METHANOL PRODUCTION FROM CARBON DIOXIDE AND WATER USING ULTRAVIOLET LIGHT

By

KENNETH WILLIAM ISCHE

Bachelor of Science in
Chemical Engineering
University of Minnesota
Minneapolis, Minnesota
1970

Submitted to the Faculty of the
Graduate College of the
Oklahoma State University
in partial fulfillment of
the requirements for
the Degree of
MASTER OF SCIENCE
December, 1982

METHANOL PRODUCTION FROM CARBON DIOXIDE AND WATER USING ULTRAVIOLET LIGHT

Thesis Approved:

Gary L Foutch
Thesis Adviser

Mayis Seapan

M G Rockley

Norman N Durham
Dean of Graduate College

PREFACE

An experimental apparatus was designed and constructed for photochemically converting carbon dioxide and water into small organic molecules such as methanol. Water to carbon dioxide molar ratios in the reactor feed ranged from 0.03 to 1.0 to the stoichiometric ratio for methanol production of 2.0 to 1.0 at 14.3 psia reactor pressure. Experiments were carried out at reactor residence times of 0.14 to 4.9 minutes. The experiments were done to study a potential method of solar capture and storage.

I would like to express my deepest appreciation to my thesis adviser, Dr. Gary L. Foutch, for his guidance and helpfulness throughout the study. He applied for and received equipment funds which allowed this study to become a reality. Appreciation is also expressed to my other committee members, Dr. Mark Rockley and Dr. Mayis Seapan for their encouragement and technical guidance. Particular thanks is due Dr. Billy L. Crynes for the assistantship which enabled me to return to college and pursue this study. Discussions with other faculty members and my fellow graduate students were also of considerable help.

I am grateful for the help of Mr. Preston Wilson, Mr. Wayne Adkins, and Mr. Charles Baker who were involved with the building and procurement of my experimental equipment.

I would also like to thank Mr. Richard Melling who introduced me to the Osborne computer and its word processing capabilities which played an extremely important role in preparing the manuscript drafts and final copy.

Financial support for the project was gratefully received from the Institute for Energy Analysis on the Oklahoma State University campus.

Finally, I owe a deep debt of gratitude to my wife, Maureen, and our daughters, Susan and Erin, for their many sacrifices.

TABLE OF CONTENTS

Chapter Page

LIST OF TABLES

LIST OF FIGURES

CHAPTER I

INTRODUCTION

This study concerns one potential process for converting carbon dioxide and water into simple hydrocarbons. Plants are normally thought of as the only means for reversing combustion; however, the process investigated is one of a number which has potential for producing organic chemicals such as methanol without going through a biological cycle.

The reverse combustion or photoreduction process could be a means of solar energy capture and storage in a readily useable and versatile form. Success in this area could help reduce dependence on foreign energy sources and also limit the buildup of carbon dioxide in the atmosphere. Carbon dioxide could be taken directly from the atmosphere or from combustion exhaust where it is in concentrated form, such as fossil fueled power plants (20). Since carbon dioxide would be captured in the process for reuse, the amount of fossil fuel required from the earth would be decreased. This results in a slowdown of the overall rate of carbon dioxide production (14, 16, 17, 18, 32, 33).

Stein (31) notes attempts at duplicating photosynthesis such as a synthetic leaf using chlorophyll. He believes that there is something to be learned by studying photosynthesis, but attempting to duplicate photosynthesis as a means for solar energy conversion and storage is not necessarily the correct path to follow.

Experiments performed for this study were patterned after work done by Aurian-Blajeni, Halmann and Manassen (2) on photoreduction of carbon dioxide saturated with water vapor. In their experiments small amounts of methanol and formaldehyde were produced on a number of semiconductor materials such as strontium titanate ($SrTiO_3$), titanium dioxide (TiO_2), ferric oxide (Fe_2O_3), calcium titanate ($CaTiO_3$), lead oxide (Pb_3O_4) and a number of other metal oxides. The reactor feed was passed through a borosilicate tube which had been coated with a water slurry of semiconductor powder. This tube was illuminated with either a high pressure mercury arc lamp or the sun, which activated the semiconductor material driving the reaction. Less than one percent of the absorbed energy was converted to product. Absorbed energy conversion of more than one percent was obtained by bubbling carbon dioxide through a suspension of semiconductor powder in liquid water.

Experiments aimed at producing methane by photoreduction of carbon dioxide and water vapor on a strontium titanate-platinum foil sandwich were performed by Hemminger, Carr, Lo and Somorjai (15). A high pressure mercury arc lamp provided reactor illumination. Methane was produced, but production stopped after a monolayer of methane was formed. Hydrogenation of carbon dioxide to formic acid or formaldehyde with further reduction to methane was believed to be the reaction path. Adsorption studies that had been done in conjunction with the methane formation studies gave some insight into the hydrogen source. Water was found to adsorb on the strontium titanate surface in a dissociated state. The hydrogen was then available for hydrogenation.

A less successful attempt to produce methanol from carbon dioxide, liquid water and light energy was performed by Åkermark, Eklund-Westlin, Baeckström and Löf (1). Only very low levels of formic acid and formaldehyde were formed by bubbling carbon dioxide through aqueous solutions of metal salts while illuminating the sample with 254 nanometer ultraviolet light.

This study extends some of the work done by Aurian-Blajeni et al. (2). Their experiments where a carbon dioxide-water vapor feedstock was used had been performed at ambient temperatures and pressures. A reactor which could be operated at temperatures and pressures above ambient was designed and built for this study. Reactor operation with water to carbon dioxide molar ratios in the reactor feed from 0.03 to 1.0 at ambient conditions of $75^{\circ}F$ and 14.3 psia to the stoichiometric ratio for methanol production of 2 : 1 at $192^{\circ}F$ and 14.3 psia was made possible (11). Methanol production could then be studied at a variety of reactor conditions in addition to ambient conditions. Only one semiconductor material, strontium titanate, was studied.

The following questions are to be addressed by this study:

1. Does a flat plate, gas phase photochemical reactor produce methanol from carbon dioxide and water?

2. What methanol yields can be expected?

3. How does the reactor perform at different operating conditions?

4. What changes might improve the reactor's operation?

Answers to these questions may help determine whether or not this potential method of solar energy storage by hydrocarbon production should be pursued further.

CHAPTER II

LITERATURE REVIEW

There have been very few investigations of nonbiological photoreduction reactions of carbon dioxide and water as indicated by the literature (1, 2, 5, 15, 38). The products from this process can be methanol, methane, formic acid, formaldehyde, or some other small hydrocarbon molecule and molecular oxygen. Work on carbon dioxide-water photoreduction is in many cases based on work done on water photolysis (5, 8, 12, 21, 23, 24, 25, 26, 28, 35, 36, 38, 39, 40). Here the intended products are hydrogen and oxygen molecules. In most cases the motivating force is the possibility of finding a process to chemically store solar energy.

The following basic reactions are involved in the efforts to photochemically convert carbon dioxide and water to organic molecules (15):

$$CO_2 + 2\ H_2O = CH_4 + 2\ O_2 \quad \Delta G^o = 8.30 \text{ eV/molecule}$$

$$CO_2 + 2\ H_2O = CH_3OH + 3/2\ O_2 \quad \Delta G^o = 7.15 \text{ eV/molecule}$$

$$CO_2 + H_2O = H_2CO + O_2 \quad \Delta G^o = 5.32 \text{ eV/molecule}$$

$$CO_2 + H_2O = HCOOH + 1/2\ O_2 \quad \Delta G^o = 2.98 \text{ eV/molecule}$$

Photoreduction reactions have been carried out with water in the liquid phase (1, 2) and also in the vapor phase (2, 15).

Photoreduction of Carbon Dioxide and Water

The thermodynamically uphill reactions of reverse combustion are powered by light energy. Eventually this light energy will come from the sun, but in most experiments high-pressure mercury arc lamps which emit ultraviolet light are used. The light is beamed onto solid semiconductor material such as titanium dioxide (TiO_2) or strontium titanate ($SrTiO_3$) which excites the electrons at the surface creating mobile electrons or electron-hole pairs. These excited electrons can then flow to or from the molecules adsorbed on the semiconductor surface making possible surface reactions. The adsorbed molecules may also be directly excited by light. Light energy greater than the band gap must be used. Band gap energy is the difference in energy between the semiconductor's valence band and conduction band. Light having greater than band gap energy can excite electrons from the semiconductor's completely filled valence band to the partially filled conduction band forming electron-hole pairs. Before their recombination occurs, some of these electron-hole pairs can be combined with the molecules adsorbed on the semiconductor surface (15, 38).

Previous Experimental Work

Aurian-Blajeni et al. (2) investigated the photoreduction of carbon dioxide and water to formaldehyde and methanol on semiconductor materials. The reactants were carbon dioxide with liquid water in some cases and water vapor in other cases.

In the cases where liquid water was used, the reaction cell was made of borosilicate glass which contained the water and photoactive materials which were held in suspension by the bubbling carbon dioxide reactant. The light source was a 70 watt high-pressure mercury arc lamp which was immersed in the glass reaction cell. The photoactive semiconductor materials used were: strontium titanate ($SrTiO_3$), tungsten trioxide (WO_3), titanium dioxide (TiO_2), calcium titanate ($CaTiO_3$), barium titanate/mercuric sulfide ($BaTiO_3/HgS$), zinc oxide/titanium dioxide (ZnO/TiO_2), silicon carbide (SiC), ferric oxide (Fe_2O_3), mercuric sulfide (HgS), and lead tetroxide (Pb_3O_4). Some of the photoactive materials were thermally treated by heating to approximately 600^oC in a vacuum or in air. Vacuum thermal treatment resulted in higher activity than heating in air. Thermal treatment did not seem to affect the light absorptive properties of the materials except for tungsten trioxide. Rapid removal of the reaction products from the irradiation zone to prevent re-oxidation of the products was emphasized. Reaction products, methanol and methane, were analyzed by gas chromatography on a Porapak Q column with flame ionization detection. Formaldehyde was determined colorimetrically after reaction with chromotropic acid. Methane was also detected using mass-spectrometry.

In the case where the reactants were carbon dioxide and water vapor, the photoactive materials were mixed with water to form a slurry and painted on the surface of a cylindrical borosilicate glass tube. This tube was placed in the photochemical cell instead of the aqueous suspension used in the liquid water experiments. Also, two of the sunlight powered experiments were performed by coating the inner back surface of a borosilicate glass tube with titanium dioxide powder and passing carbon dioxide saturated with water through the tube. The tube was inclined at an angle of 30 degrees from vertical to face the sun.

Results of the Aurian-Blajeni et al. (2) experiments employing aqueous suspensions of photoactive materials could be used as a basis for comparing the photoactivity of the semiconductor powders tested. Products yielded were methanol and formaldehyde. The highest yield was 7.16 micromoles per hour with a carbon dioxide circulation rate of 164 milliliters per minute using strontium titanate semiconductor suspended in liquid water. In this experiment 0.1 micromole per hour of methane was produced. The carbon dioxide and water vapor reaction with the largest conversion produced 0.25 micromole per hour of methanol and 0.09 micromole per hour of formaldehyde using a carbon dioxide flow rate of 3 milliliters per minute and calcium titanate semiconductor. The highest yields were obtained from the experiments where carbon dioxide was bubbled through aqueous suspensions of the photoactive powders.

Another aspect of photoreduction which was investigated was the effect of light intensity. It was believed that there may have been a lack of yield improvement with more intense radiation from a 500 watt high-pressure mercury arc lamp due to the possible photodissociation or oxidation processes on methanol adsorbed on the semiconductor surface.

Hemminger et al. (15) also carried out thermodynamically uphill chemical reactions at solid surfaces with light energy. Specifically, methane production from carbon dioxide and water vapor in contact with a sandwich consisting of single-crystal strontium titanate and platinum foil was investigated.

A gas phase photoreaction was chosen because there are a number of advantages compared to reactions occurring at the solid-liquid interface that had been studied in electrochemical liquid water splitting cells (12, 23, 24, 28, 35, 40). The surface composition and its changes can be analyzed by sophisticated techniques including electron loss spectroscopy, UV photoelectron spectroscopy, auger electron spectroscopy and low-energy electron diffraction. Therefore, the reaction mechanisms can be more easily studied. The dissolution of the active surface and the absorption of the incident light by the electrolyte are absent. Also, the diffusion of reactants and products to and from the surface is more rapid which may be an important consideration affecting the rate of the photochemical reaction.

Since photoelectrochemical cells have been successfully used to dissociate water using only light without an external potential, Hemminger et al. (15) believed there was the possibility of carrying out photochemical surface reactions with gaseous reactants. Not only had the photoelectrochemical work shown that no external potential was required, but also, that hydrogen and oxygen were evolved at the aqueous electrolyte interface even when the oxide ($SrTiO_3$, TiO_2) anode and the platinum cathode were touching each other or short-circuited. This operation with anode-cathode short-circuiting indicated that charge transfer at the metal-semiconductor interfaces may cause adequate charge separation and formation of a space charge barrier at the surface to cause water photodissociation. It was believed that an electrolyte might not be necessary when there was semiconductor-metal contact.

Using gaseous water instead of an aqueous electrolyte solution was a deviation from normal photoelectrochemistry procedures involving water dissociation. Hydroxide ions which are normally present in the basic photoelectrochemical cell solution would have to be formed by dissociation of water molecules adsorbed on the oxide surface from the gas phase.

Since reactions on the oxide surface are very important, the adsorption characteristics of carbon dioxide, water, carbon monoxide, and oxygen on strontium titanate and titanium dioxide single-crystal surfaces were investigated by a combination of techniques. The surface area of the oxide sample used for desorption studies was approximately one square centimeter which made it difficult to obtain products in detectable concentrations.

The photoreaction was carried out at near atmospheric pressure in a specially constructed cell located in the center of an ultrahigh vacuum chamber. The strontium titanate crystal samples were made in the form of a one centimeter diameter disk of one millimeter thickness. A disk of 0.001 inch thick platinum foil was attached to the strontium titanate disk by two platinum foil strips. The oxide surface was illuminated through a sapphire window using a 500 watt high-pressure mercury lamp. Temperature of the sample could be controlled by a tungsten heater wire located at the back of the sample. An infrared filter consisting of a quartz cell filled with nickel sulfate solution was used to absorb heat from the light beam and transmit the near UV.

Water adsorbs in a dissociated state on strontium titanate and oxidizes Ti^{3+} to Ti^{4+}. Ti^{3+} is only partly regenerated upon illumination. Oxygen adsorbs in several states. Not all of the adsorbed oxygen is removed by photodesorption. Carbon monoxide and carbon dioxide form the same species on the oxide surface. Carbon monoxide is probably converted to carbon dioxide by a slow surface reaction.

Water remains molecular on the platinum surface and is bound only weakly. Oxygen was found to be chemisorbed on the platinum surface. Carbon monoxide chemisorbs strongly in molecular form on the platinum surface. Carbon dioxide adsorbs poorly on the platinum surface and remains largely in molecular form.

A total of about one monolayer of methane was produced during the first 10 minutes of illumination after which production stopped. The initial rate of formation was 2 X 10^{14} molecules per minute which corresponds to a quantum yield of one methane molecule per 10^4 photons. The reaction stoppage was caused by a tenacious poison since reintroducing fresh reactants failed to regenerate the chemical activity of the surfaces. There was also the buildup of a monolayer of carbon on the platinum.

Methane was also thermally generated when a reduced strontium titanate sample was used in the oxide-metal sandwich. A monolayer of methane was generated by heating the sandwich to 600 K in the dark. The light powered reaction had been carried out at 300 K. Again methane production stopped after formation of one monolayer of methane, and there was a monolayer deposit of carbon on the platinum. It appeared that the same poisoning occurred as with the light-driven reaction. Substitution of carbon monoxide for carbon dioxide did not increase the methane yield.

The following experiments were done to determine if methane could be generated without the metal-oxide contact; however, no methane production resulted.

1. Only carbon dioxide (no water) was fed to the metal-oxide sandwich while illuminated or heated to 450 K.

2. No platinum foil was used in conjunction with the strontium titanate when carbon dioxide and water was fed to the reactor.

3. No strontium titanate was used in conjunction with the platinum foil when carbon dioxide and water was fed to the reactor.

4. Light energy less than the band gap of strontium titanate was used.

Hemminger et al. (15) concluded that the photochemical process leading to methane formation was made up of two parts the exact mechanism of which is still unknown: (A) water dissociation to oxygen and hydrogen on the semiconductor surface and (B) the reduction of carbon dioxide with the hydrogen.

As in the two previously summarized experiments, work done by Åkermark et al. (1) was to find a method of photochemically converting carbon dioxide into fuels as a method of solar energy storage. Methods slightly different from the previous two studies were used.

Researchers bubbled carbon dioxide through an aqueous solution of metal salt (iron II, cobalt II and chromium II) saturated with carbon dioxide and irradiated the sample with 254 nanometer ultraviolet light. No semiconductor material was used in these experiments. In some cases visible light was used. The reduction using iron II quickly yielded a low stationary concentration of formic acid and formaldehyde. Similar results occurred with cobalt II and chromium II. No reduction occurred at all in the absence of metal ions. The researchers believed that the oxidized form iron III might oxidize the reduced products so reducing agents (metallic iron and zinc amalgam) were employed. Neither of the reducing agents was capable of increasing the yield of formaldehyde, and reduction products like methanol could not be detected. Another measure to scavenge iron III by addition of fluoride led to a sharp decrease in reaction products. It was decided that iron III was not the major factor causing low yields of formic acid and formaldehyde.

Since neither methanol nor methane could be detected as a result of carbon dioxide reduction, more concentrated solutions of formaldehyde (than were achieved by direct carbon dioxide reduction) were studied. In this case a low stationary level of methanol was produced. The level was sufficiently low to cause analytical problems.

Finally, photoreduction of methanol was studied. Only very low yields of methane were obtained. Åkermark et al. (1) concluded that a more sophisticated reducing method was required to improve methanol yield.

Of the three attempts at carbon dioxide photoreduction described above, an experimental system similar to that of Aurian-Blajeni et al. (2) was most economical to construct and appeared to have the greatest probability for methanol production. Water vapor as opposed to liquid water was chosen for the reactor feed mixture because Hemminger et al. (15) believed a gaseous reaction had potential since reactants and products could diffuse to and from the semiconductor surface more easily than in the case where liquid water reactant was used. Also, despite Aurian-Blajeni et al.'s (2) less successful attempts at producing methanol using water vapor as opposed to liquid water, it was possible that a change in reactor design and operating conditions may have been able to improve this situation. Since Aurian-Blajeni et al.'s (2) experiments had been carried out at ambient conditions, experiments at a variety of water to carbon dioxide ratios and reactor residence times were a logical extension of the search for higher methanol yields from carbon dioxide photoreduction.

CHAPTER III

EXPERIMENTAL APPARATUS

An apparatus was designed and constructed for photochemically reacting carbon dioxide and water vapor to form hydrocarbons. A diagram of the apparatus is shown in Figures 1 and 2, and its major components are described below.

Carbon Dioxide Flowmeter

The flowmeter was a model F3060 compact shielded microflowmeter manufactured by Gilmont Instruments, Inc. The instrument range is 0.02 to 15 milliliters per minute of air at standard conditions. A Gilmont model F3080A static eliminator was used to prevent buildup of electrostatic charges which might have caused the flowmeter ball to stick.

Carbon Dioxide Saturator

The vessel used for carbon dioxide humidification was a Hoke model DOT 3 E 1800 stainless steel bomb measuring 2 inches outside diameter by 12 1/2 inches long. Saturator volume is 500 milliliters. Dry carbon dioxide entered the bottom of the vessel and humidified gas exited from the top of the vessel. A small glass wool filter was placed in the

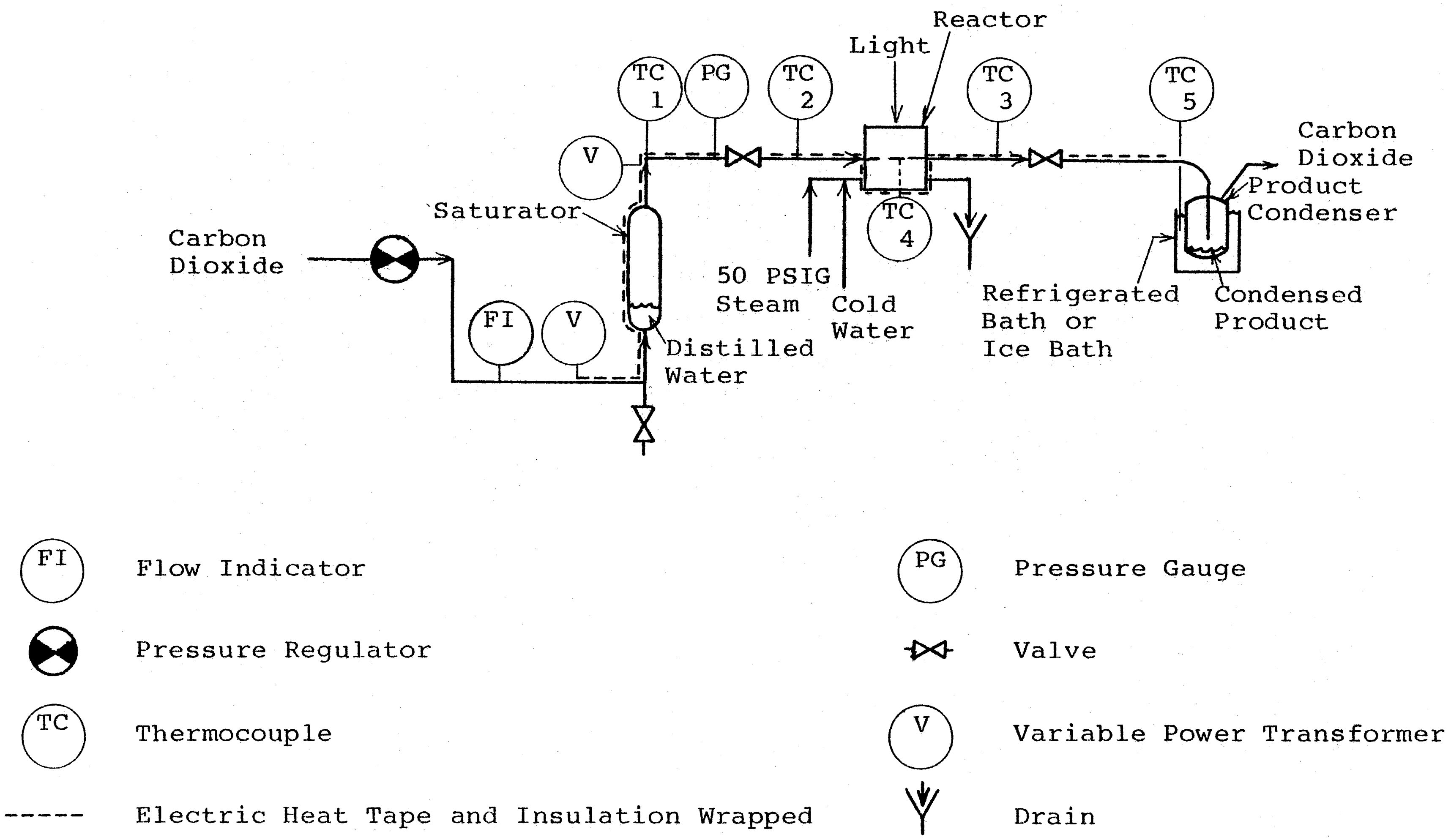


Figure 1. Schematic Flow Diagram of the Experimental System (Continuous Flow Operation)

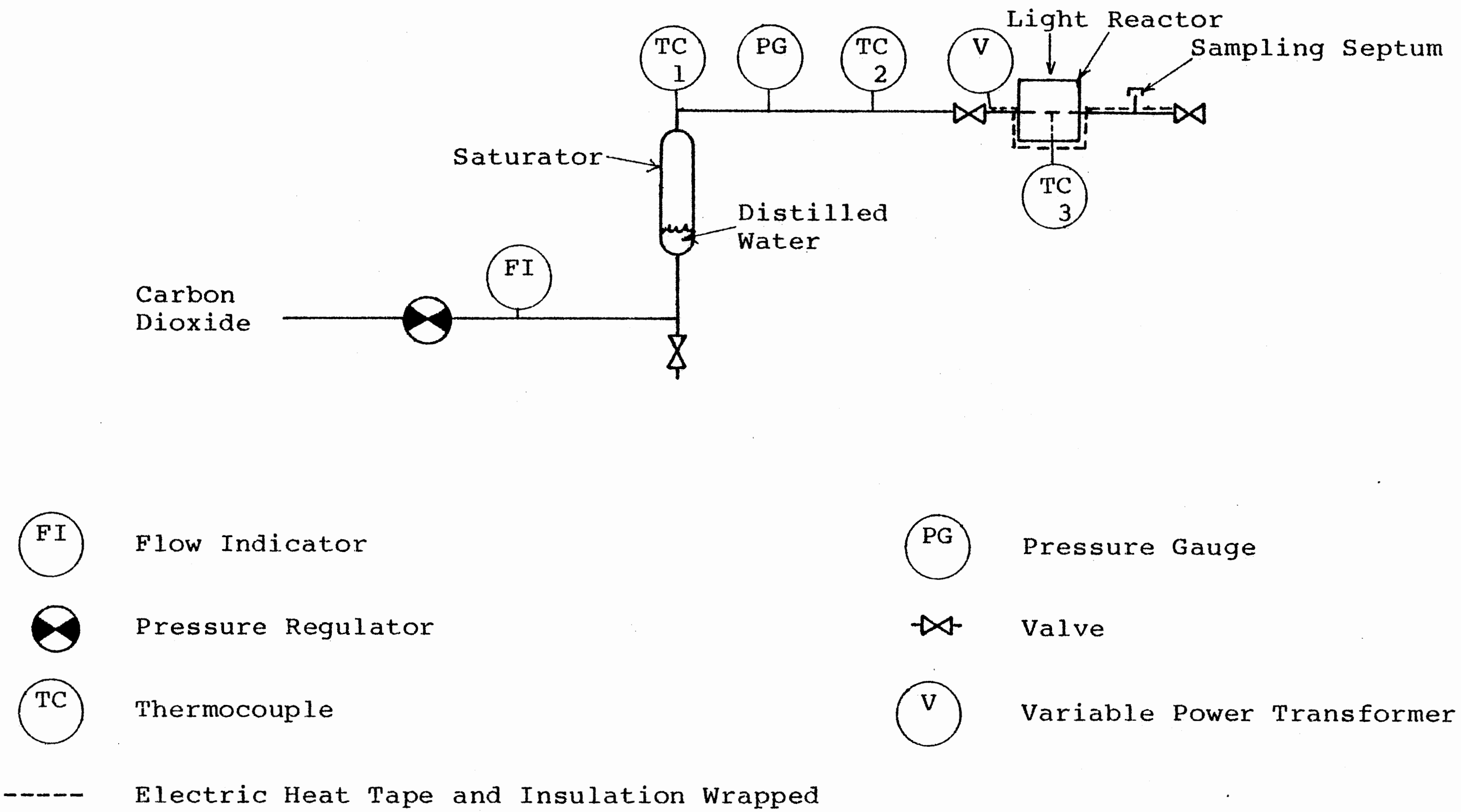


Figure 2. Schematic Flow Diagram of the Experimental System (Batch Flow Operation)

inlet tubing and acted to disperse the entering carbon dioxide assuring good gas-liquid contact. The vessel was charged with two hundred milliliters of distilled water.

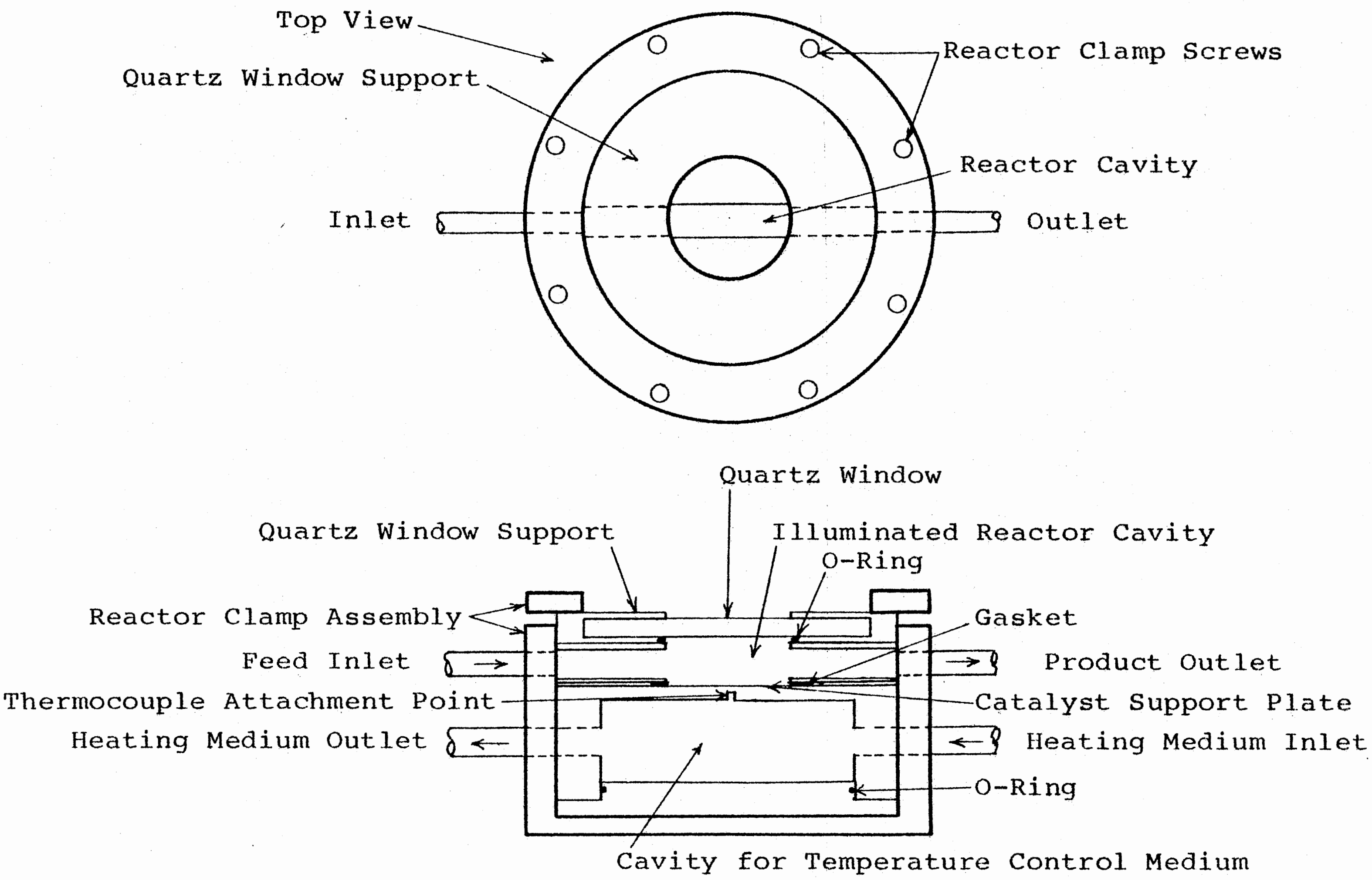
Pressure Gauge

Pressure was measured immediately upstream of the reactor using a Marsh Safecase Type 210-C 60 psig pressure gauge. The gauge has 0.2 psi divisions.

Reactor

The reactor was a specially designed (See Figure 3) photochemical reactor manufactured from stainless steel by the Oklahoma State University Mechanical Engineering Laboratory Shop. The dimensions of the reaction compartment are 9 millimeters wide by 32 millimeters long by 12 millimeters deep. Reactor volume is 3.5 milliliters.

Catalyst in the form of a water slurry was brushed onto the flat surface opposite a quartz window and allowed to dry before reactor reassembly. For some experiments the catalyst-water slurry was brushed onto a one-eighth inch thick glass plate, and the glass plate was placed on the stainless steel surface opposite the quartz window. The one-eighth inch thick quartz window allowed ultraviolet light below 400 nanometers to enter the reactor and energize the carbon dioxide photoreduction process. Approximate catalyst surface temperature was measured by a one-sixteenth inch O.D. type J thermocouple silver soldered to the underside of the



Scale: 1 cm. = 0.7 in.

Figure 3. Reactor Design

stainless steel catalyst support surface. The reactor was operated in both batch and flow modes.

Light Sources

Two light sources were used during these experiments. The first was a quartz tungsten-halogen filament lamp, and the second was a high pressure xenon arc lamp.

Quartz Tungsten-Halogen Filament Lamp

This light source was a Smith-Victor model Q250 with a DYH 120 volt quartz-tungsten-halogen lamp intended for use as a video light. This lamp did emit some light at wavelengths below 413 nanometers which is desirable since this represents band gap energy for strontium titanate. See the spectral distribution curve, Figure 11, Appendix C. This curve was obtained from the Oriel Corporation catalog (27).

Xenon Arc Lamp

The light source was an Osram XBO75W/2 high pressure xenon arc lamp in an Oriel Model 6302 lamp housing. The lamp was powered by an Oriel Model 8510-1 power supply. Accessories included an Oriel Model 6304 condensing lens assembly, an Oriel Model 6194 liquid filter, and an Oriel Model 6204 90° light tube. See spectral intensity distribution curve, Figure 12, Appendix C. This curve was obtained from the Oriel Corporation catalog (27).

Valves and Tubing

All valves were 0.25 inch stainless steel valves manufactured by Parker-Hannifin Tube Fittings Division. Tubing from the carbon dioxide cylinder through the reactor was 0.25 inch O.D. stainless steel tubing with 0.035 inch wall thickness.

Reactor Product Condenser System

The glass condenser (See Figure 4) used to condense water and reaction products out of the reactor effluent stream was built by the Oklahoma State University Chemistry Department Glass Shop. The condenser was placed in an ice bath for some experiments and in a refrigerated bath for other experiments after the refrigerated bath became available. A six inch long, one-sixteenth inch O.D. type J thermocouple was used to measure the bath temperature.

Refrigerated Bath

This refrigerated bath is catalog number S-84890 manufactured by E. H. Sargent & Company. Bath dimensions are 12 inches wide by 20 inches long by 11 inches deep. The bath had a small centrifugal pump which was used to circulate salt brine from the bath to a miniature bath made from a small metal can. The sample condenser was placed in this small metal can which had salt brine at approximately 32°F flowing through it.

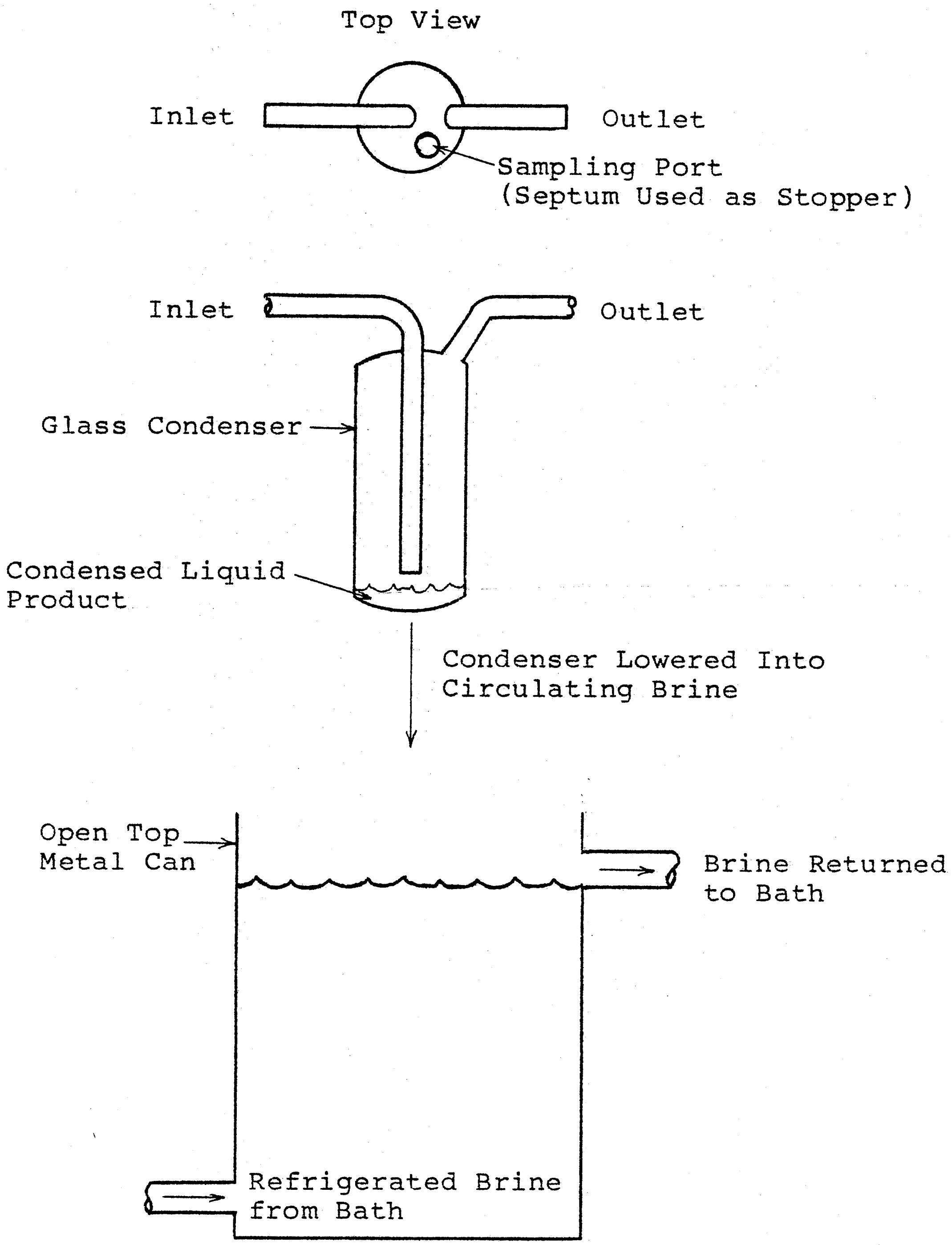


Figure 4. Reactor Product Condenser System

Thermocouples and Thermocouple Digital Readout

All except one of the thermocouples used were six inch long, one-sixteenth inch O.D. iron constantan type J thermocouples manufactured by Omega Engineering Inc. One thermocouple each was located in the reactor feed inlet tubing and the reactor product outlet tubing. Another was located at the outlet of the carbon dioxide saturator. A fourth was located in the reactor product condenser ice bath. A Honeywell thirty-six inch long, one-sixteenth inch O.D. type J thermocouple was silver-soldered to the reactor catalyst support plate. The digital thermocouple readout was a Model 199 JF-X-X manufactured by Omega Engineering Inc.

Gas-Liquid Chromatograph

The gas-liquid chromatograph used was a Model 5880A Level Four manufactured by Hewlett-Packard. It was equipped with two-five foot long one-eighth inch O.D. stainless steel columns containing 80/100 mesh Porapak Q column packing material obtained from Varian Instrument Service Center. The chromatograph was equipped with both a thermal conductivity and a flame ionization detector.

Heating Tape

The heating tape used was four feet long, silicon rubber coated and had a maximum operating temperature of 260°C. It was manufactured by Glas Col Apparatus Company.

The tape was wrapped around the carbon dioxide saturator and the reactor inlet and outlet tubing to keep water from condensing.

Variable Power Transformers

Powerstat 116B variable power transformers were used to control power to the heating tapes. Each was capable of supplying eight amps at 110 volts into transformer and 0-140 volts out of transformer. Transformers were manufactured by The Superior Electric Company.

Sampling Syringes

Gas sampling was performed using a 25 microliter gas-tight syringe manufactured by Unimetrics Corporation. A ten microliter liquid syringe manufactured by Hamilton Company was used to inject liquid water, methanol and formaldehyde solutions, and condensed reactor product into the gas chromatograph.

Chemicals

Liquid carbon dioxide was ultra high purity grade from Big 3 Industries, Inc. Single distilled water was obtained from the still in the chemical engineering stockroom. Strontium titanate came from Pfaltz & Bauer, Inc. Methanol used for chromatograph calibration was spectrophotometric grade manufactured by Mallinckrodt, Inc. A reagent grade 37 percent formaldehyde solution used for chromatograph calibration was also manufactured by Mallinckrodt.

CHAPTER IV

EXPERIMENTAL PROCEDURE

Two procedural aspects are covered in this chapter. These are: (A) Calibration and (B) Operation.

Calibration Procedure

Pressure Gauge Calibration

The 60 psig Marsh pressure gauge was calibrated from zero to thirty psig using a mercury manometer. Results are given in Table VI, Appendix E.

Thermocouple Calibration

The five thermocouples used in this experiment were calibrated by placing them in an ice water bath and a beaker of boiling water and noting the temperature indication on the thermocouple readout. The data obtained from this procedure are given in Table VII and Figure 14, Appendix F.

Carbon Dioxide Flowmeter Calibration

Carbon dioxide flow rate was read from the calibration chart supplied with the flowmeter and reproduced as Figure 13, Appendix D. Flow was corrected for temperature and pressure using the formulas given in Appendix G.

Chromatograph Calibration

Methanol response factors were determined by making three dilutions of spectrophotometric grade methanol in distilled water. Methanol solutions of 10, 100, and 500 parts per million were made. One, three, and five microliter sample volumes were injected into the five foot Porapak Q column ahead of the flame ionization detector. The methanol peak area obtained was plotted against moles of methanol in each sample. See Table V and Figure 10, Appendix B.

Formaldehyde solutions containing 10, 100, and 500 parts per million by volume were made using a formaldehyde solution containing 37 percent by volume formaldehyde and 10 percent by volume methanol. The only peaks observed after injecting varying solution volumes were due to the methanol in the solution. A formaldehyde peak was not observed. Aurian-Blajeni et al. (2) used a colorimetric determination of formaldehyde and only used the chromatograph for methanol and methane analysis.

Operating Procedure

The photochemical reactor shown in Figures 1, 2, and 3 of Chapter III was designed as a continuous flow reactor but was operated in both a batch and a continuous mode. Experimental procedure involved preparation, operation, and sample analysis. Strontium titanate semiconductor catalyst material was tested using different carbon dioxide and water ratios in the two operating modes. The batch reactor runs were performed while awaiting delivery of the xenon arc lamp. See Figures 5 and 6 for lighting arrangement.

Batch Reactor Experiments

Experimental preparation involved the following items. After removal from the system, the reactor was disassembled and rinsed with distilled water. Strontium titanate from the previous experiment was washed from the stainless steel catalyst support plate. Fresh untreated catalyst was mixed with distilled water to form a slurry and brushed onto the catalyst support surface with a small paint brush. After waiting anywhere from one hour to overnight for the catalyst to dry, the reactor was reassembled and reconnected to the system. Occasionally, the same catalyst was kept in the reactor for up to three experiments. After approximately every five experiments, saturator water was drained and replaced by a fresh 200 milliliter charge of distilled water. A sample of water used to fill the saturator and a sample of the water removed from the saturator was retained for analysis. The reactor was wrapped with heating tape and insulation for those runs where the reactor was heated.

Carbon dioxide was bubbled through water in the saturator at room temperature (approximately 75^{o}F) and then flowed through the reactor at approximately two milliliters per minute. Chromatographic analyses of the carbon dioxide-water gaseous feed mixture were done until there was

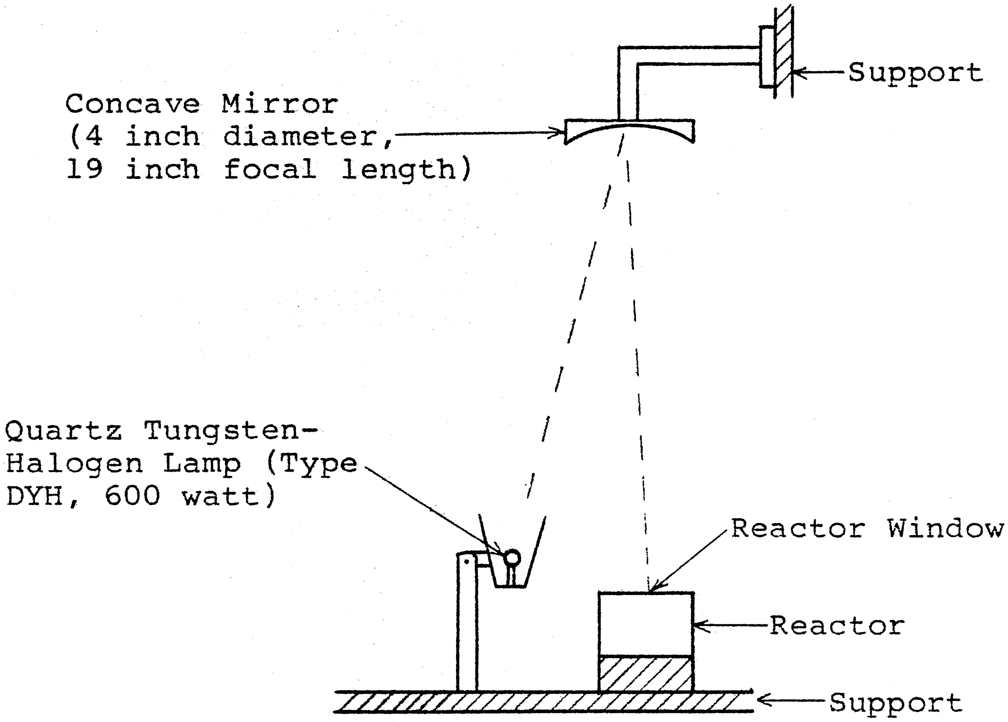


Figure 5. Quartz Tungsten-Halogen Light Source with Reactor

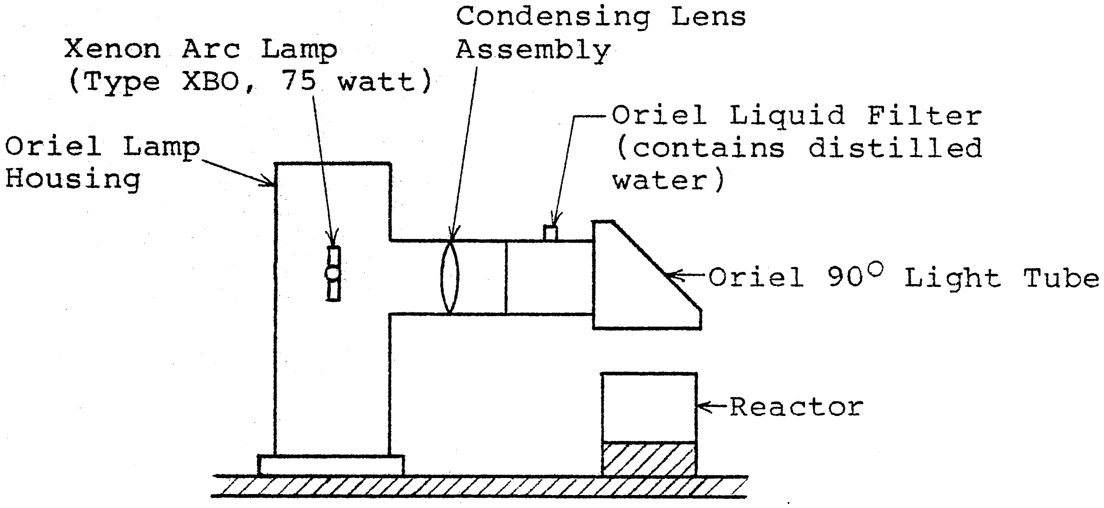


Figure 6. Xenon Arc Light Source with Reactor

reproducibility between samples. Flow through the reactor was stopped by closing inlet and outlet valves, and the reactor was illuminated using the 600 watt quartz tungsten-halogen light source.

After illuminating the reactor for ten minutes, the light source was turned off, and the reactor was allowed to set for five minutes so that any product formed could diffuse to the sampling location (See Figure 2, Reactor system in batch operating mode). For some experiments the light was on continuously throughout the experiment. A 25 microliter gas sample was drawn through a septum in the tubing next to the reactor vessel using a gas-tight syringe. The sample was then injected into the five foot Porapak Q column ahead of the flame ionization detector. This procedure was repeated until the reactor had been illuminated for an hour or more.

During the batch experiments, only approximate catalyst surface temperature was measured using the thermocouple attached to the underside of the catalyst support plate. Reactor pressure was not measured since attaching a pressure gauge or manometer would have increased the reactor volume. Reactor volume was minimized so that any buildup in reaction products could be detected more quickly than with a larger system volume. The reactor would have had difficulty attaining pressures higher than atmospheric because samples were taken using a gas-tight syringe inserted through a rubber septum into the reactor. The repeated insertions of the sampling syringe during the experiments would have had a depressuring effect.

A variation of this method involved changing the carbon dioxide to water ratio in the reactor from its initial ratio at laboratory ambient conditions. The reactor was wrapped with a four foot long electric heat tape and covered by fiber glass insulation. Initially, carbon dioxide saturated with water at room temperature was flowed through the reactor until there was composition reproducibility between reactor gas samples. Reactor inlet and outlet valves were then closed. One or two microliters of distilled water were injected into the reactor through the sampling septum. The heating tape connected to a variable power supply was turned on at the beginning of each experiment. The reactor temperature kept increasing during the whole experiment. Therefore, the amount of water in the vapor phase should have kept increasing over the initial water of saturation at ambient conditions as long as some liquid water remained in the reactor. The reactor was illuminated at intermittent intervals as it was in the ambient temperature experiments.

There were a number of other variations of the batch reactor experiments. To establish a baseline, no light and no catalyst were used in some experiments. Catalyst was coated with a couple of drops of saturated sodium hydroxide solution in other experiments. Heat treating the catalyst was attempted. In one run the catalyst used was heat treated in air at 500°C. Some catalyst was heat treated in a 15 inch Hg vacuum at an unmeasured temperature. Other catalyst was heat treated at 250^{o}F in an unmeasured vacuum. In one case titanium dioxide was used as a catalyst.

A more detailed description of each batch reactor experiment is given in Appendix A. The reason for doing each run is given there.

The chromatograph operating conditions were as follows: The carrier gas (nitrogen) flow rate was 21 milliliters per minute. The injector and detector temperatures were 130^{o}C. The oven was operated isothermally at 100^{o}C. At these conditions any methanol formed would have eluted from the column at 2.0 minutes residence time. Methane, if present, would have eluted at 0.35 minutes, approximately the same as carbon dioxide. Since carbon dioxide passing through a flame ionization detector produces a very small signal, any methane in the sample would have been noticed by an increase in the area under the peak at 0.35 minute residence time.

Continuous Flow Reactor Experiments

The same equipment and piping configuration as in the batch experiments was used up to and including the reactor (See Figure 1, Reactor system in continuous flow operating mode). Downstream of the reactor, the two operating modes differed in their product sample collection methods. In the batch operation a gas sample had been collected through a septum located near the reactor. In the continuous flow experiments reactor effluent passed through a glass condenser where water and any methanol formed could be collected for the duration of the experiment.

Experiments to test the effect of reactor residence time and feed water to carbon dioxide ratio were performed at atmospheric pressure. Dry carbon dioxide flow rates of 18.7, 2.6, and 0.55 standard (70°F, 1 atmosphere) milliliters per minute were tested. These flow rates translated into reactor residence times of 0.14, 1.0, and 5.0 minutes respectively. Water to carbon dioxide mole ratios of 0.03, 0.29, 0.9, and 2.0 to 1 were tested. These feed ratios were achieved by operating the saturator vessel at ambient temperature (approximately 75°F), 146°F, 177°F, and 192°F respectively.

The following system features allowed operation at the above ambient temperatures necessary for the water to carbon dioxide ratios above 0.03 to 1. The carbon dioxide saturator vessel, the reactor, and the tubing upstream and downstream of the reactor was wrapped with electric heating tape and covered with insulation. Also, a heating medium consisting of a mixture of steam and cold water was passed through the cavity beneath the catalyst support surface to keep water in the feed from condensing. To increase the ratio of water to carbon dioxide, the voltage from the variable power transformer supplying power to the heating tape surrounding the carbon dioxide saturator was increased causing a corresponding temperature increase. The voltage from the variable power transformer supplying power to the heating tape surrounding the reactor and the tubing to and from the reactor was also increased. The temperature of the stream from the carbon dioxide saturator, through the reactor, and on to the sample condenser was maintained slightly above the saturator temperature so that condensation would not occur. Steam and cold water flow to the cavity beneath the catalyst support surface was also adjusted to maintain the desired reactor temperature.

Experimental preparation consisted of the following items. Following removal from the system, the reactor was disassembled and rinsed with distilled water. Strontium titanate catalyst from the previous experiment was washed from the glass catalyst support. Fresh untreated catalyst was mixed with distilled water to form a slurry and brushed onto the glass plate with a small paint brush. After waiting approximately ten minutes for the catalyst to partially dry, the reactor was reassembled. The glass product condenser was rinsed with distilled water and placed in an oven to dry for approximately one hour at 200°F. The saturator water was pressured out of the saturator vessel using carbon dioxide to overcome the pressure drop caused by the glass wool filter at the bottom of the vessel. At this time a sample of saturator water from the previous experiment was collected to be analyzed. A new 200 milliliter charge of distilled water was drawn into the saturator with vacuum supplied from an aspirator. The reactor vessel was then reconnected to the system. Heating tape and insulation was reapplied to the reactor and tubing downstream of the reactor.

System operation involved bringing the system to chosen steady state conditions and then maintaining these steady state conditions until enough liquid sample was collected for chromatographic analysis. Carbon dioxide flow was started at a rate higher than the highest flowmeter reading to purge air from the system. This rate was maintained for approximately an hour. Electricity to the heating tapes was turned on. Steam and cold water flow was started to the cavity below the catalyst support plate. Variable power transformer settings along with steam and cold water valves were adjusted until the desired steady state temperatures were achieved. At this time the xenon arc lamp was started. The glass product condenser was connected to the tubing downstream of the reactor and surrounded by the cooling medium consisting of either crushed ice in a beaker or 32^{o}F salt brine pumped from the refrigerated bath.

Steady state operation was maintained until an adequate or more than adequate amount of liquid (approximately 100 to 500 microliters) for chromatographic analysis had accumulated in the glass product condenser. The experiments where a higher water to carbon dioxide ratio and higher carbon dioxide flow rates were run for shorter periods of time since less time was required to collect an adequate sample.

After an experiment was completed, the xenon arc light and the variable power transformers were turned off, and the carbon dioxide flow was turned off. The liquid product condenser was removed from its cooling medium and allowed to warm to room temperature.

Chromatographic analyses were done on the following streams: (A) the gas stream out of the product condenser during steady state operation when the chromatograph was available, (B) the distilled water used to charge the carbon dioxide saturator, (C) the saturator water after completion of an experimental run, and (D) the liquid collected in the product condenser. All sample injections were made into the Porapak Q column upstream of the flame ionization detector. The gas stream out of the product condenser was analyzed for methane by injecting a 25 microliter gas sample into the chromatograph using a gas-tight syringe. This was done after an hour or more of steady state operation on the days when the chromatograph was available. The distilled water was analyzed to be sure it contained no methanol. Liquid sample volumes were usually five microliters. Saturator water was analyzed for methanol after each experiment since the carbon dioxide feed appeared to contain trace amounts of methanol which could have built up in the saturator water over the duration of the experiment. Liquid samples were drawn from the product condenser and analyzed for methanol. Any methanol produced was expected to condense along with the water in the reactor effluent stream. Methanol production rates were calculated as shown in Appendix G. Experiments using ultraviolet light and catalyst at the various residence times and water to carbon dioxide ratios were performed twice.

Blank experiments were run using no light and no catalyst. These experiments were performed at all four water to carbon dioxide ratios at the longest and second longest reactor residence times. These experiments were intended to see if methanol production was due to light and catalyst or some other factors.

CHAPTER V

EXPERIMENTAL RESULTS

Experiments were designed to determine (A) if a flat plate, gas phase photochemical reactor can produce methanol from carbon dioxide and water, (B) what yields might be expected, (C) the effect of different operating conditions on yields, and (D) what changes might improve the reactor's operation. The batch experiments involved trying a variety of reactor conditions in hopes of detecting any methanol production. The continuous flow reactor experiments were attempts at not only finding reactor conditions at which methanol was produced, but also quantifying methanol production.

Batch Reactor Experiments

The analyses of the reactor contents would at times indicate the presence of trace quantities of methanol. None of the methanol peaks were large enough to be integrated by the chromatograph. The smallest amount of methanol that could be detected and integrated was 5×10^{-4} micromoles which is 450 parts per million by volume in a 25 microliter vapor sample. Therefore, any methanol produced was present at less than this concentration in the 25 microliter vapor samples drawn during the experiments.

After successfully producing a small amount of methanol during the first experiment following approximately an hour of illumination, the goal became discovering conditions which would increase the amount of methanol produced. However, after intermittently producing the same size methanol peaks in three experiments, a period of a month was spent performing fifteen experiments where not even a slight indication of methanol appeared. One other experiment produced a methanol peak. Table I lists the results for each experiment described in Appendix A.

Continuous Flow Reactor Experiments

The continuous flow reactor experiments produced a liquid product. This liquid product was analyzed for methanol. Methanol peak area from the chromatograph was converted to a methanol production rate in micromoles per hour by the method described in Appendix G. Reactor residence time calculations are also described in Appendix G. Since reactor feed rate varied, the best way of comparing methanol from the different experiments was to calculate the micromoles of methanol produced per mole of carbon dioxide in the reactor feed.

Experimental results using ultraviolet light and catalyst are given in Table II. For comparison purposes, experimental results where no light or catalyst was used are

TABLE I

RESULTS OF BATCH REACTOR EXPERIMENTS

Experiment Number	Methanol Production Indicated	Comments
1	Yes	Unintegrated methanol peak after 50 minutes of illumination.
2	Yes	Unintegrated methanol peaks after 50 minutes of illumination.
3	No	
4	Yes	Unintegrated methanol peaks after 51 minutes of illumination.
5	Yes	Unintegrated methanol peaks after 50 minutes of illumination.
6-17	No	
18	Yes	An unintegrated methanol peak appeared and grew slightly after 125 minutes of illumination. Another unidentified peak at 1.3 minutes residence time appeared after 125 minutes of illumination.
19	No	There was no methanol peak, but the unidentified peak at 1.3 minutes appeared again after 10 minutes of illumination.
20	No	There was no methanol peak, but the unidentified peak appeared 56 minutes after the experiment began. There was no light used for this experiment, just reactor heat. The size of the peak grew for a while after the beginning of the experiment and decreased toward the end of the experiment.
21	No	There was no methanol peak, but the unidentified peak appeared after 10 minutes of illumination. This experiment used no catalyst.

TABLE I (Continued)

Experiment Number	Methanol Production Indicated	Comments
22	No	There was no methanol peak, but the unidentified peak at about 1.3 minutes residence time appeared approximately 52 minutes after the beginning of the experiment.
23	No	There was no methanol peak, but the unidentified peak at 1.3 minutes residence time appeared after approximately 40 minutes of illumination and got larger and then smaller during the experiment. It was never large enough to integrate.
24	No	There was no methanol peak. There was a small unidentified peak which appeared after about 73 minutes of illumination.
25	No	There were no peaks of any kind.

For chronology of experiments, see Table IX, Appendix I.

given in Table III. For any one sample, chromatographic analyses would sometimes give quite large variations in methanol peak area. Usually this variation was due to the chromatograph interpreting and integrating the peaks differently on any successive sample injection. For this reason maximum and minimum methanol production rates are given in Table II and III corresponding to maximum minimum peak areas listed by the chromatograph.

TABLE II

METHANOL PRODUCTION FROM CONTINUOUS FLOW REACTOR EXPERIMENTS, CATALYST AND ULTRAVIOLET LIGHT USED

Experiment Number	Reactor Residence Time (minutes)	Molar Water to Carbon Dioxide Ratio	Methanol Production Rate (Micromoles per hour) max.	Methanol Production Rate (Micromoles per hour) min.	Micromoles Methanol Produced Per Mole of Carbon Dioxide max.	Micromoles Methanol Produced Per Mole of Carbon Dioxide min.
1	0.14	0.3	0.028	0.024	0.61	0.53
2	0.14	0.3	0.031	0.024	0.69	0.53
3	0.14	0.3	0.041	0.040	0.90	0.88
4	0.14	0.3	0.034	0.033	0.76	0.74
5	0.14	0.3	0.019	0.018	0.43	0.40
6	0.14	0.3	0.023	0.020	0.51	0.45
7	0.14	0.9	0.074	0.071	1.65	1.59
8	0.14	0.9	0.187	0.069	4.14	1.53
9	0.14	2.0	0.144	0.140	3.28	3.18
10	0.14	2.0	0.435	0.215	9.74	4.83
11	0.14	0.03	0.002	0.002	0.05	0.05
12	1.06	0.9	0.009		1.47	
13	1.06	0.9	0.026	0.011	4.11	1.71
14	1.06	0.3	0.003	0.003	0.55	0.47
15	1.06	0.3	0.021	0.011	3.42	1.75
16	1.06	2.0	0.028	0.018	4.40	2.90
17	1.06	2.0	0.080	0.031	12.94	4.99
18	1.06	0.03	0.0003	0.0003	0.05	0.05
19	1.06	0.03	0.0003	0	0.05	0

TABLE II (Continued)

Experiment Number	Reactor Residence Time (minutes)	Molar Water to Carbon Dioxide Ratio	Methanol Production Rate (Micromoles per hour) max.	min.	Micromoles Methanol Produced Per Mole of Carbon Dioxide max.	min.
20	5.07	2.0	0.009	0.005	7.20	3.84
21	5.03	0.9	0.003	0.003	2.31	2.24
22	5.06	0.3	0.0008	0.0007	0.64	0.56
23	5.01	0.03	0.0001	0.0001	0.05	0.04
24	4.98	0.03	0.0001	0.	0.08	0.
25	5.02	2.0	0.010	0.010	7.83	7.33
26	4.99	0.9	0.002	0.002	1.79	1.65
27	4.98	0.3	0.001	0.001	1.02	0.72

For chronology of experiments, see Table IX, Appendix I.

There were a few extremely small indications of methanol in the distilled and saturator water that had been retained after an experiment. The highest quantum yield for the formation of methanol was 0.30. No methane was detected in any of the experiments. There was not sufficient time to perform experiments using no catalyst and no light at all the conditions for which experiments using catalyst and light had been performed.

TABLE III

METHANOL PRODUCTION FROM CONTINUOUS FLOW REACTOR EXPERIMENTS, NO CATALYST OR ULTRAVIOLET LIGHT USED

Experiment Number	Reactor Residence Time (minutes)	Molar Water to Carbon Dioxide Ratio	Methanol Production Rate (Micromoles per hour) max.	min.	Micromoles Methanol Produced Per Mole of Carbon Dioxide max.	min.
1	4.99	0.03	0.0002	0.0001	0.13	0.06
2	4.98	0.3	0.002	0.001	1.65	1.03
3	5.01	0.9	0.003	0.002	2.06	1.48
4	4.97	2.0	0.012	0.006	8.89	4.53
5	1.06	0.3	0.004	0.003	0.61	0.53
6	1.06	0.9	0.009	0.009	1.38	1.37
7	1.06	2.0	0.027	0.022	4.32	3.42
8	0.14	2.0	0.184	0.160	4.19	3.64

For chronology of experiments, see Table IX, Appendix I.

CHAPTER VI

DISCUSSION

In this chapter the results of the batch reactor experiments and the continuous flow reactor experiments will be discussed. These results will partially answer the questions posed in the introduction. A comparison of these results to those of Aurian-Blajeni et al. (2) will be made.

The questions which were to be answered by this study are:

1. Does a flat plate, gas phase photochemical reactor produce methanol from carbon dioxide and water?
2. What methanol yields can be expected?
3. How does the reactor perform at different operating conditions?
4. What changes might improve the reactor's operation?

Finding answers to these questions was rather difficult. The following short answers will be followed by a more detailed discussion. In answer to the first question, methanol was produced, but it was probably not produced by a photochemical reaction. Methanol yields of up to 12.9 micromoles per mole of carbon dioxide were obtained. These yields are of the same order of magnitude as yields indicated by Aurian-Blajeni et al. (2). Highest methanol yields resulted when the highest water to carbon dioxide ratios existed in the reactor feed. There was also an indication that longer reactor residence times resulted in higher methanol yields. Answering the fourth question involves trying modes of operation different from those used in experiments performed for this study such as operating a higher pressure reactor, operating with longer residence times, and finding a better means of catalyst support which would allow more catalyst-reactant contact.

Batch Reactor Experiments

The batch reactor experiments were done using a quartz-tungsten-halogen light source with no filtration. This lamp did emit light in the wavelengths below 413 nanometers, the wavelength corresponding to the band gap energy for strontium titanate. This light was used because the xenon arc lamp used in the continuous flow reactor experiments had not yet arrived from the manufacturer.

After performing the first batch experiment and getting a very small non-integrated peak on the chromatograph following approximately 60 minutes of reactor illumination, it was hoped that some modification to the experiment would increase the amount of product formed. The peak appeared to have been caused by methanol since injections of methanol solutions into the chromatograph had produced a similar residence time. A second experiment using the same semiconductor material and water charge gave approximately the same results.

Before the next batch experiment, a continuous flow experiment was performed using the same catalyst. No indication of methanol could be found by injecting gas samples taking from the reactor outlet tubing.

Batch experiment number 3 was done immediately after the flow reactor experiment. The same catalyst and water charge which had been used in all of the previous experiments was also used for this experiment. No indication of methanol production was found. There was a possibility that the catalyst had been deactivated so the catalyst was removed from the reactor.

Before another catalyst charge was attached to the catalyst support plate, an experiment using no catalyst was performed. A small non-integrated peak of approximately the same size and residence time as in previous experiments appeared. This result tended to indicate that possibly the catalyst had not been involved in producing the peaks found in earlier experiments. Wagner and Somorjai (36), involved in photocatalytic hydrogen production from water on strontium titanate single crystals, obtained a low rate of hydrogen production from their reactor loop in the absence of strontium titanate. Their reaction chamber was made of stainless steel, but the materials used in the remainder of the reactor loop were not listed. The very small non-integrated peaks that had been produced in this study could possibly have been some sort of background methanol production.

A new catalyst and water charge was used in the fifth experiment. Again after approximately 50 minutes of reactor illumination a small methanol peak emerged as had occurred with the first catalyst and water charge. This result gave some confidence in the reproducibility of the experiment. Now measures needed to be taken for yield improvement. In water splitting studies using strontium titanate single crystals, Wagner and Somorjai (36) found it necessary to coat the crystals with sodium hydroxide to achieve hydrogen production. Although strontium titanate powder rather than single crystals were used for this study, there was a chance that coating the powder with sodium hydroxide could enhance hydrogenation of carbon dioxide into methanol. In the sixth experiment where two drops of saturated sodium hydroxide solution were placed on the catalyst still in place from experiment 5 and allowed to dry, no peaks were produced. Perhaps the entire catalyst surface had been covered with sodium hydroxide leaving none of the semiconductor powder exposed.

For the next eleven experiments, no indication of methanol or any other substance was found. The problem had reverted back to finding conditions in which methanol could be produced rather than trying to improve methanol yield in a batch reactor. Heat treating catalyst and providing higher water to carbon dioxide molar ratios were the two major efforts tried to obtain methanol production.

Aurian-Blajeni et al. (2) had observed the greatest methanol production, when the semiconductor powders used had been heat treated in a vacuum at 600°C for six hours. Facilities to provide this type of heat treatment were not available, but it was believed that any heat treatment could not hurt and would probably be better than none at all. The strontium titanate may have adsorbed oxygen from the atmosphere when the strontium titanate container was opened to remove the powder for the earlier experiments; however, it is very unlikely that the strontium titanate had been kept from exposure to air from the time of its manufacture to its arrival at Oklahoma State University. A few different catalyst treatment conditions were used as described in Appendix A, Description of Batch Reactor Experiments. The use of treated catalyst alone made no difference. No methanol was produced.

Another possible method of improving methanol production chances was to inject distilled water into the reactor and then heat the reactor to drive more and more water into the vapor phase. Experiment number 18 was the first where this technique was tried. Water had been injected in experiment 17, but the reactor had not been heated. Approximately two hours after the start of the experiment, 0.7 microliter of water was injected into the reactor. Approximately fifty minutes later, one microliter of distilled water was injected into the reactor. In order to vaporize some of the water which had been injected, the reactor was wrapped with heat tape and insulated. The heat tape was turned on approximately 45 minutes after the last water injection. Within 25 minutes after the heat tape was turned on, both an unintegrated methanol peak at approximately 4.9 minutes and another unidentified peak of approximately 1.8 minutes residence time appeared on the chromatogram. The experiment was continued for two more hours during which both peaks remained. The following day a 0.5 microliter sample of the saturator water was injected into the chromatograph. A very slight bump was observed at the expected methanol residence time and the earlier unidentified peak could have been hidden in the water peak. The column had not been conditioned sufficiently so the water peak was broad enough at the bottom to have included the unknown peak. A sample of the distilled water which had been injected was not analyzed.

There is the possibility that the material causing the two peaks could have been in the water which had been injected or that a very small amount of methanol actually was being formed and was concentrated by a method described below. As the reactor was heated, more water would go into the vapor phase raising the dew point of the reactor contents. When the syringe at ambient temperature was used for reactor gas sampling, the syringe could have condensed water out of the gas. Condensation may have created a driving force capable of drawing into the syringe a larger sample than would have been collected if no condensation had occurred. As the gas sample dew point was raised, the driving force and the actual sample amount would have increased because the increased water condensation would make room available in the syringe for additional sample. Assuming methanol formed would also condense with the water, the amount of methanol injected into the chromatograph would have increased over time by virtue of more methanol being formed by reaction and the concentration effect just described. This concentration effect may have been responsible for the slightly increasing peak area with time. Nevertheless, the peak areas were too small to be integrated even at very high chromatograph sensitivity settings.

None of the remaining seven experiments produced methanol. The small unidentified peak did appear again in most of the remaining experiments, but only at very low levels. Also, in all of the experiments where water was injected followed by reactor heating, there was no way of avoiding liquid condensation in the gas sampling syringe because the syringe was below the dew point temperature of the mixture. This problem was avoided in the continuous flow experiments by condensing and analyzing a liquid rather than a vapor product. Condensing water and reaction products out of the reactor effluent stream acted to concentrate these products making them easier to detect.

Continuous Flow Reactor Experiments

The continuous flow reactor experiments did produce detectable, integrateable levels of methanol. A comparison of Table II and Table IV indicates that some of the methanol production rates expressed as micromoles of methanol produced per mole of carbon dioxide feed are of the same order of magnitude as the results obtained by Aurian-Blajeni et al. (2). The actual rates of methanol production in micromoles of methanol produced per hour are usually much lower due to the lower carbon dioxide feed rates and smaller reactor used for this study.

An approximate quantum yield for methanol production was calculated for the highest methanol production rate. The reactor was not designed to be able to acquire light absorption information required for quantum yield calculation. Instead, information concerning light intensity was obtained from the Oriel catalog (27). Light absorption by the strontium titanate was assumed to be 100 percent. A description of quantum yield calculations is given in Appendix G.

Figures 7, 8, and 9 indicate a trend to higher methanol production as the water to carbon dioxide mole ratio in the reactor feed increases. This result seems reasonable since the higher the water to carbon dioxide ratios, the higher the hydrogen to oxygen ratio. A higher hydrogen to oxygen ratio would be more conducive to the reduction process. It

TABLE IV

METHANOL PRODUCTION REPORTED BY AURIAN-BLAJENI ET AL. (2) FOR EXPERIMENTS WHERE CARBON DIOXIDE FLOW RATE IS LISTED

Catalyst Used	Experiment Type*	Methanol Production Rate (Micromoles per hour)	Micromoles Methanol Produced Per Mole of Carbon Dioxide
$SrTiO_3$	1	7.16	16.3
$SrTiO_3$	1	6.85	15.6
TiO_2	1	0.56	3.37
$BaTiO_3/HgS$	1	0.29	1.15
SiC	1	0.1	0.44
$BaTiO_3$	2	<0.01	<0.41
$CaTiO_3$	2	0.25	31.1
Fe_2O_3	2	0.06	0.86
TiO_2	2	0.04	1.87
TiO_2	2	<0.01	0.83
Pb_3O_4	2	2.6-1.3	10.2-5.11
TiO_2	3	0.56	0.84

*Experiment Types

1 - Carbon dioxide bubbled through liquid water with semiconductor powder suspended in water.

2 - Carbon dioxide saturated with water vapor with catalyst slurry brushed onto glass tube.

3 - Carbon dioxide saturated with water vapor with catalyst slurry brushed onto glass tube.

Type 1 and 2 light source - 70 watt mercury arc lamp.
Type 3 light source - direct sunlight.

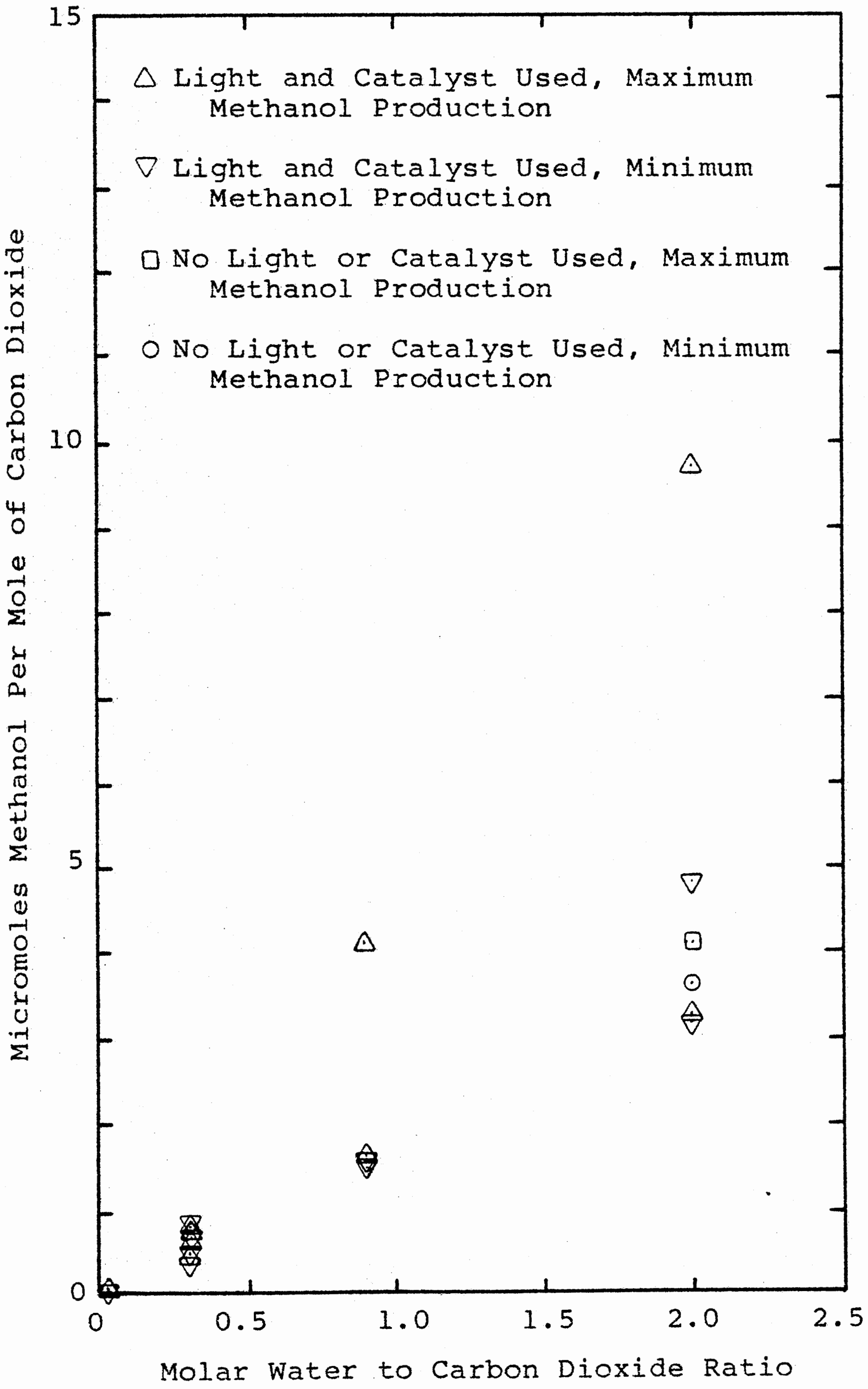


Figure 7. Continuous Flow Reactor Experiment Results, 0.14 Minute Reactor Residence Time

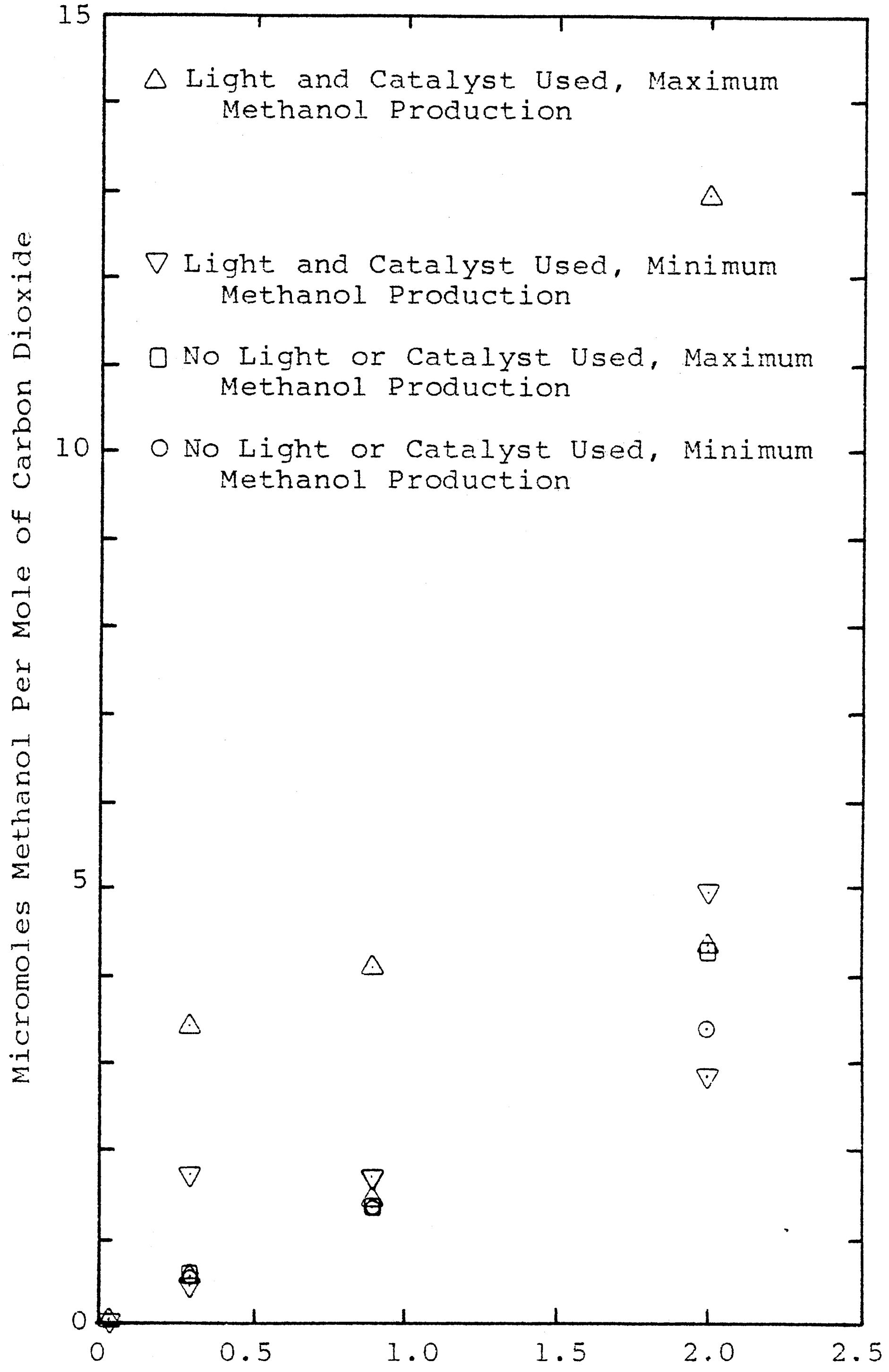


Figure 8. Continuous Flow Reactor Experiment Results, 1.06 Minutes Reactor Residence Time

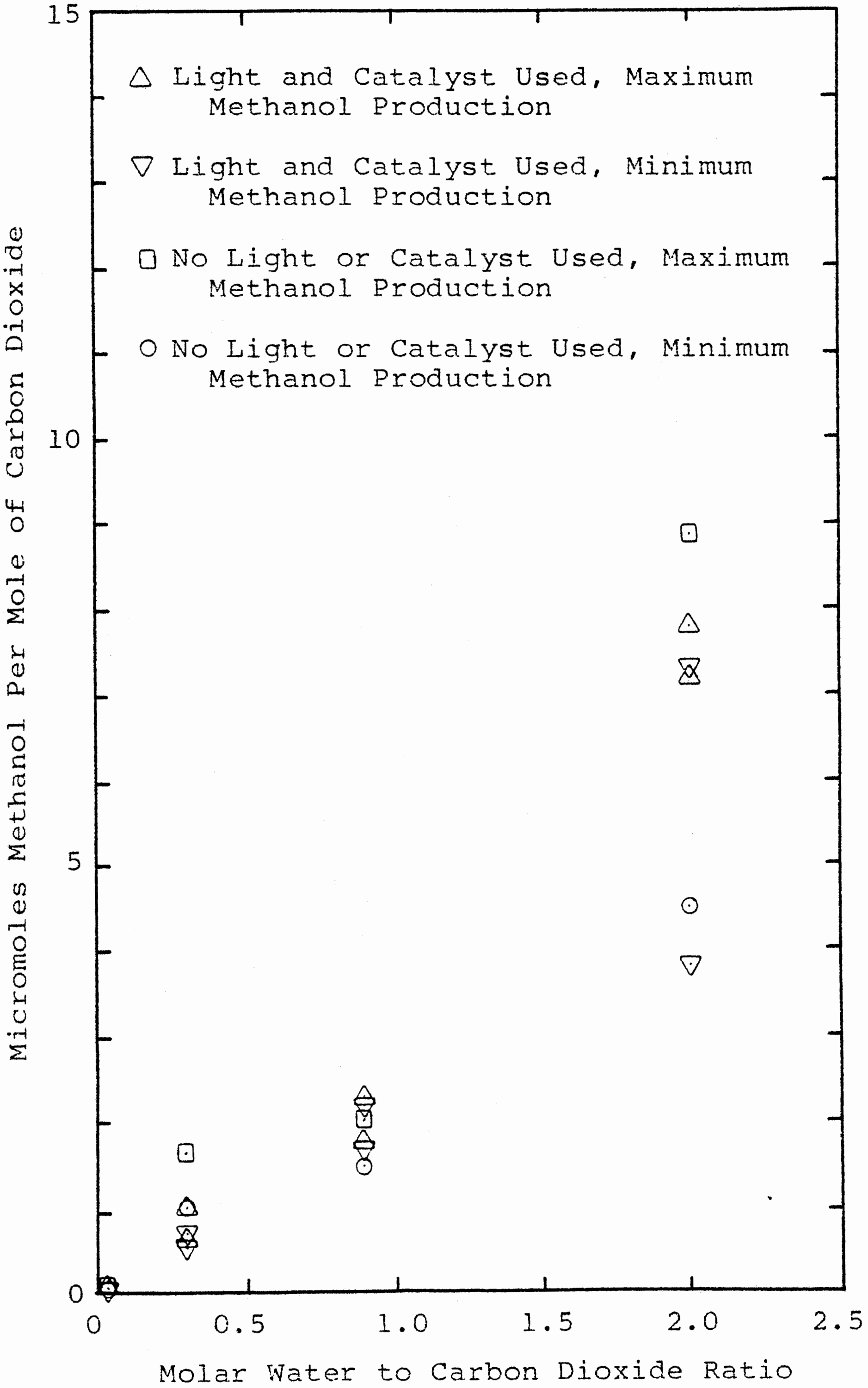


Figure 9. Continuous Flow Reactor Experiment Results, 5.0 Minutes Reactor Residence Time

is difficult to notice a trend with respect to reactor residence time. The higher residence times appear, in most cases, to give the greatest methanol yields at any water to carbon dioxide ratio.

Experiments where no light or strontium titanate were used in the reactor indicate that photoreduction on a semiconductor powder is not the driving force behind the methanol formation reaction observed in this study. The eleven experiments conducted without either light or catalyst produced methanol amounts in the same order of magnitude as the experiments where the reactor contained strontium titanate and the reactor was illuminated with the xenon arc lamp. The experiments not employing strontium titanate or reactor illumination showed the same methanol yield increase with increasing water to carbon dioxide ratios as did the experiments where strontium titanate and reactor illumination was used. Aurian-Blajeni et al. (2) do not mention any experiments performed without catalyst or reactor illumination.

The results from this study appear to indicate that the methanol produced may not be due to a photocatalytic reaction. The thermodynamic equilibrium constant calculated for the methanol formation reaction is less than 9×10^{-99} at 192°F as would be expected for a reaction reversing combustion (29). The stainless steel tubing, saturator and reactor are not necessarily chemically inert, and there is a slight possibility that these components may have been involved in the methanol forming reaction. The effect, if any, of the stainless steel system on the experiment results could be determined by replacing the stainless steel tubing with glass tubing and repeating experiments. Any significant change in results would signal the influence of the metal system. If the whole system volume downstream of the carbon dioxide saturator could be considered the reactor, then the reactor residence time would be 30.8 minutes instead of approximately five minutes when only the reactor cavity is considered for the highest residence time experiments performed for this study.

Another possible reason why methanol production was indicated in the experiments might have been the use of carbon dioxide contaminated with methanol. No indication of methanol was found when 25 microliter samples of the carbon dioxide used in the experiments were injected into the column upstream of the chromatograph's flame ionization detector. However, the experimental method used could have concentrated methanol whether it had been introduced into the system along with the carbon dioxide or had been produced in the reactor. Also, the increase in methanol production with increasing system temperature appears possible if the carbon dioxide was contaminated with methanol. As the system temperature was increased, the methanol coming into the system with the carbon dioxide would have been decreasingly soluble in the saturator water and more methanol would have passed on to the product condenser. Big Three Industries, the carbon dioxide supplier, indicated that the carbon dioxide was a byproduct of a natural gas separation plant. Although no further investigation into the gas's origin was done, methanol may have been used in the natural gas separation process as a hydrate formation preventative and could have remained with the carbon dioxide stream in trace amounts (10). Saturator water was analyzed after every experiment, and a few analyses indicated a trace of methanol. If methanol had been entering the system with the carbon dioxide, its buildup would probably not have been noticed in the 200 milliliters of saturator water since this water was replaced after every continuous flow experiment.

As can be seen from the results, Tables II and III, there was quite a lot of variation in the analysis of product from one experiment. This variation was usually due to the way in which the chromatograph defined and integrated the methanol peak. Peak areas for the same peak definition method and integration were nearly the same. However, different peak definition methods could cause peak areas to vary by as much as 75 percent.

In cases where duplicate experiments were run, there is even more variation. The difference may, in part, be explained by the difficulty in maintaining steady state operation throughout the duration of the experiment. There was no automatic control of carbon dioxide flow rate or system temperatures. In experiments where the reactor residence time was approximately five minutes, experiments would have to run overnight or over a weekend just to get a large enough sample to inject into the chromatograph. This meant that the system had to operate unattended for hours and in a few instances days at a time because there was no additional manpower available to continuously monitor the system. In nearly every case the saturator temperature which determines the water to carbon dioxide ratio was within 15°F of the desired temperature and usually within 10°F of this temperature upon resumption of system monitoring. The carbon dioxide flow rate was usually the same before and after a period during which the experiment ran without monitoring.

CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

Batch Reactor Experiments

1. Product sampling from reactor where contents are above the dew point temperature at atmospheric pressure is very difficult due to moisture condensation in sampling syringe.

2. If the reactor had been cooled sufficiently to condense any water and reaction products, the condensed material would have been spread too thin to collect it in a liquid sampling syringe. With a feed water to carbon dioxide ratio of 0.03 to 1.0 (at 75°F) and a total batch reactor volume (illuminated and un-illuminated sections) of 6.7 milliliters, there would have been 0.15 microliters of water in the reactor. This amount is hardly enough liquid for one sample even if it could be collected from all areas of the reactor.

3. In this reactor, residence time is difficult to determine because the path the reactant molecule takes into and out of the illuminated region of the reactor is difficult to determine.

4. Due to a reactant dew point temperature which is above ambient temperature at some system operating conditions and extremely low product yields, this reaction vessel and system appear to be better suited for continuous operation.

Continuous Flow Reactor Experiments

The four questions posed in the Introduction are best answered at this point. The numbers correspond to those earlier question numbers.

1. The system used for this study did produce methanol. The observed methanol production was probably not due to photoreduction of the carbon dioxide on strontium titanate since experiments with and without reactor illumination and strontium titanate on the catalyst support plate yielded approximately the same methanol amounts. There is a slight chance that methanol may have been produced by catalytic action of the stainless steel tubing and reactor. Another possibility is that methanol production detected may have come from carbon dioxide contaminated with trace amounts of methanol.

2. Extremely small yields can be expected. The maximum yield obtained was 12.9 micromoles of methanol per mole of carbon dioxide.

3. Higher methanol yields were obtained as the water to carbon dioxide ratio in the feed and system temperature increased. This result appears reasonable since the higher

water to carbon dioxide ratio corresponds to a higher hydrogen to carbon dioxide ratio as stated in the Discussion. The effect of residence time is much less pronounced, but it appears that higher residence times may result in slightly higher methanol production.

4. Changes which might improve the reactor's operation are described in item numbers 3, 4, 5, 6 and 7 below.

Recommendations

Batch Reactor Experiments

1. If experiments are performed in a batch mode in this reaction vessel, longer illumination periods should be used since very little product had been indicated in the usual two hour total of the 10 minute illumination periods used for this study.

2. This reactor vessel should probably not be used as a batch reactor because of the difficulty in product sampling.

Continuous Flow Reactor Experiments

1. Replace the stainless steel tubing in the system with glass tubing in a couple of increments to determine if a change in stainless steel surface area has an effect on methanol production.

2. To determine whether or not trace amounts of methanol exist in the carbon dioxide feed, bubble carbon dioxide through approximately five milliliters of water for a day.

Analyze this water for methanol content. A potential method for removing methanol from a contaminated carbon dioxide stream might be to bubble carbon dioxide through a large volume of cool water to absorb methanol before sending the carbon dioxide on to the saturator.

3. Develop an apparatus which can be used to heat treat the semiconductor powder catalyst in a vacuum and use these heat treated powders in the reactor.

4. Try using other semiconductor powders. Powders used by Aurian-Blajeni et al. (2) would be good choices initially.

5. Use platinized semiconductor powders to repeat the experiments done for this study (3).

6. Develop the capability to flow reactants through catalyst powder rather than over a catalyst-covered surface. This catalyst arrangement might provide better reactant-photoactivated catalyst contact and measureable photoreduction of carbon dioxide. A glass tube with catalyst retainers at either end of the catalyst charge might suffice. Aurian-Blajeni et al. (2) propose that "possibly by packing thicker layers of the semiconductor coatings for the gas-solid reactions, comparable yields [comparable to liquid water-solid reactions] of reduced carbon products may be achieved."

7. Future experiments should include system operation at higher than atmospheric pressure. For an increase in pressure in gas reactions, conversion should rise since the

number of moles decreases with the methanol formation reaction (19).

8. Repeating the experiments at least three times for each set of conditions would help increase confidence in the results.

9. The origin of chromatograph peaks arising in addition to the methanol peak should be determined. During this study, usually two other peaks were integrated. The peak areas were usually the same order of magnitude or less than the methanol peak area. Due to the very low threshhold setting of the chromatograph, the peaks may or may not have been caused by a chemical substance. There is a possibility that chromatograph pressure fluctuations caused by the vaporization of the liquid sample in the sample injection port could have caused at least one of the peaks.

10. Control elements in the apparatus should be replaced with control elements allowing tighter control of system conditions. Install a micrometer flow control valve on the carbon dioxide line upstream of the carbon dioxide flowmeter. Install needle valves in the steam tubing and cold water tubing going to the reactor for tighter control of reactor temperature. Ideally a reactor temperature control system should be installed to vary cold water flow rate at some fixed steam rate. Also, a refrigerated bath thermostat with a temperature range of one to two degrees Farenheit rather than ten would be desirable although not as necessary as better control valves.

11. Replace the Teflon gasket material in the reactor with material that does not permanently deform when the reactor clamp is tightened. This is especially important for reactor operation above atmospheric pressure. Although experiments at pressures above atmospheric were not done for these studies, some reactor pressure testing was done. After a couple of experiments, reactor pressure testing at pressures around 15 psig usually indicated leaks which were significant in size compared to the normal carbon dioxide flow rate through the reactor. Replacement with another new Teflon gasket would stop the leak. However, it became a nuisance to replace the gasket after every three or four experiments so the Teflon gasket was used for approximately 10 experiments since reactor operation was at atmospheric pressure. A more permanent gasket able to continue sealing the reactor for twenty experiments or more would be desirable.

Summary

In summary, the small amounts of methanol produced in this study appear to have resulted from catalytic action by the stainless steel in the system or contaminated carbon dioxide rather than from a photocatalytic reaction. This was indicated after obtaining approximately the same results with or without reactor illumination and strontium titanate in the reactor.

A SELECTED BIBLIOGRAPHY

1. Åkermark, B., U. Eklund-Westlin, P. Baeckström and R. Löf. "Photochemical, Metal-promoted Reduction of Carbon Dioxide and Formaldehyde in Aqueous Solution." Acta Chemica Scandinavica, B 34, (1980), pp 27-30.

2. Aurian-Blajeni, B., M. Halmann, and J. Manassen. "Photoreduction of Carbon Dioxide and Water into Formaldehyde and Methanol on Semiconductor Materials." Solar Energy, Vol. 25, (1980), pp 165-170.

3. Bard, A. J. "Solar Energy Conversion At Semiconductor Electrodes." The Third Conference On Cooperative Advances In Chemical Science And Technology Proceedings., (1981), pp 28-35.

4. Boer, K. W. "The Solar Spectrum at Typical Clear Weather Days." Solar Energy, Vol. 19, (1977), pp 525-538.

5. Bolton, J. R. "Photochemical Conversion and Storage of Solar Energy." Journal of Solid State Chemistry, Vol. 22, (1977), pp 3-8.

6. Bolton, J. R. "Solar Fuels." Science, Vol. 202, (1978), pp 705-711.

7. Calvert, J. G. and J. N. Pitts, Jr. Photochemistry. New York: John Wiley and Sons, 1966.

8. Carr, R. G. and G. A. Somorjai. "Hydrogen Production from Photolysis of Steam Adsorbed Onto Platinized $SrTiO_3$." Nature, Vol. 290, (1981), pp 576-577.

9. Castellan, G. W. Physical Chemistry. Reading, Massachusetts: Addison-Wesley Publishing Company, 1964.

10. Engineering Data Book. 9th Ed. Tulsa, Oklahoma: Gas Processors Suppliers Association, 1972.

11. Erbar, J. H. Documentation of the GPA*SIM Program. Tulsa, Oklahoma: Gas Processors Association, August, 1980.

12. Fujishima, A. and K. Honda. "Electrochemical Photolysis of Water at a Semiconductor Electrode." Nature, Vol. 238, (1972), pp 37-38.

13. Garrison, L. M., L. E. Murray and A. E. S. Green. "Ultraviolet Limit of Solar Radiation at the Earth's Surface With a Photon Counting Monochromator." Applied Optics, Vol. 17, No. 5, (1978), pp 683-684.

14. Gribbin, J. "Fossil Fuel: Future Shock?" New Scientist, Vol. 79, (1978), pp 541-543.

15. Hemminger, J. C., R. Carr, W. J. Lo and G. A. Somorjai. "Photochemical Processes at the Solid-Gas Interface--The Adsorption and Reactions of Gaseous CO_2 and H_2O on Pt-$SrTiO_3$ Single-Crystal Sandwiches." Interfacial Photoprocesses: Energy Conversion and Synthesis, ed. M. S. Wrighton. Advances in Chemistry Series No. 184. Washington, D. C.: American Chemical Society, 1980.

16. "Recent Energy Outlook is More Reassuring." Industry Week, March 23, 1981, pp 46 and 49.

17. Janssen-Hering, A. and H. Janssen. "Kohlendioxid als Chemierohstoff." Umschau, Vol. 81, (1981), pp 67-70.

18. Keeling, C. D. "Atmospheric Carbon Dioxide in the 19th Century." Science, Vol. 202, (1978), p 1109.

19. Levenspiel, O. Chemical Reaction Engineering. New York: John Wiley & Sons, 1972.

20. Martin, L. R. "Use of Solar Energy to Reduce Carbon Dioxide." Solar Energy, Vol. 24, (1980), pp 271-277.

21. Mavroides, J. G., J. A. Kafalas and D. F. Kolesar. "Photoelectrolysis of Water in Cells With $SrTiO_3$ Anodes." Applied Physics Letters, Vol. 28, (1976), pp 241-243.

22. Munroe, M. and W. Shepherd. "An Assessment of Solar Energy Availability in Different Regions of the Solar Spectrum." Solar Energy, Vol. 26, (1981), pp 41-47.

23. Nozik, A. J. "Photochemical Diodes." Applied Physics Letters, Vol. 30, (1977), pp 567-569.

24. Nozik, A. J. "Photoelectrochemistry: Applications to Solar Energy Conversion." Annual Review of Physical Chemistry, Vol. 29, (1978), pp 189-222.

25. Nozik, A. J. "Photoelectrolysis of Water Using Semiconducting TiO_2 Crystals." Nature, Vol. 257, (1975), pp 383-386.

26. Nozik, A. J. "P-N Photoelectrolysis Cells." Applied Physics Letters, Vol. 29, (1976), pp 150-153.

27. Oriel Corporation Complete Catalog of Optical Systems & Components. Stamford: Oriel Corporation, 1979.

28. Schrauzer, G. N. and T. D. Guth. "Photolysis of Water and Photoreduction of Nitrogen on Titanium Dioxide." Journal of the American Chemical Society, Vol. 99, (1977), pp 7189-7193.

29. Smith, J. M. and H. C. Van Ness. Introduction to Chemical Engineering Thermodynamics. 2nd Ed. New York: McGraw-Hill Book Company, 1959.

30. Spinhirne, J. D. and A. E. S. Green. "Calculation of the Relative Influence of Cloud Layers on Received Ultraviolet and Integrated Solar Radiation." Atmospheric Environment, Vol. 12, (1978), pp 2449-2454.

31. Stein, G. "Photochemical Conversion and Storage of Solar Energy." Solar Power and Fuels ed. J. R. Bolton. New York: Academic Press, Inc., 1977.

32. Stuiver, M. "Atmospheric Carbon Dioxide and Carbon Reservoir Changes." Science, Vol. 199, (1978), pp 253-258.

33. "Costing the CO_2." Technology Review, Vol. 81, (1979), p 72.

34. Tiné, G. Gas Sampling and Chemical Analysis in Combustion Processes. New York: Pergamon Press, 1961.

35. Van Damme, H. and W. K. Hall. "On the Photoassisted Decomposition of Water at the Gas-Solid Interface on TiO_2." Journal of the American Chemical Society, Vol. 101, (1979), pp 4373-4374.

36. Wagner, F. T. and G. A. Somorjai. "Photocatalytic and Photoelectochemical Hydrogen Production on Strontium Titanate Single Crystals." Journal of the American Chemical Society, Vol. 102, (1980), pp 5494-5502.

37. Williams, R., R. S. Crandall and A. Bloom. "Use of Carbon Dioxide in Energy Storage." Applied Physics Letters, Vol. 33, (1978), pp 381383.

38. Wrighton, M. S. "The Chemical Conversion of Sunlight." Technology Review, May 1977, pp 30-37.

39. Wrighton, M. S., A. B. Ellis, P. T. Wolczanski, D. L. Morse, H. B. Abrahamson and D. S. Ginley. "Strontium Titanate Photoelectrodes. Efficient Photoassisted Electrolysis of Water at Zero Applied Potential." Journal of the American Chemical Society, Vol. 98, (1976), pp 2774-2779.

40. Wrighton, M. S., P. T. Wolczanski and A. B. Ellis. "Photoelectrolysis of Water by Irradiation of Platinized n-Type Semiconducting Metal Oxides." Journal of Solid State Chemistry, Vol. 22, (1977), pp 17-29.

APPENDIX A

DESCRIPTION OF BATCH REACTOR EXPERIMENTS

All the batch reactor experiments were done to determine (A) what operating conditions would produce methanol and (B) what conditions would affect methanol yield. A variety of conditions were tested and a description of each run is given below:

Experiment 1

Catalyst Charge Number: 1 Water Charge Number: 1

Mole Ratio of Water to Carbon Dioxide: 0.03 : 1

Lighting: Intermittent

Total Illumination Time (min.): 117

Reactor Heating: No Water Injection Into Reactor: No

Maximum Catalyst Surface Temperature (^{O}F): 93

Description

Reactor was filled and illuminated until product peaks appeared. The purpose of the experiment was to determine if product could be detected and the illumination time required for product to be detected.

Experiment 2

Catalyst Charge Number: 1 Water Charge Number: 1

Mole Ratio of Water to Carbon Dioxide: 0.03 : 1

Lighting: Intermittent

Total Illumination Time (min.): 50

Reactor Heating: No Water Injection Into Reactor: No

Maximum Catalyst Surface Temperature (^{O}F): 92

Description

This was an attempt at producing the same results as in Experiment 1.

Experiment 3

Catalyst Charge Number: 1 Water Charge Number: 1

Mole Ratio of Water to Carbon Dioxide: 0.03 : 1

Lighting: Intermittent

Total Illumination Time (min.): 68

Reactor Heating: No Water Injection Into Reactor: No

Maximum Catalyst Surface Temperature (^{o}F): 99

Description

This was the second attempt at duplicating Experiment 1. A continuous flow reactor experiment had been performed just prior to this batch experiment. This was the last experiment to use the first catalyst charge.

Experiment 4

Catalyst Charge Number: None Water Charge Number: 1

Mole Ratio of Water to Carbon Dioxide: 0.03 : 1

Lighting: Intermittent

Total Illumination Time (min.): 114

Reactor Heating: No Water Injection Into Reactor: No

Maximum Catalyst Surface Temperature (^{o}F): 97

Description

No catalyst was used in this experiment to see if methanol was produced without catalyst. All other conditions were the same as in Experiments 1 through 3.

Experiment 5

Catalyst Charge Number: 2 Water Charge Number: 2

Mole Ratio of Water to Carbon Dioxide: 0.03 : 1

Lighting: Intermittent

Total Illumination Time (min.): 85

Reactor Heating: No Water Injection Into Reactor: No

Maximum Catalyst Surface Temperature ($^{\circ}$F): 103

Description

This experiment was the first use of the second new catalyst charge. This experiment was an attempt to duplicate the experimental conditions and results of Experiment 1.

Experiment 6

Catalyst Charge Number: 2 Water Charge Number: 2

Mole Ratio of Water to Carbon Dioxide: 0.03 : 1

Lighting: Continuous

Total Illumination Time (min.): 85

Reactor Heating: No Water Injection Into Reactor: No

Maximum Catalyst Surface Temperature ($^{\circ}$F): 95

Description

Two drops of saturated sodium hydroxide solution were placed on the catalyst from Experiment 5 and allowed to dry. Sodium hydroxide application was tried due to its success at promoting hydrogen production from water using illuminated strontium titanate single crystals coated with sodium hydroxide or other basic deliquescent compounds (36). It is the first experiment during which the reactor was illuminated continuously. Reactor sampling was performed approximately every ten minutes.

Experiment 7

Catalyst Charge Number: 3 Water Charge Number: 2

Mole Ratio of Water to Carbon Dioxide: 0.03 : 1

Lighting: Continuous

Total Illumination Time (min.): 149

Reactor Heating: No Water Injection Into Reactor: No

Maximum Catalyst Surface Temperature (^{O}F): 100

Description

Conditions for this experiment were the same as for Experiment 1 except that continuous lighting was used, and samples were drawn from the reactor every ten minutes.

Experiment 8

Catalyst Charge Number: 3 Water Charge Number: 2

Mole Ratio of Water to Carbon Dioxide: 0.03 : 1

Lighting: Intermittent

Total Illumination Time (min.): 110

Reactor Heating: No Water Injection Into Reactor: No

Maximum Catalyst Surface Temperature (°F): 91

Description

This is an attempt at producing methanol peaks as in the early experiments. The only difference between conditions for this experiment and Experiment 1 is the reuse of catalyst from Experiment 7.

Experiment 9

Catalyst Charge Number: 3 Water Charge Number: 3

Mole Ratio of Water to Carbon Dioxide: 0.03 : 1

Lighting: Continuous

Total Illumination Time (min.): 154

Reactor Heating: No Water Injection Into Reactor: No

Maximum Catalyst Surface Temperature (°F): 102

Description

This experiment was a repetition of Experiment 6 except that this was the third use of catalyst charge number 3. Two drops of saturated sodium hydroxide solution were placed on the catalyst surface and allowed to dry as was done in Experiment 6.

Experiment 10

Catalyst Charge Number: 4 Water Charge Number: 3

Mole Ratio of Water to Carbon Dioxide: 0.03 : 1

Lighting: Intermittent

Total Illumination Time (min.): 80

Reactor Heating: No Water Injection Into Reactor: No

Maximum Catalyst Surface Temperature (°F): 89

Description

This was the first attempt at testing heat treated catalyst. The catalyst was heat treated by covering the bottom of a two inch diameter crucible with a thin layer of strontium titanate and placing it in an oven at 540°C for two hours using no vacuum. Treating catalyst was attempted because Aurian-Blajeni et al. (2) claimed much higher activity for vacuum heat treated titanium dioxide catalyst (600°C, for two hours in a vacuum) than for catalyst heated in air (550°C, for twenty hours). Since there were no facilities to vacuum heat treat the strontium titanate catalyst at the same conditions as Aurian-Blajeni et al. (2), heat treatment at milder conditions was performed for some of the following experiments.

Experiment 11

Catalyst Charge Number: 5 Water Charge Number: 3

Mole Ratio of Water to Carbon Dioxide: 0.03 : 1

Lighting: Intermittent

Total Illumination Time (min.): 110

Reactor Heating: No Water Injection Into Reactor: No

Maximum Catalyst Surface Temperature (^{o}F): 86

Description

Catalyst used in this experiment was heat treated by placing it in a crucible and heating in an oven at 500^{o}C for two hours and fifteen minutes. After removal from the oven, the crucible was covered with an inverted glass beaker. Helium was flowed into the beaker forming an inert gas blanket as the catalyst was cooling. Instead of making a water slurry with this catalyst, the dry catalyst powder was spread on the catalyst support plate.

Experiment 12

Catalyst Charge Number: 1 Water Charge Number: 3

Mole Ratio of Water to Carbon Dioxide: 0.03 : 1

Lighting: Intermittent

Total Illumination Time (min.): 117

Reactor Heating: No Water Injection Into Reactor: No

Maximum Catalyst Surface Temperature (^{o}F): 99

Description

This was the only experiment where titanium dioxide catalyst was used. No heat treatment was done on the catalyst.

Experiment 13

Catalyst Charge Number: 6 Water Charge Number: 3

Mole Ratio of Water to Carbon Dioxide: 0.03 : 1

Lighting: Intermittent

Total Illumination Time (min.): 90

Reactor Heating: No Water Injection Into Reactor: No

Maximum Catalyst Surface Temperature (^{o}F): 93

Description

This was an attempt to duplicate Experiment 1 conditions to see if the product peaks could be produced again. A new O-ring was placed under the quartz reactor window. The new O-ring was used because there was suspicion that some previous product peaks may have been chemicals which had been driven out of the O-ring material by heat from the light source. There was no catalyst treatment.

Experiment 14

Catalyst Charge Number: 6 Water Charge Number: 3

Mole Ratio of Water to Carbon Dioxide: 0.03 : 1

Lighting: Intermittent

Total Illumination Time (min.): 60

Reactor Heating: No Water Injection Into Reactor: No

Maximum Catalyst Surface Temperature (^{o}F): 90

Description

This again was an attempt to duplicate Experiment 1. Since all the batch experiments began by flowing the reaction mixture through the reactor and then closing first the reactor outlet valve and then the reactor inlet valve, there was a possibility that pressure could have built up in the reactor between the time the outlet valve and the inlet valve was closed. In this experiment a slightly longer than normal time (approximately 30 seconds) was taken to close the reactor inlet valve after having closed the outlet valve. Pressure built up to 0.1 psig, and the experiment was run. Untreated catalyst was used for this experiment.

Experiment 15

Catalyst Charge Number: None Water Charge Number: 3
Mole Ratio of Water to Carbon Dioxide: 0.03 : 1
Lighting: Intermittent
Total Illumination Time (min.): 92
Reactor Heating: No Water Injection Into Reactor: No
Maximum Catalyst Surface Temperature (^{o}F): 93

Description

This experiment was done to duplicate Experiment 4. No catalyst was used in this experiment.

Experiment 16

Catalyst Charge Number: 7 Water Charge Number: 3

Mole Ratio of Water to Carbon Dioxide: 0.03 : 1

Lighting: Intermittent

Total Illumination Time (min.): 100

Reactor Heating: No Water Injection Into Reactor: No

Maximum Catalyst Surface Temperature ($^{\circ}$F): 89

Description

This experiment was the first use of another vacuum heat treated catalyst. The catalyst was placed in an uncovered vial which was placed in a glass container connected to a vacuum pump. The glass container was placed in an oven at 250°F. There was no vacuum gauge on the vacuum system. If positive results had been obtained from this catalyst, heat treating conditions could have been duplicated and the vacuum could have been measured.

Experiment 17

Catalyst Charge Number: 7 Water Charge Number: 3

Mole Ratio of Water to Carbon Dioxide: 0.03 : 1

Lighting: Intermittent

Total Illumination Time (min.): 103

Reactor Heating: No Water Injection Into Reactor: No

Maximum Catalyst Surface Temperature ($^{\circ}$F): 90

Description

This is a repeat of Experiment 16 using the catalyst from that experiment. This experiment was run because in Experiment 16, relatively large peaks were were produced at a residence time where methanol was expected. Experiment 17 was to verify or disprove the results of Experiment 16.

Experiment 18

Catalyst Charge Number: 8 Water Charge Number: 3

Mole Ratio of Water to Carbon Dioxide: Initially 0.03 : 1; then steadily increased throughout the experiment.

Lighting: Intermittent

Total Illumination Time (min.): 145

Reactor Heating: Yes Water Injection Into Reactor: Yes

Maximum Catalyst Surface Temperature (^{O}F): 132

Description

This was the first of a number of experiments where liquid distilled water was injected into the reactor during the experiment, and the reactor was heated to drive more and more water into the vapor phase. More water in the vapor phase gave a steadily increasing water to carbon dioxide ratio. Since the increase in water vapor tended to bring the reactants closer to a stoichiometric ratio for methanol production, there could have been an increased methanol yield. A total of 1.7 microliters of distilled water was injected into the reactor. A new charge of the same treated catalyst as was used in Experiments 16 and 17 was used in this experiment.

Experiment 19

Catalyst Charge Number: 8 Water Charge Number: 4

Mole Ratio of Water to Carbon Dioxide: Initially 0.03 : 1; then steadily increased throughout the experiment.

Lighting: Intermittent

Total Illumination Time (min.): 100

Reactor Heating: Yes Water Injection Into Reactor: Yes

Maximum Catalyst Surface Temperature (^{O}F): 118

Description

This was the second experiment where liquid water was injected into the reactor at the beginning of the experiment. Distilled water volume injected was one microliter. A new 200 milliliter distilled water charge replaced the old charge in the saturator. The reactor was again wrapped in heat tape and insulation and heated for the duration of the experiment. This experiment was essentially the same as Experiment 19 except for the new water charge in the saturator.

Experiment 20

Catalyst Charge Number: 8 Water Charge Number: 4

Mole Ratio of Water to Carbon Dioxide: Initially 0.03 : 1; then steadily increased throughout the experiment.

Lighting: None

Total Illumination Time (min.): 0

Reactor Heating: Yes Water Injection Into Reactor: Yes

Maximum Catalyst Surface Temperature (^{O}F): 96

Description

This experiment was performed exactly like Experiment 19 except no illumination was used. This was done to compare results with and without the use of a light source.

Experiment 21

Catalyst Charge Number: None Water Charge Number: 4

Mole Ratio of Water to Carbon Dioxide: Initially 0.03 : 1; then steadily increased throughout the experiment.

Lighting: Intermittent

Total Illumination Time (min.): 82

Reactor Heating: Yes Water Injection Into Reactor: Yes

Maximum Catalyst Surface Temperature (^{O}F): 119

Description

This experiment was done in the same manner and under the same conditions as Experiments 18, 19, and 20 except no catalyst was used. No catalyst was used in this experiment so that the effect of the catalyst in Experiments 18 and 19 could be determined.

Experiment 22

Catalyst Charge Number: 9 Water Charge Number: 4

Mole Ratio of Water to Carbon Dioxide: Initially 0.03 : 1; then steadily increased throughout the experiment.

Lighting: None

Total Illumination Time (min.): 0

Reactor Heating: Yes Water Injection Into Reactor: Yes

Maximum Catalyst Surface Temperature (°F): 147

Description

This experiment was performed exactly like Experiment 20 except that a new charge of catalyst was used. The catalyst in Experiment 20 had been used two times previously.

Experiment 23

Catalyst Charge Number: 9 Water Charge Number: 4

Mole Ratio of Water to Carbon Dioxide: Initially 0.03 : 1; then steadily increased throughout the experiment.

Lighting: Intermittent

Total Illumination Time (min.): 120

Reactor Heating: Yes Water Injection Into Reactor: Yes

Maximum Catalyst Surface Temperature (°F): 126

Description

This experiment was done at the same conditions as Experiment 19.

Experiment 24

Catalyst Charge Number: 10 Water Charge Number: 5

Mole Ratio of Water to Carbon Dioxide: Initially 0.03 : 1; then steadily increased throughout the experiment.

Lighting: Intermittent

Total Illumination Time (min.): 115

Reactor Heating: Yes Water Injection Into Reactor: No

Maximum Catalyst Surface Temperature (^{o}F): 128

Description

In this experiment the catalyst slurry was spread on a one-eighth inch thick piece of Pyrex glass the same size as the reactor cavity. Since the semiconductor powder slurries in the Aurian-Blajeni et al. work had always been brushed onto a glass tube rather than a metal surface, a piece of glass which would electrically insulate the semiconductor material from the stainless steel reactor was placed on the catalyst support plate. Untreated catalyst was used in this experiment. The remainder of the experimental procedure was the same as that of Experiment 19.

Experiment 25

Catalyst Charge Number: 11 Water Charge Number: 5

Mole Ratio of Water to Carbon Dioxide: 0.03 : 1

Lighting: Intermittent

Total Illumination Time (min.): 84

Reactor Heating: No Water Injection Into Reactor: No

Maximum Catalyst Surface Temperature (^{o}F): 95

Description

This experiment was like Experiment 1 except the catalyst was spread on the glass plate used in Experiment 24 instead of being spread directly on the stainless steel catalyst support plate. Untreated catalyst was used. There was no reactor heating or water injection into the reactor. The catalyst charge had not been used in previous experiments. This was the last batch experiment.

APPENDIX B

METHANOL RESPONSE FACTORS

TABLE V

METHANOL RESPONSE FACTORS

Sample Injection Number	Sample Volume (Microliters)	Methanol Concentration (Parts per Million)	Moles of Methanol in Sample	Peak Area
1	3	10	7.45×10^{-10}	60
2	3	10	7.45×10^{-10}	54
3	3	10	7.45×10^{-10}	61
4	5	10	1.24×10^{-9}	112
5	5	10	1.24×10^{-9}	109
6	5	10	1.24×10^{-9}	108
7	1	100	2.48×10^{-9}	243
8	1	100	2.48×10^{-9}	260
9	1	100	2.48×10^{-9}	267
10	3	100	7.45×10^{-9}	883
11	3	100	7.45×10^{-9}	898
12	3	100	7.45×10^{-9}	897

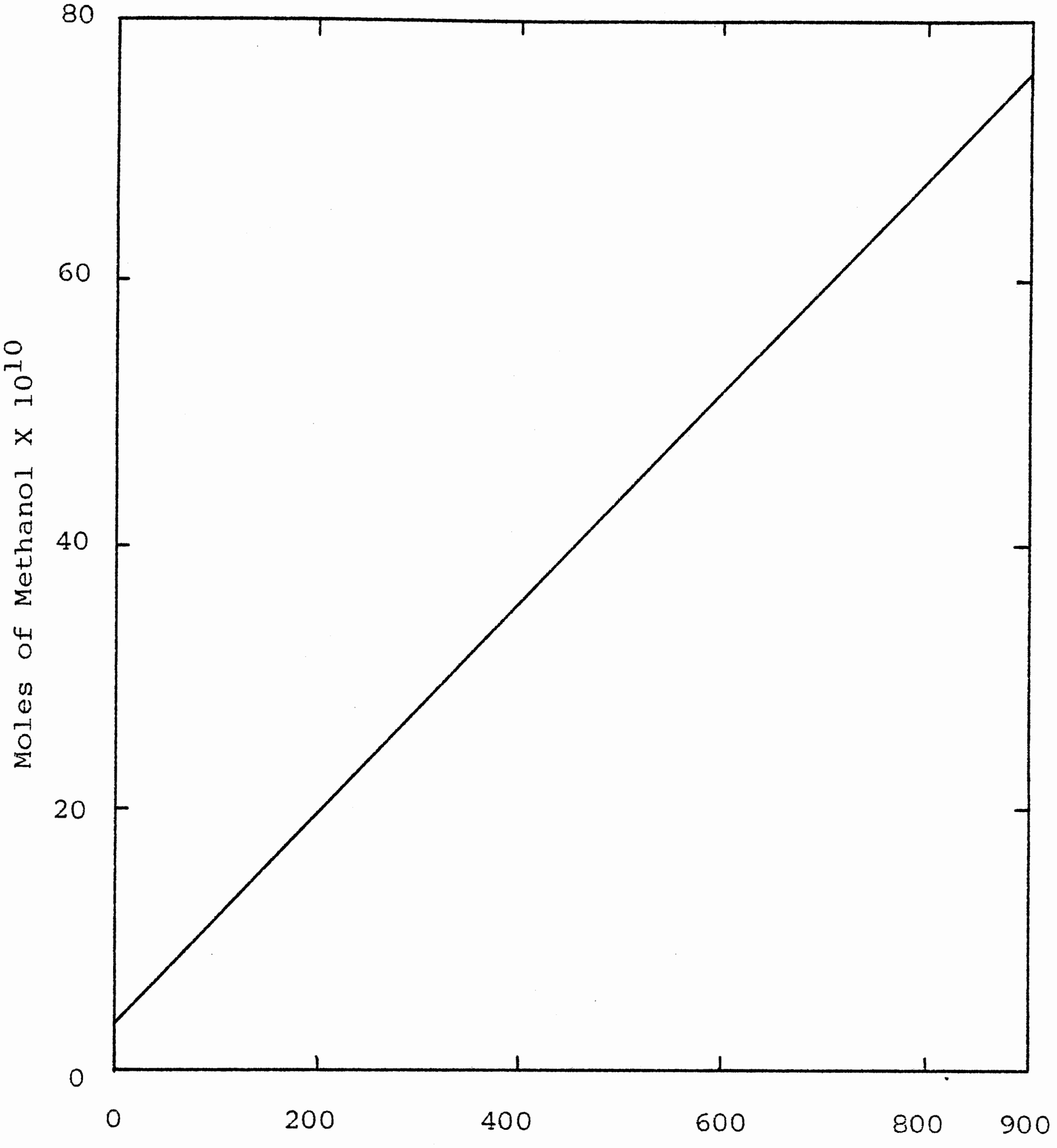


Figure 10. Methanol Response Factors

APPENDIX C

SPECTRAL IRRADIANCE OF LIGHT SOURCES

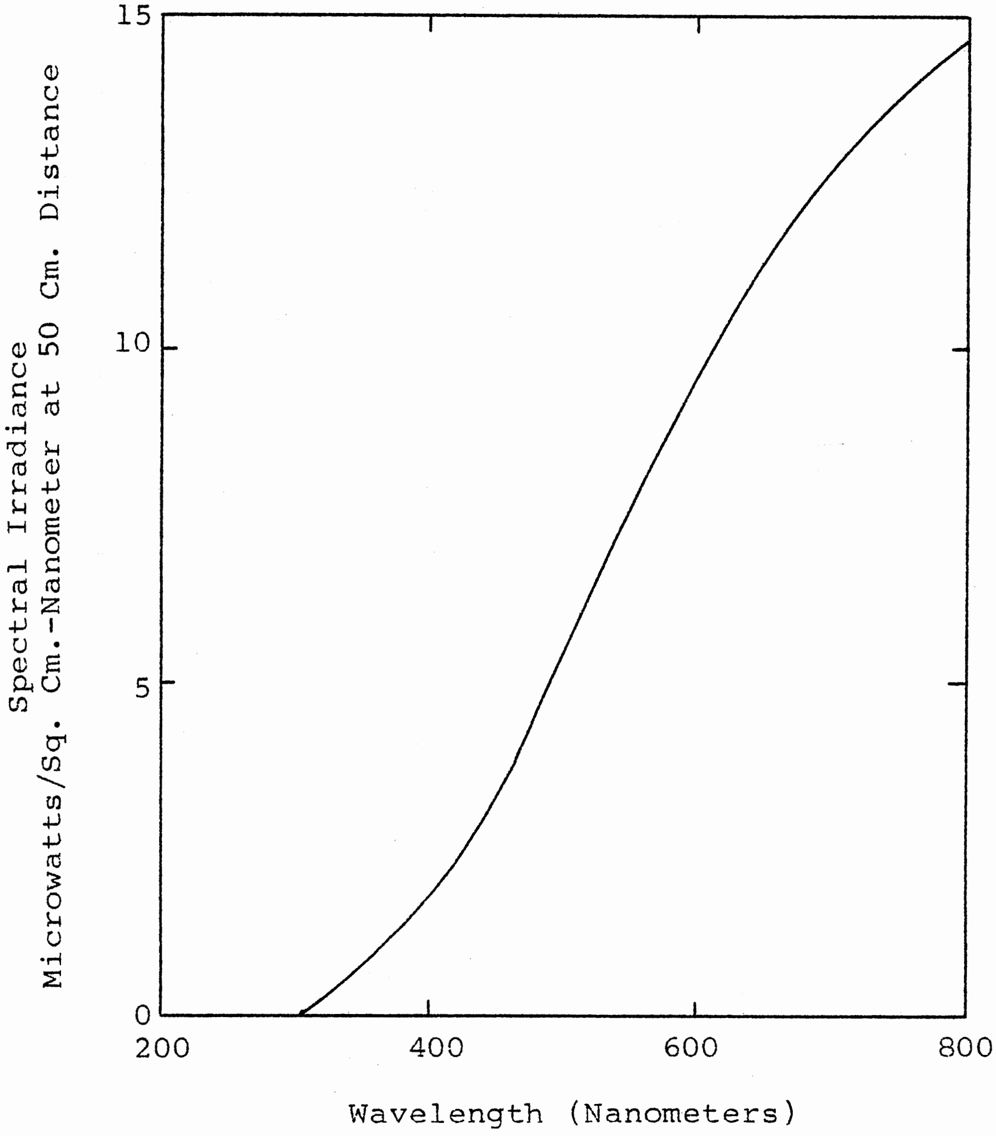


Figure 11. Output Spectra for Quartz Tungsten-Halogen Light Source

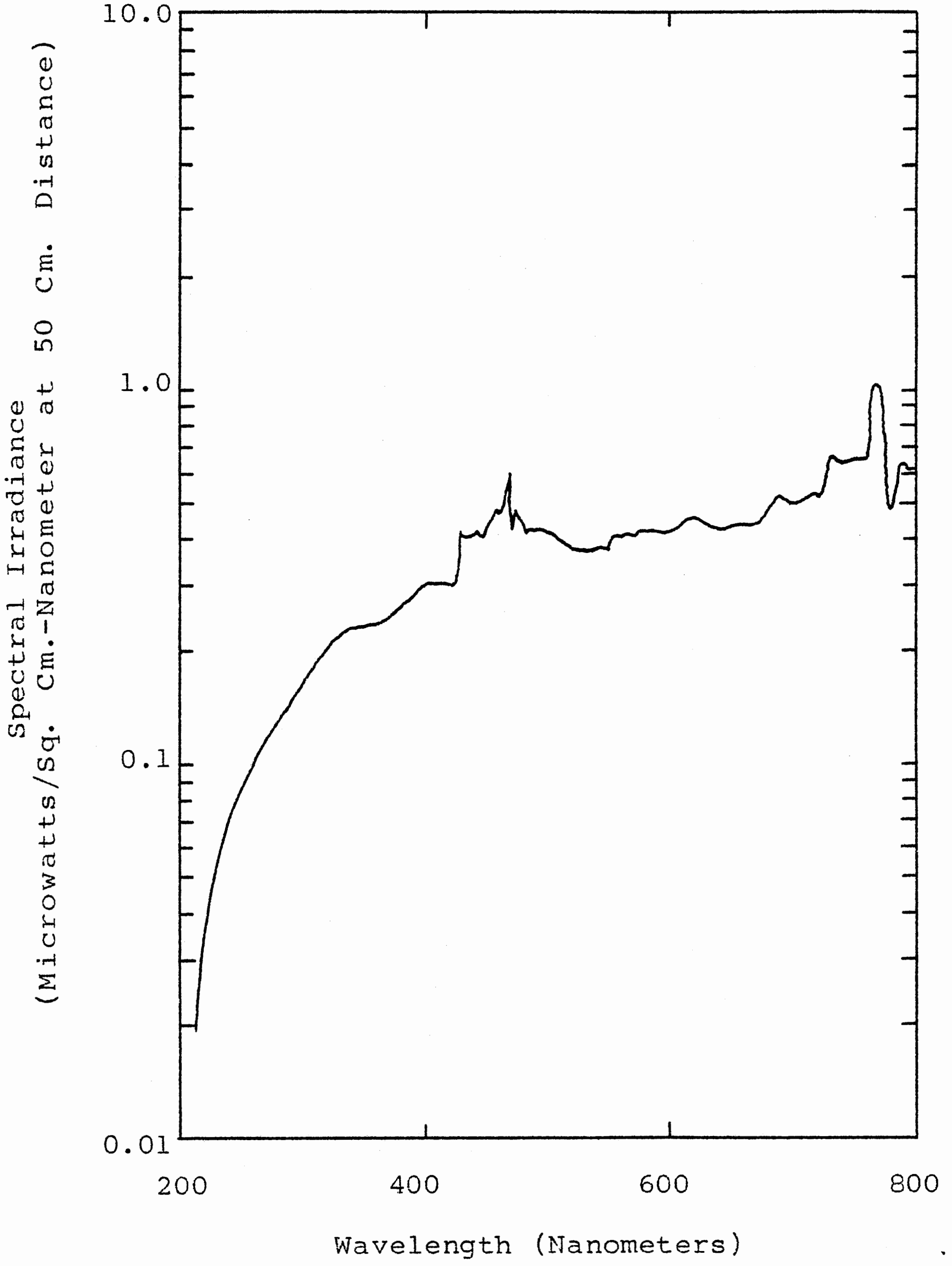


Figure 12. Output Spectra for Xenon Arc Light Source

APPENDIX D

CARBON DIOXIDE FLOWMETER CALIBRATION CHART

GILMONT
INSTRUMENTS, INC.

Calibration Chart
Flowmeter Catalog No. F3000

Serial No. J - 2857

$D_1 = .0394''$ $W_1 = .00209$ GM $\rho_1 = 3.98$ GM/ML

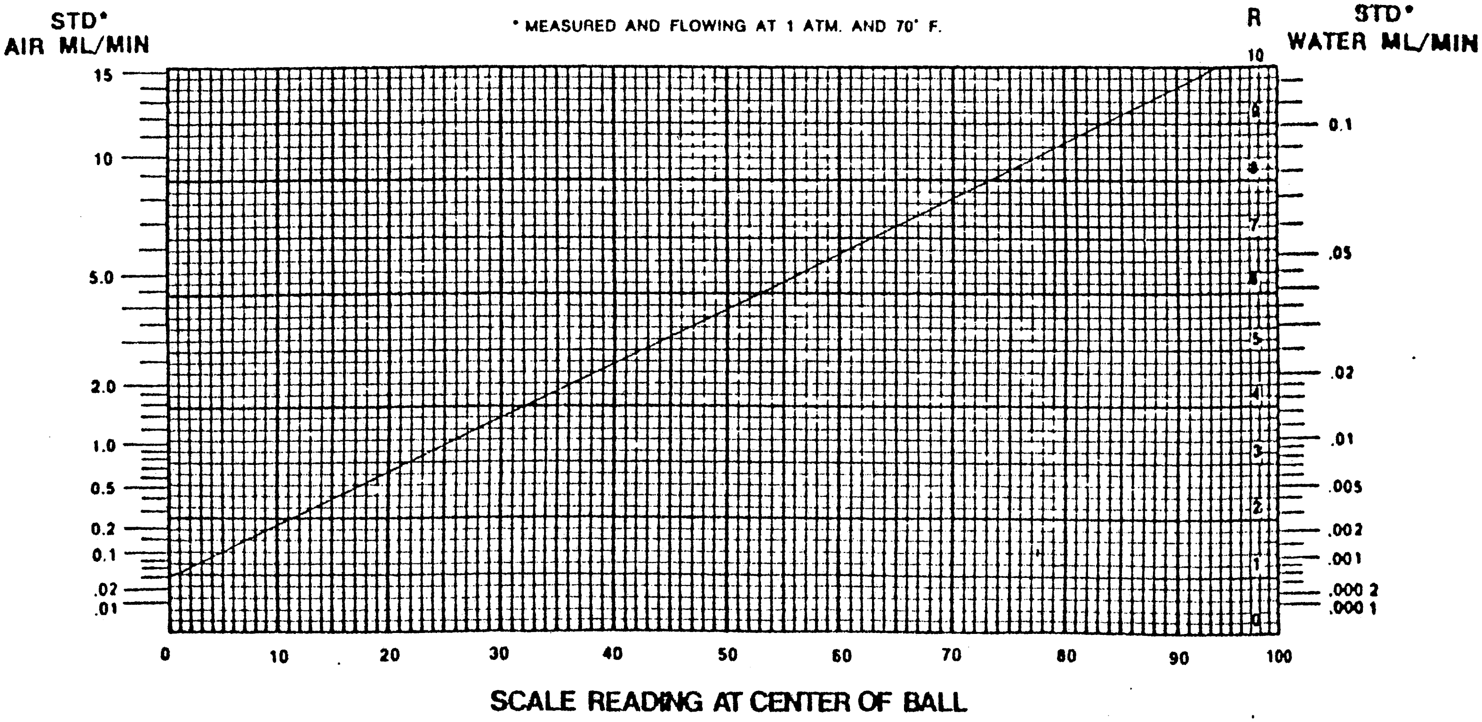


Figure 13. Carbon Dioxide Flowmeter Calibration Chart

APPENDIX E

CALIBRATION OF PRESSURE GAUGE USING MERCURY MANOMETER

TABLE VI

CALIBRATION OF PRESSURE GAUGE USING MERCURY MANOMETER

	Manometer Low in Hg	Manometer High in Hg	Total in Hg	Total PSI	Gauge PSI
1	15.79	16.72	32.51	16.0	16.0
2	14.76	15.66	30.42	14.9	15.1
3	13.88	14.80	28.68	14.1	14.2
4	12.94	13.83	26.77	13.1	13.3
5	11.78	12.65	24.43	12.0	12.2
6	10.69	11.57	22.26	10.9	11.1
7	9.59	10.46	20.05	9.8	10.1
8	8.53	9.37	17.90	8.8	9.0
9	7.53	8.36	15.89	7.8	8.1
10	6.53	7.35	13.88	6.8	7.1
11	5.52	6.34	11.86	5.8	6.0
12	4.41	5.21	9.62	4.7	5.0
13	3.54	4.32	7.86	3.4	4.0
14	2.52	3.26	5.78	2.8	3.0
15	1.55	2.28	3.83	1.9	2.0
16	0.60	1.30	1.90	0.9	1.1
17	0.12	0.82	0.94	0.5	0.6

Atmospheric Pressure = 29.0 in Hg
1 in Hg = 0.4912 PSI

APPENDIX F

THERMOCOUPLE CALIBRATION

TABLE VII

CALIBRATION OF IRON-CONSTANTAN THERMOCOUPLES AND THERMOCOUPLE READOUT USING AN ICE BATH AND BOILING WATER

		Temperature Displayed by Thermocouple Readout	
Thermocouple No.	Thermocouple Location	In ice (^{o}F)	In Boiling Water (^{o}F)
1	CO2 Saturator Outlet	37	215
2	Reactor Inlet	37	215
3	Reactor Outlet	37	216
4	Reactor Catalyst Support Surface	37	216
5	Refrigerated Bath	37	216

Barometric pressure at time of experiment = 28.96 in Hg

Water Boiling Point at Atmospheric Pressure = 210.1^{o}F

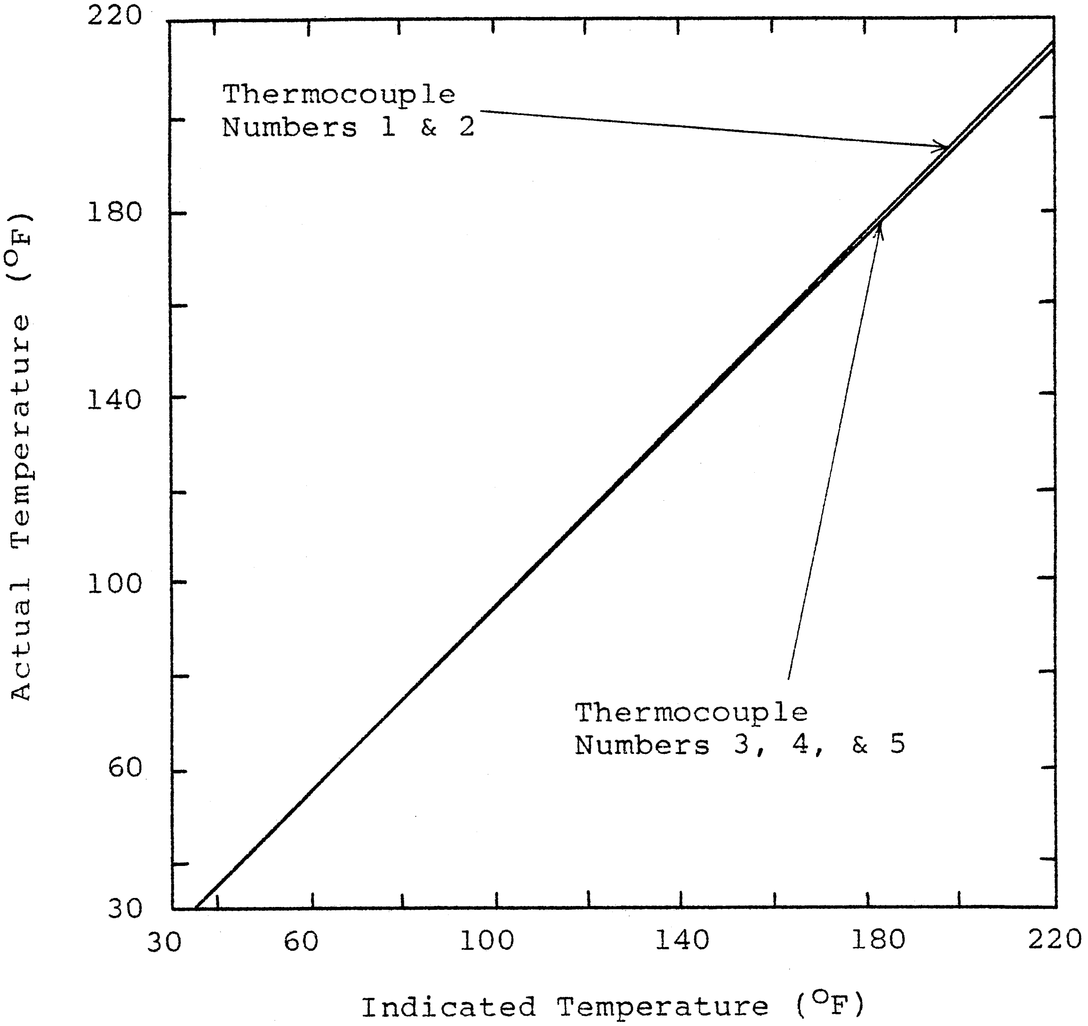


Figure 14. Actual Temperature Versus Temperature Indicated by Thermocouple Readout

APPENDIX G

SAMPLE CALCULATIONS

Calculation of Reactor Residence Time

This calculation of reactor residence time is for the illuminated reactor volume which includes a glass catalyst support plate. The residence time is based on carbon dioxide flow only at $70^{o}F$ and 1 atmosphere.

Calculation of Reactor Volume

Volume of Reactor Cavity = Length X Width X Depth

= 32 mm X 9 mm X 12 mm

= 3500 cu. mm.

$$3456 \text{ cu. mm.} \times \frac{1 \text{ milliliter}}{1000 \text{ cu. mm}} = 3.46 \text{ milliliters}$$

Calculation of Glass Catalyst Support Plate Volume

Volume of Glass Plate = Length X Width X Thickness

= 3.2 cm X 0.9 cm X 0.3 cm

= 0.86 cu. cm

Reactor Cavity Volume with Glass Plate Inserted

V = 3.5 ml - 0.86 ml = 2.64 ml

where,

V = reactor cavity volume

Calculation of Carbon Dioxide Volumetric Flow Rate at 70°F And One Atmosphere

1. Convert carbon dioxide flowmeter reading to a standard air flow rate in milliliters per minute using the Carbon Dioxide Flowmeter Calibration Chart, Figure 13, Appendix D.
2. Convert the standard air rate to standard gas rate in milliliters per minute.

   $$q_G^{o} = q_A^{o} \frac{0.0181}{\mu_G^{o}}$$

   where,

   q_A^{o} = standard air flow rate as read from calibration chart, milliliters per minute.

   q_G^{o} = standard gas flow rate, milliliters per minute

   μ_G^{o} = viscosity of carbon dioxide in centipoises at 70°F and 1 atmosphere
3. Correct the standard gas rate for temperature and pressure.

   $$q_G' = q_G^{o} \frac{(P)}{(760)} \frac{(530)}{(T)}^{1.5}$$

   where,

   q_G' = gas flowing at T and P with volumetric flow rate converted to measurement at 70°F and 1 atmosphere, milliliters per minute

P = absolute pressure of gas inlet in mm of Hg

T = absolute temperature in $^{\circ}R$

Calculation of Illuminated Reactor Residence Time

$$t = \frac{V}{q_G'}$$

where,

t = carbon dioxide residence time in minutes

V = reactor cavity volume in milliliters

Example

Carbon dioxide flowmeter reading - 37

Standard air rate from calibration chart = $q_A^{\circ} = 2.1$ milliliters per minute

$$q_G^{\circ} = 2.1 \; \frac{0.0181}{0.0145}$$

= 2.6 milliliters per minute

$P = 739$ mm Hg

$T = 540^{\circ}R$

$$q_G' = 2.6 \; \frac{(730)}{(760)} \; \frac{(530)}{(540)}^{1.5}$$

= 2.5 milliliters per minute

$$t = \frac{2.64 \text{ milliliters}}{2.5 \text{ milliliters per minute}} = 1.06 \text{ minutes}$$

Calculation of Methanol Production

Calculation of Carbon Dioxide Molar Flow Rate

$$m(CO_2) = q_G' \times \frac{492^{\circ}R}{530^{\circ}R} \times \frac{1\ \text{gmole}}{22.4\ \text{liters}} \times \frac{1\ \text{liter}}{1000\ \text{milliliters}}$$

where,

$m(CO_2)$ = molar flow rate of carbon dioxide in gram moles per minute

q_G' = standard carbon dioxide flow rate in milliliters per minute from above

Calculation of Water Molar Flow Rate

Using the mole ratio of water to carbon dioxide given by Figure 14, Appendix H at the desired saturator temperature, determine the molar flow rate of water.

$$m(H_2O) = m(CO_2) \times \frac{H_2O}{CO_2}$$

where,

H_2O/CO_2 = mole ratio of water to carbon dioxide

$m(H_2O)$ = molar flow rate of water in gram moles per minute

Calculation of Methanol Product Yield

Performing linear regression on values from Table V, Appendix B yields the following formula relating moles of methanol to methanol peak area on chromatograph:

$$y = (0.0797\ x + 3.55) \times 10^{-10}$$

where,

y = moles of methanol

x = methanol peak area from chromatograph

$$mm(CH_3OH) = y \times \frac{1}{S} \times m(H_2O) \times \frac{1 \times 10^6 \text{ micromoles}}{1 \text{ mole}}$$

$$\times \frac{18 \text{ gm}}{\text{mole}} \times \frac{\text{milliliter}}{1 \text{ gm } H_2O} \times \frac{1 \times 10^3 \text{ microliters}}{\text{milliliter}}$$

where,

$mm(CH_3OH)$ = micromoles methanol per hour

S = reactor product liquid sample volume in microliters

Micromoles of methanol formed per gram mole of carbon dioxide feed $= mm(CH_3OH) \times \frac{1 \text{ hr}}{60 \text{ min}} \times \frac{1}{m(CO_2)}$

Calculation of Quantum Yield (9)

Calculation of Number of Molecules of Methanol Formed

$$M(CH_3OH) = mm(CH_3OH) \times N_A \times \frac{1 \times 10^{-6} \text{ mole}}{\text{micromole}} \times \frac{\text{hour}}{3600 \text{ sec.}}$$

where,

M(CH3OH) = molecules of methanol formed per second

N_A = Avogadro's number, 6.023×10^{23} molecules per mole

$m(CH_3OH)$ = micromoles methanol per hour

Calculation of number of quanta (photons) absorbed by Strontium Titanate

The wavelength of light energy considered ranged from 250 nanometers to 400 nanometers. Below 250 nanometers the quartz transmittance began dropping quickly. Above 400 nanometers the light energy is not sufficient to produce chemically reactive electron-hole pairs. Spectral irradiances of 0.122, 0.205 and 0.255 microwatts per square centimeter-nanometer were chosen from Figure 12 at 275, 325 and 375 nanometers. These wavelengths represent the midpoints of the 250 to 300, 300 to 350 and 350 to 400 nanometer wavelength ranges. These irradiances were corrected for distance by using the inverse square law. The distance between the lamp and reactor was approximately 30 centimeters instead of 50 centimeters for the quoted irradiances. An irradiance correction factor of 2.78 was used. Quartz transmittance was determined to be approximately 86 percent based on an ultraviolet spectrophotometer scan of the quartz window. Collimated beam power factors of 0.754, 0.709 and 0.689 were obtained from the Oriel catalog at the midpoint wavelengths (27). Irradiance was multiplied by the quartz transmittance factor and the collimated beam power factor at each of the three midpoint wavelengths to get a corrected irradiance. Absorption of light by the strontium titanate was assumed to be 100 percent. Light absorbing area was 2.9 square centimeters.

Example Calculation of Energy Absorbed in One Wavelength Range (250 to 300 Nanometers)

Energy Absorbed = 3.19×10^{-5} joules per second = 31.9 microwatts = 0.122 microwatts per square centimeter-nanometer X 2.78 X 0.86 X 0.754 X 2.9 square centimeters X 50 nanometers

Example Calculation of Energy of One Quantum or Photon at Midpoint Wavelength

$$E = 7.23 \times 10^{-19} \text{ joules per quanta} = \frac{h\,c}{\lambda \times 10^{-9}} = 6.63 \times 10^{-34} \text{ joule-second} \times 3 \times 10^{8} \frac{\text{meters}}{\text{second}} \times \frac{1}{275 \text{ nanometers}} \times \frac{\text{nanometer}}{10 \text{ Angstroms}} \times \frac{1 \text{ Angstrom}}{10^{-10} \text{ meter}}$$

where,

E = energy per quantum

h = Planck's constant, 6.63×10^{-34} joule-second

c = velocity of light, 3×10^{8} meters per second

λ = midpoint wavelength, nanometers

To get total quanta per second absorbed by the strontium titanate, the total energy in each wavelength range is divided by the energy per quantum in each wavelength range, and the results for each wavelength range are added. The total quanta per second absorbed by the strontium titanate for all experiments where the xenon arc lamp was used are approximately 2.41 X 10^{14} quanta per second.

Formula for Methanol Formation Reaction Quantum Yield Calculation

$$Q = \frac{M(CH_3OH)}{q/s}$$

where,

Q = quantum yield in molecules of methanol formed per quantum

$M(CH_3OH)$ = molecules of methanol formed per second

q/s = total quanta per second absorbed by strontium titanate in reactor

APPENDIX H

WATER TO CARBON DIOXIDE MOLE RATIO IN REACTOR FEED

TABLE VIII

WATER TO CARBON DIOXIDE MOLE RATIO IN REACTOR FEED

Temperature (°F)	Moles H_2O per Mole CO_2
70	0.03
80	0.04
90	0.05
100	0.07
110	0.10
120	0.13
130	0.18
140	0.25
150	0.35
155	0.42
160	0.50
165	0.60
170	0.72
175	0.89
180	1.11
185	1.42
190	1.89
195	2.66
200	4.15

Pressure = 14.3 PSIA (Atmospheric Pressure in Stillwater, Oklahoma)

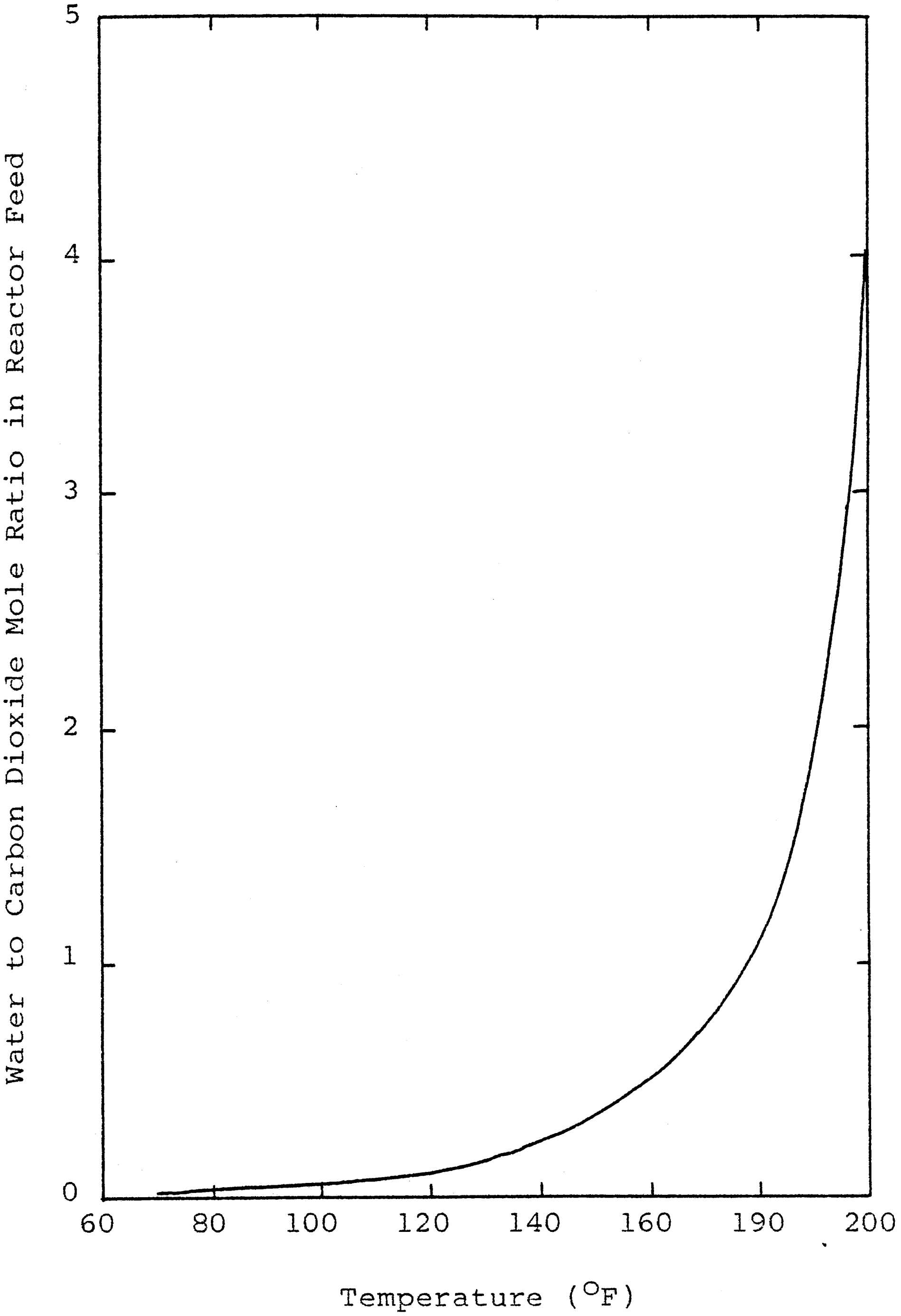


Figure 15. Water to Carbon Dioxide Mole Ratio in Reactor Feed at 14.3 PSIA

APPENDIX I

CHRONOLOGICAL ORDER OF EXPERIMENTS

TABLE IX

CHRONOLOGICAL ORDER OF EXPERIMENTS

Experiment Number	Date Experiment Performed (1982)		
	TABLE I	TABLE II	TABLE III
1	13 Apr	14 Jul	13 Aug
2	16 Apr	16 Jul	11 Aug
3	19 Apr	19 Jul	10 Aug
4	21 Apr	20 Jul	9 Aug
5	27 Apr	21 Jul	1 Sep
6	5 May	22 Jul	31 Aug
7	7 May	23 Jul	30 Aug
8	10 May	26 Aug	2 Sep
9	17 May	26 Jul	
10	17 May	25 Aug	
11	18 May	27 Jul	
12	19 May	28 Jul	
13	20 May	23 Aug	
14	21 May	29 Jul	
15	24 May	24 Aug	
16	25 May	30 Jul	
17	26 May	19 Aug	
18	27 May	2 Aug	
19	1 Jun	27 Aug	
20	2 Jun	3 Aug	
21	3 Jun	4 Aug	
22	4 Jun	5 Aug	

TABLE IX (Continued)

Experiment Number	Date Experiment Performed (1982)		
	TABLE I	TABLE II	TABLE III
23	7 Jun	6 Aug	
24	9 Jun	20 Aug	
25	11 Jun	16 Aug	
26		17 Aug	
27		18 Aug	

VITA 2

Kenneth William Ische

Candidate for the Degree of

Master of Science

Thesis: METHANOL PRODUCTION FROM CARBON DIOXIDE AND WATER USING ULTRAVIOLET LIGHT

Major Field: Chemical Engineering

Biographical:

Personal Data: Born in Shakopee, Minnesota, August 23, 1948, the son of Mr. and Mrs. W. L. Ische. Married to Maureen L. O'Donnell, August 1, 1970.

Education: Graduated from Central High School, Norwood, Minnesota, in June, 1966; received Bachelor of Science in Chemical Engineering degree from the University of Minnesota in June, 1970; completed requirements for the Master of Science degree at Oklahoma State University in December, 1982.

Professional Experience: Laborer, Green Giant Company, Glencoe, Minnesota, summers of 1966, 1967, and 1968; Summer Engineer, St. Regis Paper Company, West Nyack, New York, summer of 1969; Refrigeration and Air Conditioning Specialist, U.S. Air Force, Cannon Air Force Base, New Mexico, 1970-71; Bioenvironmental Engineer, U.S. Air Force, Carswell Air Force Base, Texas, 1971-74; Process Engineer, CONOCO INC., Ponca City, Oklahoma, 1974-81; graduate research assistant, Oklahoma State University, Stillwater, Oklahoma, 1981-82.