorable for producing high molecular weight hydrocarbons.

D.) Variation of the CO_2/H_2 Ratio with the Concentration of Carbon Dioxide Held Constant

In this part of the study, liquid phase hydrogenation of carbon dioxide was evaluated as a function of hydrogen concentration while the carbon dioxide concentration was held constant. In order to keep the total pressure of the system constant, an inert gas (N_2) was employed.

Results for the variation of the hydrogen concentration in the range of 2-4 times that of the carbon dioxide concentration, and its effect on the conversion of carbon dioxide are listed in Table XVI.

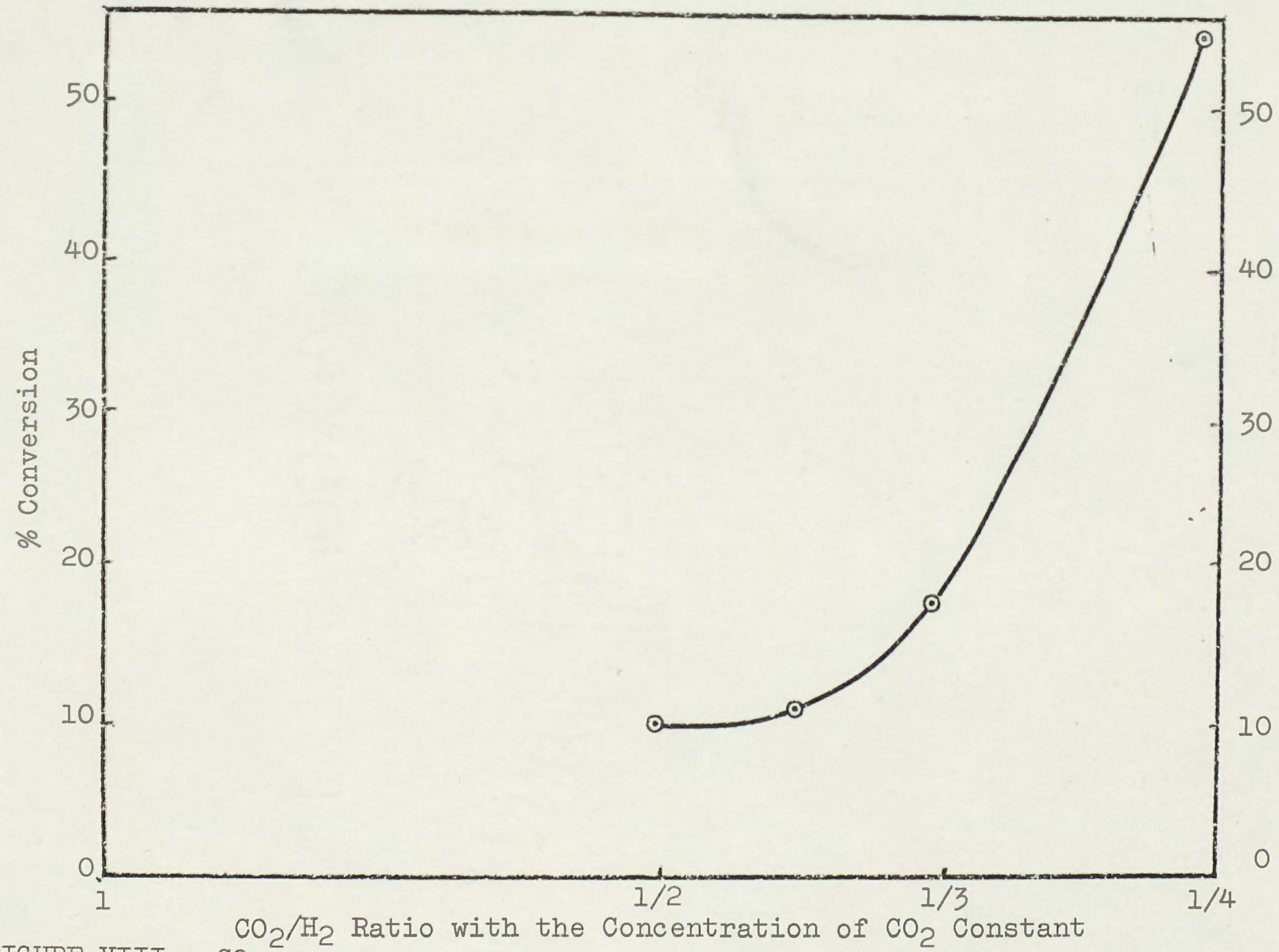


FIGURE VIII.--CO_2 Conversion as a Function of the Hydrogen Concentration

TABLE XVI

Results for the Variation of the Hydrogen Concentration with the Concentration of Carbon Dioxide Held Constant

No.	Series	H_2 (psi)	CO_2 (psi)	N_2 (psi)	Total Pressure (psi)	% Conversion after 2 hours
17	101	100	50	100	250	12.9
18	102	125	50	75	250	13.59
19	103	150	50	50	250	17.94
20	104	200	50	--	250	55.58

The data plotted in Figure VIII indicate that conversion of carbon dioxide increases as the concentration of hydrogen increases. The highest conversion of carbon dioxide was observed at a 1/4 ratio of carbon dioxide to hydrogen concentration which corresponds to the stoichiometric ratio for the hydrogenation reaction of carbon dioxide to methane.

E.) H_2/CO_2 Ratio

A $RuCl_3$ catalyst was tested at a constant total pressure of 250 psi, using various H_2/CO_2 ratios. The H_2/CO_2 ratio was observed to have a significant influence on the product distributions.

TABLE XVII

Carbon Dioxide Conversion and Product Distribution as a Function of H_2/CO_2 Ratio

No.	Series	H_2/CO_2 Ratio	% Yields						% Conversion after 2 hours
			C_1	C_2	C_3	C_4	C_5	C_6	
24	108	2/3	96.4	2.6	0.5	0.3	0.1	0.1	4.01
25	107	3/2	98.2	1.4	0.2	0.1	0.1	trace	36.99
26	106	4/1	99.1	0.8	0.06	0.04	trace	---	55.58
27	105	9/1	99.9	0.1	trace	---	---	---	82.98

Low H_2/CO_2 ratios gave larger amounts of higher molecular weight products while relatively more methane was formed at high H_2/CO_2 ratios. Conversion data vs. H_2/CO_2 ratio are plotted in Figure IX.

F.) Temperature

Conversions and yields of products as a function of temperature in the range of 100-200°C are listed in Table XVIII.

Figure X indicates that the conversion in the hydrogenation of carbon dioxide over ruthenium (III) chloride is kinetically favored by higher temperatures. The data indicate that very little reaction is expected for temperatures below 100°C.

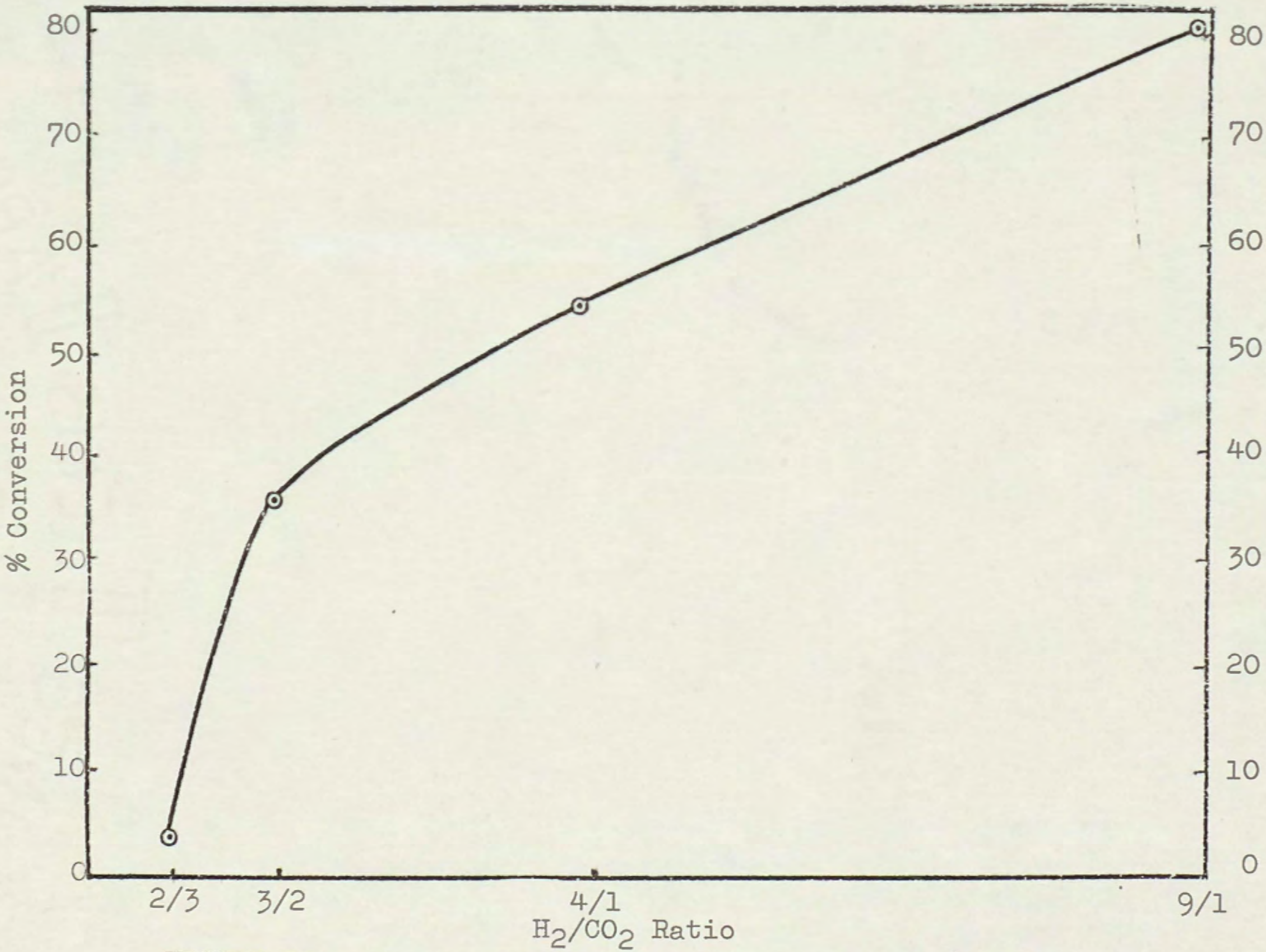


FIGURE IX.--CO_2 Conversion as a Function of H_2/CO_2 Ratio

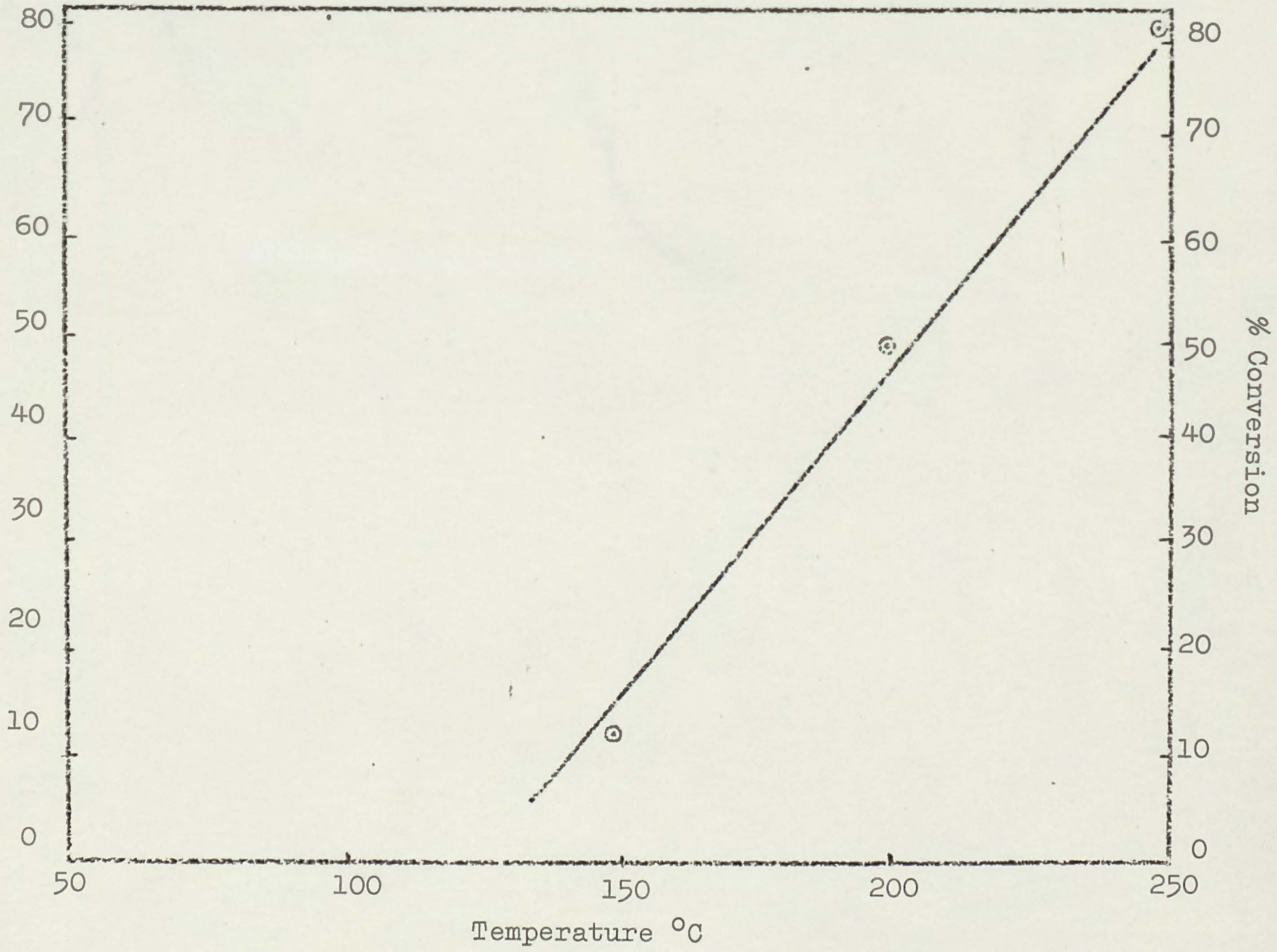


FIGURE X.--CO_2 Conversion as a Function of Temperature

TABLE XVIII

Carbon Dioxide Conversion and Yield of Product as a Function of Temperature

No.	Series	Temperature °C	% Yields C_1	C_2	C_3	C_4	% Conversion after 2 hrs.
25	2017	100	99.15	0.75	0.01	---	12.8
26	2049	150	98.87	1.08	0.057	trace	50.02
27	2050	200	98.38	1.57	0.03	trace	80.78

In summary, it appears that the hydrogenation of carbon dioxide in the presence of a system consisting of a ruthenium (III) chloride catalyst and a sodium hydroxide solution takes place through a HCO_3^- species in solution.

The reaction is first order in catalyst concentration and kinetically favored by high temperatures. The system achieved equilibrium with a 70% conversion of carbon dioxide after 24 hours at a temperature of 150°C and a catalyst concentration of 0.75 gram catalyst/mole CO_2.

The product distribution was found to be a function of the sodium hydroxide solution, temperature and H_2/CO_2 ratio. In general, high NaOH molarities, high temperatures and low H_2/CO_2 ratios give the largest yield of high molecular weight products.

System II: Three catalyst systems, $RuCl_3$, Ru metal and 1% Ru on graphite, were evaluated for the hydrogenation of carbon dioxide in a sodium hydroxide solution.

Data for the conversion and yield of products as a function of time are represented in Table XIX.

Comparisons were made between the three ruthenium catalyst systems--$RuCl_3$, Ru metal, and 1% Ru supported on graphite--under the same catalyst content and reaction conditions. One percent Ru on graphite showed the best reaction results. This system reached equilibrium after 24 hours, with 76.86% conversion of carbon dioxide to methand and higher hydrocarbons. $RuCl_3$ in the same time gave a 70% conversion, which was observed to increase to 73% after 48 hours. The activity of Ru metal was observed to change during the course of the reaction. The free Ru metal catalyst exhibited a greater conversion than $RuCl_3$ during the first eight hours of reaction. However, after eight hours, the activity of the free Ru metal catalyst began to decline. The loss in activity probably results from the loss of active catalyst sites, due to fusion of the catalyst on the surface of the glass ware inside the reactor.

Comparisons of the three catalytic systems for the

TABLE XIX

Rate of Hydrogenation Reaction Over Three Catalyst Systems

No.	Series	Catalyst	Time (hr)	% Yields					% Conversion
				C_1	C_2	C_3	C_4	C_5	
28	2018	$RuCl_3$	5/6	99.9	0.1	---	---	---	0.17
29	2019	$RuCl_3$	2	99.02	0.68	0.1	0.2	---	12.21
30	2020	$RuCl_3$	4	99.12	0.77	0.07	0.04	---	32.64
31	2021	$RuCl_3$	8	99.26	0.65	0.06	0.03	---	42.07
32	2022	$RuCl_3$	16	99.59	0.37	0.02	0.02	---	64.22
33	2023	$RuCl_3$	24	99.45	0.46	0.04	0.04	0.01	70.22
34	2024	$RuCl_3$	48	99.45	0.46	0.04	0.04	0.01	73.58
35	2025	Ru metal	5/6	99.4	0.6	---	---	---	2.01
36	2026	Ru metal	2	99.2	0.7	0.1	---	---	15.29
37	2027	Ru metal	4	99.2	0.7	0.1	---	---	34.24
38	2028	Ru metal	8	99.3	0.6	0.1	---	---	47.00
39	2029	Ru metal	16	99.38	0.5	0.04	0.04	0.04	63.32
40	2030	Ru metal	24	99.52	0.42	0.02	0.02	0.02	63.57
41	2031	Ru metal	48	99.36	0.52	0.04	0.04	0.04	66.84
42	2032	1% Ru on graphite	5/6	99.14	0.86	---	---	---	3.77

(Continued)

TABLE XIX (Continued)

No.	Series	Catalyst	Time (hr)	% Yields					% Conversion
				C_1	C_2	C_3	C_4	C_5	
43	2033	1% Ru on graphite	2	98.5	1.32	0.12	0.06	---	20.81
44	2034	1% Ru on graphite	4	99.16	0.7	0.08	0.03	0.03	42.61
45	2035	1% Ru on graphite	8	98.56	1.3	0.1	0.02	0.02	49.84
46	2036	1% Ru on graphite	16	99.29	0.61	0.06	0.02	0.02	74.45
47	2037	1% Ru on graphite	24	99.36	0.55	0.06	0.03	0.01	76.86
48	2038	1% Ru on graphite	48	99.30	0.6	0.07	0.4	0.07	77

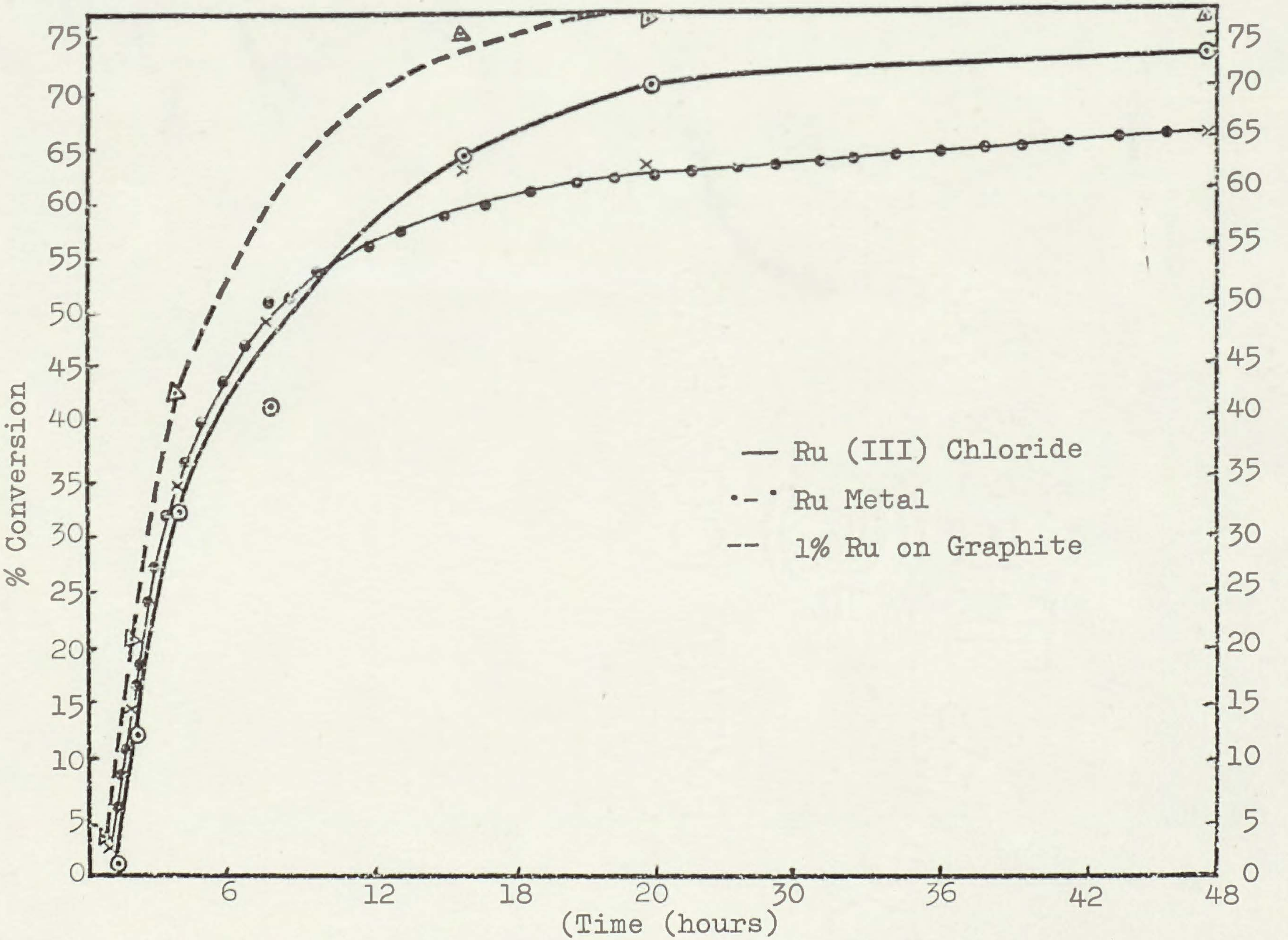


FIGURE XI.--Rate of Hydrogenation Reaction: Over the Three Catalytic Systems hydrogenation of carbon dioxide solution are represented in Figure XI.

System III: A study of sodium carbonate, sodium bicarbonate solutions, and hydrogen gas, as starting materials for hydrocarbon production.

A.) Sodium Carbonate and Hydrogen

A hydrogenation run using a sodium carbonate solution and a ruthenium (III) chloride catalyst was made. In order to make a comparison between the rate of this system with the rate of hydrogenation of carbon dioxide, the solution was made up to contain the same number of CO_3^{-2} species as carbon dioxide molecules in previous runs. In order to keep the total pressure of the system and the partial pressure of hydrogen constant, an inert gas (N_2) was employed.

1. Catalyst concentration

The influence of catalyst concentration on the carbonate conversion is represented in Table XX.

TABLE XX

Sodium Carbonate Conversion as a Function of Catalyst Concentration

No.	Series	Catalyst Concentration (grams)	n_1	n_2	n_3	% Conversion after 2 hours
50	2040	0.05	100	---	---	0.96
51	2041	0.2	99.87	0.13	trace	10.68
52	2042	0.3	99.9	0.1	trace	14.77

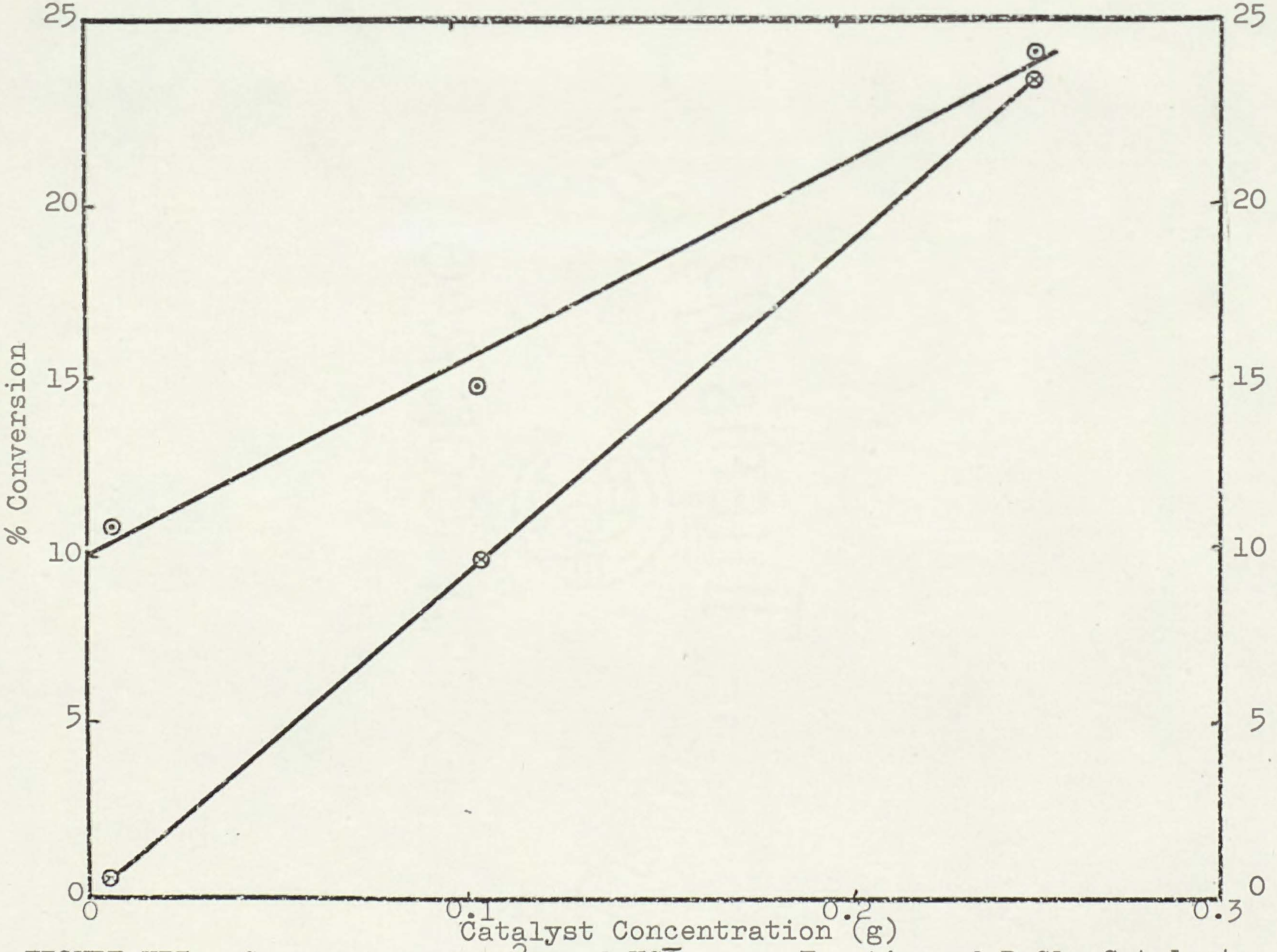


FIGURE XII.--Conversion of CO_3^{2-} and $HC\overline{O}_3$ as a Function of $RuCl_3$ Catalyst

The data of Table XX are plotted in Figure XII and indicate that the rate of hydrogenation of the carbonate species in solution over the $RuCl_3$ catalyst is first order in catalyst concentration.

2. Temperature

The rate of hydrogenation of sodium carbonate solution over ruthenium (III) chloride was tested over two different reaction temperatures. The result indicates that this reaction is kinetically favorable by high temperature (Table XXI).

TABLE XXI

Sodium Carbonate Conversion as a Function of Temperature

No.	Series	Temperature °C	C_1	C_2	C_3	% Conversion after 2 hours
51	2041	150	99.87	0.13	trace	10.68
53	2043	300	99.9	0.1	trace	19.70

The conversion increases by 0.07% per 10°C increase in temperature; because the increase in conversion with temperature is so small, it is very unlikely that temperatures above 150°C would be very economical in an industrial process.

B.) Sodium Bicarbonate and Hydrogen

The same experimental procedure described in Part A was used to study the hydrogenation of a bicarbonate solution over a $RuCl_3$ catalyst. The number of moles of bicarbonate in the solution was equal to the number of moles of carbonate used in the previous experiment.

1. Catalyst concentration

The data presented in Table XXII describes the influence of catalyst concentration on yield and product distribution. It was observed that the rate of the hydrogenation reaction is first order in catalyst concentration.

TABLE XXII

Sodium Bicarbonate Conversion on a Function of the Catalyst Concentration

No.	Series	Catalyst Concentration (grams)	% Yields C_1	C_2	C_3	C_4	% Conversion After 2 hrs.
54	2044	0.05	99.99	trace	---	---	1.5
55	2045	0.2	99.05	0.85	0.1	trace	15.88
56	2046	0.3	99.1	0.83	0.07	trace	29.31

This indicates that catalyst site availability can limit the rate of the hydrogenation reaction. Future studies on this project should focus attention on methods for improving the number of catalyst sites in the reaction mixture, either by increasing the surface area of the present catalyst systems or by increasing their concentration.

2. Molarity of bicarbonate solution

The conversion of sodium bicarbonate to hydrocarbons was observed to decrease as the molarity of the bicarbonate solution increases. However, the actual quantities of hydrocarbons produced in each run remained nearly constant. This suggests that the concentration of $HC\bar{O}_3$ species in solution is not the rate determining element under the reaction conditions studied. The rate limiting elements as observed for other reaction conditions in this study, are the catalyst and H_2 concentration. This indicates that the rate of hydrogenation is regulated by the rate of diffusion of H_2 to the actual catalyst sites and the number of catalyst sites available.

TABLE XXIII

Sodium Bicarbonate Conversion as a Function of Molarity of Sodium Bicarbonate

No.	Series	Molarity of HCO_3	C_1	C_2	C_3	C_4	% Conversion after 2 hours
56	2046	0.184	99.1	0.83	0.07	trace	29.31
57	2047	0.368	99.37	0.58	0.05	trace	17.5
58	2048	0.736	98.97	0.97	0.06	trace	5.6

System IV: Comparisons between liquid phase and gas phase hydrogenation of carbon dioxide over the three catalytic systems: Ru (III) chloride, Ru metal, and 1% Ru supported on graphite.

The gas phase hydrogenation of carbon dioxide was studied over three Ru catalyst systems. The results of these experiments are given in Table XXIV.

TABLE XXIV

Data from the Gas Phase Hydrogenation of Carbon Dioxide

No.	Series	Catalyst	% Yields C_1	C_2	C_3	C_4	C_5	% Conversion after 24 hours
59	2051	$RuCl_3$	99.45	0.51	0.02	0.02	trace	89.8
60	2052	Ru metal	99.48	0.4	0.06	0.06	trace	50.49
61	2053	1% Ru on graphite	99.31	0.6	0.06	0.03	trace	85.07

Ruthenium (III) chloride exhibited the greatest rate with the 89.8% conversion after 24 hours of reaction. The rate of the reaction between carbon dioxide and hydrogen in the gas phase over $RuCl_3$ is faster than the rate of this reaction in the liquid phase. The liquid phase system under these conditions only reached 70% conversion of carbon dioxide after 24 hours.

A 1% Ru on graphite catalyst also exhibited a faster rate of reaction in the gas phase than the liquid phase. Table XXV summarizes the comparison between the gas phase and the liquid phase hydrogenation reaction for the three catalytic systems. The comparisons are made for similar reaction conditions.

TABLE XXV

Comparison Between Gas Phase and Liquid Phase Hydrogenation Reaction

Catalyst	% Conversion After 24 Hours (gas phase)	% Conversion After 24 Hours (liquid phase)
$RuCl_3$	89.8	70.22
Ru metal	50.49	63.57
1% Ru on graphite	85.07	76.86

CONCLUSION

A.) The liquid phase hydrogenation of carbon dioxide over a $RuCl_3$ solution:

1. The hydrogenation reaction of carbon dioxide appears to take place through a bicarbonate species in solutions.
2. The rate of the reaction was found to be first order in catalyst concentration and kinetically favored by temperatures greater than $150^{\circ}C$.
3. A high NaOH normality, high temperature and low H_2/CO_2 ratio was found to give the largest yield of high molecular weight products.
4. The system was observed to reach equilibrium with a 70% conversion of carbon dioxide after 24 hours at a temperature of $150^{\circ}C$ and a catalyst concentration of 0.75 gram catalyst/mole CO_2.

B.) Comparison of the liquid phase hydrogenation reaction of carbon dioxide over $RuCl_3$, Ru metal and 1% Ru on graphite.

1. A 1% Ru on graphite catalyst exhibited the highest conversions compared with $RuCl_3$ on Ru metal. This

system reached equilibrium after 24 hours with a 76.86% conversion of carbon dioxide to methane and higher hydrocarbons.

2. A ruthenium (III) chloride catalyst was found to give a 70% conversion after 24 hours. After 48 hours, the conversion increased to 73%.
3. The activity of Ru metal was found to decrease during the course of the reaction.

C.) The gas phase hydrogenation reaction of carbon dioxide over $RuCl_3$, Ru metal, and 1% Ru on graphite.

1. A solid $RuCl_3$ catalyst exhibited the greatest rate with a conversion of 89.8% being achieved after 24 hours of reaction.
2. The rate of the reaction between carbon dioxide and hydrogen over $RuCl_3$ and 1% Ru on graphite was observed to be faster in the gas phase than in the liquid phase. However, Ru metal was observed to exhibit a faster rate of reaction in the liquid phase than in the gas phase.
3. No significant changes in the yield of products was observed between the gas phase and liquid phase hydrogenation reaction.

D.) Hydrogenation of sodium carbonate and sodium bicarbonate solution over a $RuCl_3$ catalyst.

1. $NaHCO_3$ solutions were found to undergo hydrogenation at a faster rate than sodium carbonate solutions.
2. The conversion of carbonate and bicarbonate to hydrocarbon compounds were found to be first order in catalyst concentration. The rate of the reaction was also found to increase with temperature in the range of 150-250°C.

E.) Observation

Carbon dioxide is commercially available from several sources as follows:[51]

1. Carbon dioxide recovery from flue gases; coke, coal, fuel oil, and gas.
2. Carbon dioxide as a by product of the fermentation industry.
3. Carbon dioxide from ammonia plants.
4. Carbon dioxide as a by product of lime-kiln operation.
5. Carbon dioxide from natural gas production wells.

As indicated above, there are several sources of large quantities of carbon dioxide. The most promising process for hydrocarbon production from carbon dioxide gas is recovery of pure carbon dioxide from gases containing other diluents, such as nitrogen and carbon monoxide. The recovery could be accomplished by reaction with sodium carbonate according to:

$$CO_2 + NaCO_3 + H_2O \rightleftarrows 2NaHCO_3$$

This reaction proceeds to the right at low temperatures and can take place in absorbers where the carbon dioxide bearing gases are passed countercurrent to the carbonate solution. The amount of carbon dioxide absorbed in the solution will vary with temperature, pressure, partial pressure of carbon dioxide in the gas, and solution strength.[52] Operational data on this reaction have been obtained by numerous investigations[53] and it has been demonstrated that carbon dioxide can be economically recovered by this method. When this information is combined with the results of this study, which have shown that the hydrogenation of bicarbonate solution over a ruthenium (III) chloride or 1% ruthenium on graphite catalyst produces a high conversion of the carbon to hydrocarbon compounds, one is had to believe that an industrial process for the conversion of carbon dioxide to hydrocarbons is feasible in an industrial scale.

REFERENCES

(1) Dew, J. N., White, R. R., and Slieucenich, C. M. (1955), Ind. Eng. Chem. 47 (1), 140.

(2) Sahatier, P., and Senderens, J. B. (1897), C. R. Hebd. Seances. Acad. Sci., 124, 1358.

(3) Sahatier, P., and Senderens, J. B. (1902), C. R. Hebd. Seances. Acad. Sci., 134, 514, 689.

(4) Anilin, B., and Soda-Fabrik, A. G., German Patent 293,787 (1913).

(5) Fischer, F., Tropsch, H., and Dilthey, P. (1925), Brennst.-Chem. 6, 265.

(6) Mills, G. A., and Steffgen, F. W. (1973), Catal. Reviews 8 (2), 159.

(7) Fischer, F., and Tropsch, H. (1923), Chem. Ber. 56, 2428.

(8) Hanisch, H., French Patent 571,580 (1923).

(9) Greyson, M., in Catalysis, Vol. 4, Emmett, P. H., Ed., Reinhold, New York, 1956, Chap. 6.

(10) Fischer, F., and Tropsch, H. (1926), Chem. Ber. 57, 830, 832, 923.

(11) Fischer, F., and Tropsch, H. (1928), Gesammelts Abh. Kennt. Kohle 10, 313.

(12) Fischer, F., and Tropsch, H. (1926), Brennst.-Chem. 7, 97.

(13) Fischer, F., and Meyer, K. (1931), Brennst.-Chem. 12, 255.

(14) Fischer, F., and Koch, H. (1932), Brennst.-Chem. 13, 61.

(15) Fischer, F., and Pichler, H. (1936), Brennst.-Chem. 17, 24.

(16) Fischer, F., and Pichler, H., German Patent 731,295 (1936).

(17) Fischer, F., and Pichler, H., French Patent 824,893 (1937).

(18) Fischer, F., and Pichler, H. (1939), Brennst.-Chem. 20, 41, 221, 247.

(19) Fischer, F., and Pichler, H., German Patent 888,240 (November 26, 1937) and 888,831 (August 1, 1937).

(20) Pichler, H. (1938), Brennst.-Chem. 19, 226.

(21) Shah, Y. H., and Perrotta, A. J. (1976), Ind. Eng. Chem., Prod. Res. Develop. 15 (2), 123.

(22) Pichler, H., Ziesecke, K. H., and Traeger, B. (1949), Brennst.-Chem. 31, 361.

(23) Pichler, H., and Ziesecke, K. H. (1949), Brennst.-Chem. 30, 13, 300.

(24) Pichler, H., Ziesecke, K. H., and Titzenthaler, E. (1949), Brennst.-Chem. 30, 333.

(25) Parranano, G. (1957), Ind. Eng. Chem. 49 (2), 266; Kolbel, H., and Engelhandt, F. (1951), Brennst.-Chem. 32, 150.

(26) Othmer, F. "Kirk-Othmer Encyclopedia of Chemical Technology," Vol. 4, 3rd ed., Interscience Publication, New York, 1963, p. 447.

(27) Pichler, H. (1947), Brennst.-Chem. 30, 105.

(28) Pichler, H., and Firnhabor, B. (1963), Brennst.-Chem. 44, 33.

(29) Akiers, W. W., and White, R. R. (1948), Chem. Eng. Progr. 44 (7), 553.

(30) Sabastian, J. J. S., Carnegie Institute of Technology, Coal Research Laboratory, Contribution No. 35, 1936.

(31) Karn, F. S., Shultz, J. F., Kelly, R. E., and Anderson, R. B. (1965), Ind. Eng. Chem., Prod. Res. Develop. 4 (1), 265.

(32) Randhava, S. S., Rehmat, A., and Camara, E. H. (1969), Ind. Eng. Chem., Prod. Res. Develop. 8 (4), 482.

(33) Akers, W. W., and White, R. R. (1948), Chem. Eng. Progr. 44, 554.

(34) Karm, F. S. (1963), Ind. Eng. Chem., Prod. Res. Develop. 2 (1), 43.

(35) McKee, D. W. (1967), J. Catal. 8, 240.

(36) Dalla Betta, R. A., Piken, A. G., and Shelef, M. (1974), J. Catal. 35, 54.

(37) Lunde, P. J. (1974), Ind. Eng. Chem., Process Des. Develop. 13 (3), 226.

(38) Lunde, P. J. (1974), Ind. Eng. Chem., Process Des. Develop. 13 (1), 27.

(39) Pichler, H., and Ziesecke, K. H., "The Isosynthesis," translated by Brinkley, H., and Golumbic, N., U. S. Bureau of Mines Bulletin, 488, U. S. Government Printing Office, Washington, D. C., 1950.

(40) Pichler, H., Ziesecke, K. H., and Traeger, B. (1949), Brennst.-Chem. 31, 361.

(41) Shah, Y. T., and Perrotta, A. J. (1976), Ind. Eng. Chem., Prod. Res. Develop. 15 (2), 123.

(42) Pichler, H. (1952), Advan. Catal. 4, 271.

(43) Mills, G. A., and Steffen, F. W. (1973), Catal. Reviews 8 (2), 159.

(44) Seglin, L., and Gecrits, R., "Methanation of Synthesis Gas," Advances in Chemistry Series, No. 146, American Chemical Society, Atlantic City, N. J., 1974, p. 2.

(45) Plase, R. N., and Cherehro, P. R. (1928), J. Amer. Chem. Soc. 50, 1464.

(46) Fischer, F., Bahr, T., and Meusel, A. (1935), Brennst.-Chem. 16, 466.

(47) Perrotter, A. J. (1946), Brennst.-Chem. 27, 1464.

(48) Cratty, L. E., and Russel, W. W. (1958), J. Amer. Chem. Soc. 80, 767.

(49) Medsford, M. (1923), J. Amer. Chem. Soc. 47, 1452.

(50) Gibson, E. L., and Hall, C. C. (1954), J. Appl. Chem. 4, 464.

(51) Othmer, F., "Kirk-Othmer Encyclopedia of Chemical Technology," Vol. 2, 3rd ed., Interscience Publications, New York, 1963, p. 353.

(52) "McGraw-Hill Encyclopedia of Science and Technology," Vol. 2, 3rd ed., McGraw-Hill Co., Inc., New York, 1971, p. 498.

(53) Perry, J. H., ed., "Chemical Engineering Handbook," 3rd ed., McGraw-Hill Co., Inc., New York, 1950, pp. 702-704.