FINAL TECHNICAL REPORT
October 1, 2007, through September 30, 2008

Project Title: **A NOVEL PHOTOCATALYTIC PROCESS FOR THE
CONVERSION OF CARBON DIOXIDE TO METHANOL**

ICCI Project Number: 07-1/ER4
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ABSTRACT

The aim of the exploratory research was to develop a novel process for converting carbon dioxide produced at coal-fired gasification, coal-to-liquid fuels, and coal-fired combustion plants to useful chemical feedstock. The investigation explored the possibility of utilizing light energy, specifically in the ultraviolet range, to convert this CO_2 to methanol in the presence of a photocatalyst and water. Experiments were conducted with CO_2 bubbling through a synthesized titania powder catalyst suspended in aqueous solutions with varying composition under UV irradiation. The preparation of an alumina-supported titania catalyst, along with the coating of the catalyst on a tubular filter, was also performed. Finally, the catalyst-impregnated filter was utilized in a flow-through reactor setup for the conversion of CO_2 to methanol. Such a process could pose as a viable alternative to the costly, and uncertain in the long term, carbon dioxide sequestration; while at the same time convert an otherwise waste green house gas into useful chemical feedstock.

EXECUTIVE SUMMARY

This exploratory research addressed the issue of developing a novel process that would convert carbon dioxide into a useful chemical feedstock, methanol, and provide an alternative to carbon sequestration.

The primary objective of this research was to explore a novel process along with an innovative reactor design for enhancing the process performance of recycling the CO_2 exhausted from coal-fired gasification, coal-to-liquid fuels, and coal-fired combustion plants back to a useful chemical feedstock, in particular, methanol. Technology in this arena is of utmost importance to Illinois, a state rich in coal reserves. The approach the authors focused on, similar to photosynthesis utilized by plant-life to administer growth, the conversion of CO_2 to methanol by a photocatalytic route. There exists a great demand for methanol as a chemical intermediate in the production of paints, resins, silicones, adhesives, plastics, etc. Along with hydrogen, a methanol-based energy infrastructure has also been proposed by several researchers. Regardless of the ultimate choice of replacement fuel for gasoline and diesel, a great increase in demand for both chemicals is expected in the areas of energy and fine chemicals. Methanol, like hydrogen, can be used in internal combustion engines, it can be reformed on-vehicle to power hydrogen fuel cells, and is also utilized in direct methanol fuel cells.

Carbon dioxide is a very stable molecule and requires an energy input to drive any desired transformation. Thus, the energy from photons may be exploited by utilizing a photon absorbing semi-conductor to catalyze the reduction of CO_2 to methanol. The structure of semi-conductors consists of a filled valence band and an empty conduction band. The energy separation between the valence and conduction bands is called the band gap and consists of energy levels in which electrons cannot reside. Light, a source of energy, can be used to excite an electron from the valence band into the conduction band. When an electron in the valence band absorbs a photon, the absorption of the photon increases the energy of the electron and enables the electron to move into one of the unoccupied energy levels of the conduction band, leaving an electron deficiency in the valence band referred to as a hole. However, because the energy levels of the valence band are lower than those of the conduction band, electrons in the conduction band eventually move back into the valence band (referred to as electron-hole recombination), leaving the conduction band empty.

TiO_2 is generally the preferred semi-conductor for use in commercial photocatalytic applications because of its high level of photoconductivity, ready availability, low toxicity, no consumption of chemicals, potentially long service life and low cost. It has three crystalline forms: rutile, anatase, and brookite. Studies have indicated that the anatase form provides the highest *OH formation rates. The band gap energy of anatase TiO_2 is 3.2 eV. When this material is irradiated with photons of 387.5 nm, the band gap energy is exceeded and an electron is promoted from the valence band to the conduction band. The electron-hole pair within a semi-conductor band tends to revert to a stage where the electron hole pair no longer exists because the electron is in an unstable, excited state; however, the band gap inhibits this reversal long enough to allow excited

electrons and holes near the surface of the semiconductor to participate in reactions at the surface of the semiconductor.

The mechanism for the photocatalytic conversion of CO_2 to methanol is dependent on the formation of $^•H$ (hydrogen radicals) and $^•CO_2^-$ (carbon dioxide anions). As the TiO_2 absorbs photons, the electrons (e^-) jump from the valence band to the conduction band, leaving a hole (h^+) in the valence band. Because CO_2 and H^+ are present as adsorbed species on the excited catalyst $(Ti^{3+}-O^-)^*$, they interact with the electrons to form the $^•H$ and $^•CO_2^-$ radicals. These species react at the electron hole to produce methanol by the reaction below:

$$^•CO_2^- + 6\,^•H + h^+ \rightarrow CH_3OH + H_2O$$
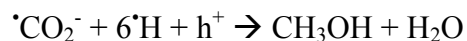
The aim of the research was to design and construct a prototype reactor and develop photocatalytic filters having good catalytic activity in the ultraviolet region, permeability, and mechanical strength to efficiently carry out the above reaction. These photocatalytically active filters were then tested for CO_2 conversion to methanol in the presence of steam and UV irradiation. The advantages of the reactor configuration researched in this work as opposed to the current designs (primarily catalyst particles suspended in aqueous solutions or catalytically active films and powders fixed in a reactor where CO_2 and steam are passed through) are: (i) the catalyst impregnated filter design forces the reactants to contact the catalyst before exiting the reactor; (ii) the UV light is evenly irradiated onto the catalyst surface, not blocked by particles closer to the light source; (iii) the catalyst could remain stable for a longer period of time when anchored on the filter; (iv) CO_2 sequestration could be drastically reduced (compared to conventional processes); and (v) elemental hydrogen is not required for the CO_2 reduction step.

γ-Al_2O_3 was synthesized and coated onto the "as-received" filters to increase the filter surface area before the anatase TiO_2 photocatalyst coating (confirmed by XRD) was applied. Preliminary experiments included testing synthesized anatase TiO_2 powders in three different aqueous solutions (H_2O, 0.2 N NaOH, and 1 M propanol) to verify their photocatalytic activity under UVC (254 nm) irradiation emitted from a penray. Carbon dioxide reduction experiments were then conducted in the newly-designed prototype reactor using a twice γ-Al_2O_3 washcoated, eight times TiO_2 impregnated tube filter. This particular experimental setup was built in such a way as to provide the greatest amount of flexibility with regards to experimental conditions. The CO_2 flowrate, CO_2:H_2O ratio, UV wavelength, intensity, temperature, and pressure can all be adjusted as needed with relative ease. In addition, a liquid/gas recycle pump was built in to the system to allow the reactor to be operated as a mixed flow with the options of 0-100 % recycle. Upon completion of the experiments, liquid product samples were collected from inside the reactor and analyzed using gas chromatography/mass spectrometry. Only formaldehyde was found in the product samples. The formaldehyde formation reaction is an intermediate reaction in the reduction steps from carbon dioxide to methanol, indicating that the reaction did not proceed to completion in the experiments.

OBJECTIVES

The main objective of this project was the development of an economically viable photocatalytic process for production of methanol from carbon dioxide (derived from coal utilization processes) in order to reduce the environmental impact of this greenhouse gas and provide an economical alternative to sequestration. The three major technical goals were: (i) to design a flexible photocatalytic filter reactor that can efficiently convert carbon dioxide to methanol in a wide range of temperatures, carbon dioxide concentrations, ultraviolet (UV) wavelengths, and flow rates; (ii) to accomplish efficient production of methanol via sustainable catalytic conversion of carbon dioxide using inexpensive, durable photocatalysts, and (iii) to evaluate the selectivity towards methanol formation. The activity and durability of the catalyst for carbon dioxide conversion needed to be demonstrated in the laboratory. The approach was based on photocatalytic conversion of carbon dioxide to hydrocarbons, specifically methanol, over novel photocatalysts to be designed at Southern Illinois University in the presence of water. The ultimate goal is to obviate the need or at least drastically reduce the need for sequestration of CO_2, by recycling the CO_2 to a value added product.

This project was executed by the following tasks:

Task 1: Acquisition of Materials

Task 2: Catalyst Preparation and Filter Coating

Task 3: Verification of Photocatalytically Active Catalyst

Task 4: Conversion of Carbon Dioxide to Methanol with Photocatalytic Filters

Task 5: Technical and Economic Feasibility Studies

Task 6: Reporting

INTRODUCTION AND BACKGROUND

The rising demand for energy globally, which in turn results in the increased use of fossil fuels, is expected to cause an emergence again in Illinois coal in light of new technologies such as gasification followed by hydrogen separation of coal to liquid fuels. Several technologies are being investigated. The production of CO_2 is inevitable when fossil fuels like coal are used. Regulatory steps have been initiated to curb this release of CO_2 since the environmental effects of this release of CO_2 into the atmosphere are believed by many to be extremely detrimental. Thus, having a technology that reduces the production of CO_2, disposes the CO_2 in an environmentally-benign fashion, or recycles the CO_2 produced is an insurance against environmental liability in the future. CO_2 sequestration, which dominates the current thinking, is only a short term solution for CO_2 disposal, and involves many uncertainties down the road. Among these uncertainties are the CO_2 mitigation effects on ground water sources, geological barrier

weakening from supercritical CO_2 pressures and corrosion from acid formation, the high cost of compression and transportation, and the lack of understanding for scale-up from laboratory experimentation under equilibrium conditions to commercial sequestration at great subsurface depths. Technologies for recycle and reuse, however, are becoming increasingly realistic for fossil fuel-based industries. The development of inexpensive technologies that can produce fuels and chemical feed stocks (methanol is both) from CO_2 will reduce the load of sequestration as well as increase productivity and viability of the use of Illinois coal and make energy production a near-green process. New market sectors in addition to the energy sector will open up for Illinois coal.

Methanol has many present and future uses. Most methanol applications are for chemical intermediates in the production of paints, resins, silicones, adhesives, plastics, etc. The drastic increases in gas prices, as well as, the concern over global climate change are part of the driving force for the shift towards U.S. energy independence from foreign petroleum. Along with hydrogen, a methanol-based energy infrastructure has also been proposed. Regardless of which fuel is ultimately chosen as the replacement for gasoline and diesel, a great increase in demand for both is expected. Methanol, like hydrogen, can be used in internal combustion engines, it can be reformed on-vehicle to power hydrogen fuel cells, and is also utilized in direct methanol fuel cells. Methanol differs from hydrogen, however, in that it is more easily transported and stored.

The utilization of carbon dioxide as a raw material, not only as a carbon source but also as a useful chemical feedstock is a more holistic approach to reduce air pollution by flue gases when compared to sequestration. Many methods have been proposed to maintain the concentration of atmospheric CO_2 or to reduce and recycle it. One of these is chemical fixation using catalysts. The conversion of CO_2 to methanol by hydrogenation over copper containing catalysts is one of the most widely studied subjects in this area. The limitation in this reaction is the low conversion of CO_2. Methanol is currently produced from CO-rich synthesis gas ($CO/CO_2/H_2$) using a catalyst at 50–100 bar and 473–523 K. CO_2 has been identified as a carbon source for methanol synthesis based on the fact that kinetic experiments, using isotope-labeled carbon oxides and spectroscopic methods, have demonstrated that methanol is produced from hydrogenation of CO_2, whereby CO merely provides a source of CO_2 and acts as a reducing agent by scavenging surface oxygen. Nevertheless, the catalyst that is active for CO-rich feedstock is not so active for CO_2-rich sources. It has been shown that the water formed as a byproduct has an inhibitory effect on methanol synthesis because it tends to oxidize the active metal during reaction. In addition, it has been reported that CO_2 keeps the metal surface partially oxidized during methanol synthesis. Within this context, there have been many claims that the catalyst performance can be improved. The majority of the modified catalysts still contain Cu and Zn as the main components, together with different modifiers such as chromium, zirconium, vanadium, cerium, titanium, and gallium. The Group VIII noble metals noble metals are excellent candidates to activate hydrogen, which could then spread over the neighboring phases through a hydrogen-spillover mechanism and may be incorporated into the catalyst matrix. This process leads to a more reduced state for the catalyst surface, a situation that may further facilitate surface hydrogenation reactions. Methanol synthesis from a CO_2/H_2 feed has already been

achieved by either physically mixing a CuO–ZnO catalyst with a Pd catalyst or by using Pd-impregnated CuO–ZnO–Al_2O_3 catalysts instead of physical mixtures.

In spite of the advances in direct hydrogenation technologies, the commercial implementation of these technologies is greatly hindered due to the cost prohibitive state of art of hydrogen production. In power plants generating hydrogen as a fuel source, the utilization of this hydrogen in reducing CO_2 is counter productive. Thus alternate methods need to be investigated that can convert CO_2 to useful chemicals without the use of molecular hydrogen as the reducing agent. Following the example provided by nature, the authors explored a photocatalytic route of converting CO_2 to methanol in the presence of light, a photocatalyst and water.

Carbon dioxide is a very stable molecule and requires an energy input to drive any desired transformation. Thus, the energy from photons may be exploited by utilizing a photon absorbing semi-conductor to catalyze the reduction of CO_2 by water to methanol. The structure of semi-conductors consists of a filled valence band and an empty conduction band. The energy separation between the valence and conduction bands is called the band gap and consists of energy levels in which electrons cannot reside. Light, a source of energy, can be used to excite an electron from the valence band into the conduction band. When an electron in the valence band absorbs a photon, the absorption of the photon increases the energy of the electron and enables the electron to move into one of the unoccupied energy levels of the conduction band. However, because the energy levels of the valence band are lower than those of the conduction band, electrons in the conduction band eventually move back into the valence band (referred to as electron-hole recombination), leaving the conduction band empty.
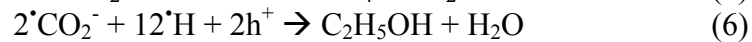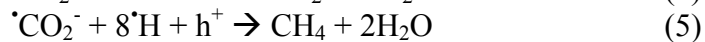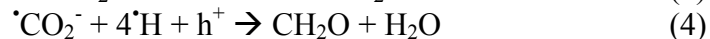
TiO_2 is generally the preferred semi-conductor for use in commercial applications because of its higher level of photoconductivity[1], ready availability, low toxicity, no consumption of chemicals, potentially long service life and low cost. It has three crystalline forms: rutile, anatase, and brookite. Studies have indicated that the anatase form provides the highest *OH formation rates. The band gap energy of anatase TiO_2 is 3.2 eV. When this material is irradiated with photons of 387.5 nm, the band gap energy is exceeded and an electron is promoted from the valence band to the conduction band. The electron-hole pair within a semi-conductor band tends to revert to a stage where the electron hole pair no longer exists because the electron is in an unstable, excited state; however, the band gap inhibits this reversal long enough to allow excited electrons and holes near the surface of the semiconductor to participate in reactions at the surface of the semiconductor. In addition, doping the TiO_2 with copper can prolong the electron-hole recombination by acting as an electron trap[2].

The mechanism for the photocatalytic conversion of CO_2 to methanol is dependent on the formation of $^\bullet H$ (hydrogen radicals) and $^\bullet CO_2^-$ (carbon dioxide anions). As the TiO_2 absorbs photons, the electrons (e^-) jump from the valence band to the conduction band, leaving a hole (h^+) in the valence band. Because CO_2 and H^+ are present as adsorbed species on the excited catalyst $(Ti^{3+}-O^-)^*$, they interact with the electrons to form the $^\bullet H$

and $^{\bullet}CO_2^-$ radicals. These species react at the electron hole to produce methanol by the reaction below:

$$^{\bullet}CO_2^- + 6^{\bullet}H + h^+ \rightarrow CH_3OH + H_2O \qquad (1)$$

However, methanol is not the only possible product from the reaction of the radicals. Below are some other reactions which may take place, making it very important to design a catalyst, and determine an adequate $CO_2:H_2O$ ratio which exhibits a high selectivity for methanol formation.

$$^{\bullet}CO_2^- + 2^{\bullet}H + h^+ \rightarrow CO + H_2O \qquad (2)$$
$$^{\bullet}CO_2^- + 2^{\bullet}H + h^+ \rightarrow HCO_2H \qquad (3)$$
$$^{\bullet}CO_2^- + 4^{\bullet}H + h^+ \rightarrow CH_2O + H_2O \qquad (4)$$
$$^{\bullet}CO_2^- + 8^{\bullet}H + h^+ \rightarrow CH_4 + 2H_2O \qquad (5)$$
$$2^{\bullet}CO_2^- + 12^{\bullet}H + 2h^+ \rightarrow C_2H_5OH + H_2O \qquad (6)$$

Several process parameters can affect the success of photocatalytic conversion to methanol using an anatase semi-conductor under UV irradiation. These parameters include $CO_2:H_2O$ ratio, UV wavelength, light intensity, temperature, and pressure. The affects of these parameters have been widely researched and a general consensus exists for each.

$CO_2:H_2O$ Ratio

Anpo, *et al.* showed that the photocatalytic reactivity on a TiO_2 catalyst was the greatest at a $CO_2:H_2O$ ratio of 1:5. The authors also noted that lower ratios suppressed the reaction rates[3]. Competition between the H_2O and CO_2 molecules adsorbing on the surface of the catalyst begins to hinder the CO_2 reduction at low ratios.

UV Wavelength

The maximum wavelength to excite the valence electron into the conduction band is indirectly proportional to the band gap energy of the semi-conductor. As stated previously, the band gap energy of anatase TiO_2 is 3.2 eV. Thus, the maximum photon wavelength is 387.5 nm. Shorter wavelength light (*e.g.* 254 nm) have been proven in several previous works to be more effective for CO_2 reduction over a TiO_2 catalyst than 350 nm wavelengths[4].

Light Intensity

The probability of electronic transitions in semi-conductors is reliant on the light intensity. At low and midrange light intensities, the CO_2 reduction rates increase with the intensity. At high light intensities, photons can be supplied at a higher rate than is actually demanded by the photo reaction, and rates are independent[5].

Temperature

While photons ultimately provide the energy for the electron-electron hole formation on the photocatalytic semi-conductor, higher temperatures provide faster CO_2 reduction kinetics. Thus, great variations in temperature can have a significant impact on methanol selectivity, and should be investigated further[5, 6].

Pressure

Increasing the CO_2 pressure increases the concentration of CO_2 absorbed into the water. In addition, by the Le Chatlier-Braun principle, higher pressures should shift the equilibrium towards more liquid products. Specifically for methanol, the yield has been found to peak in the range of 120-130 kPa when a Cu-loaded TiO_2 catalyst was used[2, 7].

EXPERIMENTAL PROCEDURES

Filters

The uncoated filters made of Kellundite® were obtained from Ferro, Inc. and weighed 110 to 130 g each. The filter dimensions were 130 mm, 52 mm OD cylinders with a thickness of 3 mm, and the total surface area was approximately 0.018 m^2. Initially, all the "as received" filter tubes were washed in acetone and dried at 80º C. The "as-received" filters made primarily of α-Al_2O_3, generally have a low specific surface area. The hurdle of low active surface area can be overcome by coating the pore walls of the "as-received" filters with a high surface area phase, such as a transition alumina. This transition alumina layer, especially γ-Al_2O_3, acted as an excellent catalyst support. The specifications of the "as received filter are provided in Table 1.

Table 1 - Technical specifications of the as-received filters

Material	Kellundite® Ceramically Bonded Alumina
Grade	FAO 70
Nominal Retention (m)	70
Maximum Pore Diameter (μ)	170
Approximate Particle Retention	7
Permeability (at 2 in water)	20-25
Porosity (%)	30-40
Max Temperature use in air (˚F)	2000
Flexural Strength (M.O.R.)	3500
Bulk Density (g/cc)	2.1-2.3
Color	Dull White
Internal Diameter (mm)	44-45
Height (mm)	130
Specific Surface Area (m^2/g)	0.30±0.05

γ-Al$_2$O$_3$ Support Preparation

Aluminum nitrate, bohemite, and urea from Aldrich for the preparation of the γ-Al$_2$O$_3$ support. An aluminum nitrate and urea aqueous solution was prepared by dissolving in water at 50 ºC. Al(NO$_3$)$_3$.9H$_2$O (close to the solubility limit) was added to the urea solution until a nitrate/urea weight ratio of about 2:1 was achieved. Al(OH)$_3$ was precipitated due to nitrate hydrolysis induced by the presence of the ammonium ion produced due to the thermal decomposition of urea. The resulting solution was heated to 90 ºC. γ-alumina powders and γ-alumina coatings for the filters were prepared from the solution. In order to coat the filters to increase their specific surface area , the "as-received" filters were dipped into the heated solution and then baked for four hours at 105 ºC followed by one hour at 260 ºC and 72 hours at 400 ºC. The baking was conducted in a furnace equipped with a temperature program to control the ram and the bake time. The resulting product had a high active surface area.

Anatase TiO$_2$ Preparation

Titanium (IV) isopropoxide, iso-propanol, and hydrochloric acid were obtained from Aldrich for the preparation of the titanium oxide catalyst. The crystalline form of TiO$_2$ for the conversion of carbon dioxide to methanol chosen for this work was anatase. In order to prepare the anatase powder and solution for filter coating, 0.15 mol titanium isopropoxide per L propanol mixture was made and hydrolyzed with 20 mol H$_2$O per mol titanium isopropoxide. This solution was then peptized with 0.17 mol HCl per mol titanium isopropoxide to create a colloidal solution. The filters, after the γ-Al$_2$O$_3$ washcoating step, were dipped in the resulting Ti(OH)$_4$ solution for 1 minute and dried at 100 ºC. This was performed up to eight times to ensure a thorough catalyst coating. The filters were then calcined at 400 ºC for one hour to form the anatase layer. Water was precipitated out of the leftover Ti(OH)$_4$ solution resulting in titania powder, and the powder was calcined at 400 ˚C to form anatase.

Preliminary Experiments to Prove Photocatalytic Activity of TiO$_2$

Two UV light penrays were purchased from UVP, one with a wavelength of 254 nm (UVC) and one with a wavelength of 365 nm (UVA). The anatase TiO$_2$ powder was tested in aqueous solutions with varying compositions to verify its photocatalytic activity under light irradiation emitted from the 254 nm wavelength penray. Figure 1 is a diagram of the experimental setup used for these preliminary tests. Three experiments were conducted for this verification. The aquesous solutions used were distilled H$_2$O, 0.2 N NaOH, and 1 M propanol. The use of an alkaline solution was used to increase the solubility of carbon dioxide while that of the propanol solution was employed to suppress the electron-hole recombination in the catalyst. 75 ml of solution were used in each experiment and the anatase powder was added to the solutions at a solids loading of 1 g anatase per L solution. After the system was purged with CO$_2$ for one hour to remove any air, the penray was switched on. 30 ml/min CO$_2$ was bubbled through the catalyst/solution mixture with the penray submerged in the center. The experiments were conducted for 2 days each, the product samples were centrifuged and filtered from the

TiO$_2$ powder, and their composition was determined by GC/MS. To avoid harmful contact with UV rays, the setup was covered with aluminum foil.
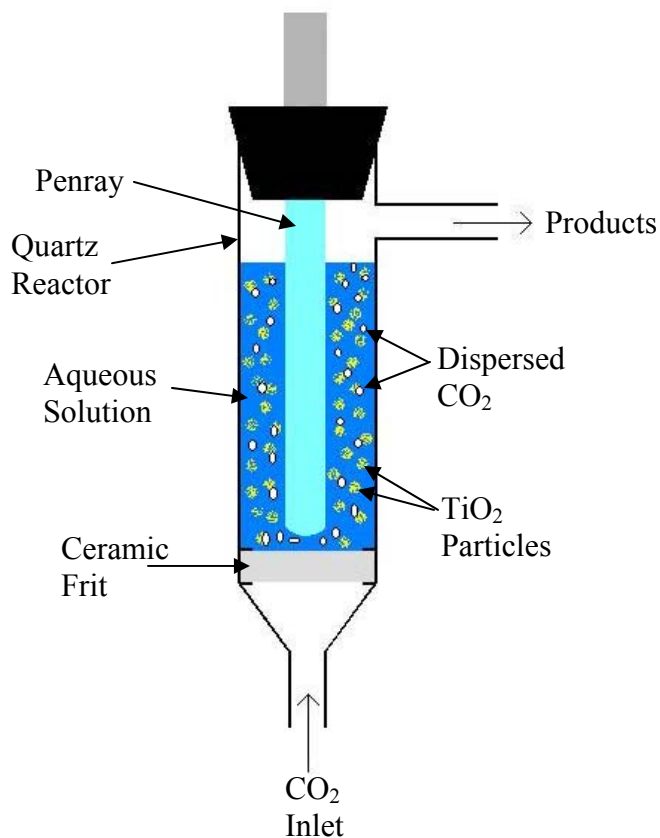

Figure 1 - Diagram of experimental setup of preliminary experiments
for TiO$_2$ powders in aqueous solution

Description of Reactor

A 5mm thick stainless steel hollow cylinder with stainless steel plates at both the top and bottom of the cylinder (held together with all-thread and nuts) was used as the reactor shell. The top and bottom of the cylinder were sealed with a silicon gasket between the cylinder and each plate. The reactor shell houses the filter, water, and the UV penray, with the penray fixed in the center of the filter. The filter length is equal to the length of the shell so that the plate gaskets also seal the filter at each end, preventing the inlet gases from bypassing the filter at either end. The inlet to the reactor is located at the bottom, consisting of a conical section into which the inlet tubing was attached. The reason for the conical section is for better axial distribution of the reactant gases as it enters the core of the reactor (see Figure 2). This in effect allows for equal distribution of the gases entering the filter reactor. Simply explained, the inlet gases are fed into the bottom center of the reactor, due to the inlet pressure, they must pass through the UV light-

energized, porous filter. Once the gases pass through the filter, they can then exit the reactor through an opening in the top plate (outside the radius of the filter).
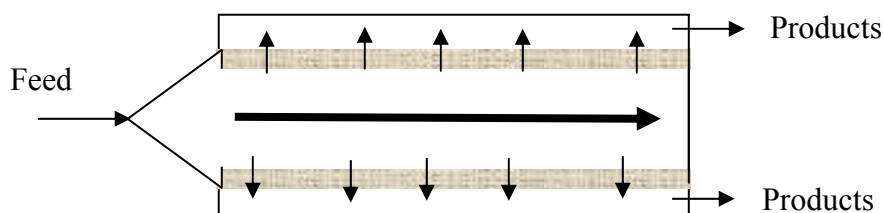

Figure 2 - Schematic of a flow through filter reactor

Description of Experimental Apparatus

Carbon dioxide (obtained from Airgas) flow from a pressurized tank was controlled with a C100 mass flow controller made by Sierra Instruments. The gas flowed through a ceramic frit and into the reactor. After bubbling through 500 ml distilled H_2O inside the reactor, the CO_2/H_2O mixture contacts the irradiated filter, reacts, passes through the filter and exits the reactor. After exiting the reactor, the product/unreacted gaseous mixture is then fed through an online gas chromatograph, which takes a 1 mL sample of the mixture at a specified frequency. The GC uses a Hayesep Q column and TCD detector for the analyses of the products. The GC has a six-way inlet valve which allows the products not used for analyses to enter a Boxer® quadhead liquid/gas recycle pump (also inline with the reactor). The products are then pumped back into the reactor, so the apparatus can best be described as a flow-through reactor with the option of 0-100 % recycle (with the exception of the 1 mL samples used for GC analyses. A schematic of the experimental apparatus is shown in Figure 3, and a picture of the reactor is given in Figure 4.
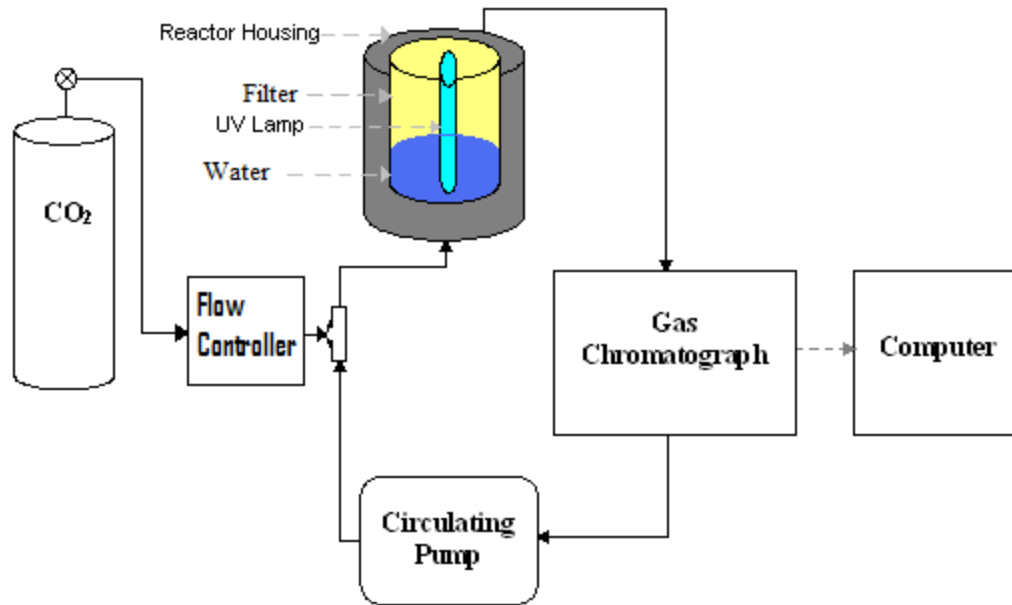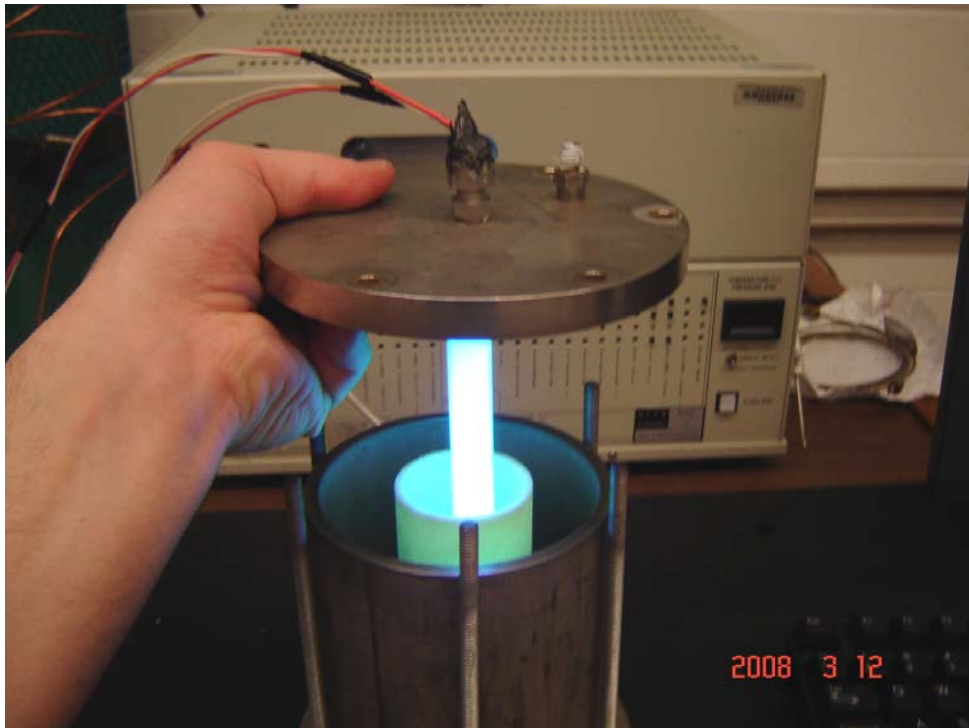
Figure 3 - Schematic of photo-catalytic reactor setup

Figure 4 - Picture of the inside of the photo-catalytic reactor

Experimental Procedure

The first step of the experimental procedure was to completely flush the reactor and tubing with the CO_2/H_2O mixture to remove any air from the system. This step was performed with the lamp turned off to prevent any reaction. A GC sample was taken every hour during the flushing, which took two hours, until the composition consisted only of the CO_2/H_2O mixture. With the lamp still turned off, the circulating pump was turned on (if desired for a particular experiment) and the reactant composition was sampled with the GC three times to confirm a thorough mixture of the reactants. The initial composition in this first experiment was 85 mol% CO_2 and 15 mol% H_2O. After verification of the reactant composition, the UV penray was switched on. Experiments were conducted for a duration of 1 week each. Liquid product samples were collected from inside the reactor and analyzed using gas chromatography/mass spectrometry.

RESULTS AND DISCUSSION

Task 1 Acquisition of Materials

The uncoated filters made of Kellundite® were obtained from Ferro, Inc. and weighed 110 to 130 g each. The filter dimensions were 130 mm, 52 mm OD cylinders with a thickness of 3 mm, resulting in a total surface area of approximately 0.018 m^2. Aluminum nitrate, bohemite, urea, titanium (IV) isopropoxide, iso-propanol, and hydrochloric acid were obtained from Aldrich for the preparation of the γ-alumina support and the titanium oxide catalyst. Two UV light penrays were purchased from UVP, one with a wavelength of 254 nm (UVC) and one with a wavelength of 365 nm (UVA). Also, two digital UV light intensities meters were purchased, one from Solartech for measuring light intensity in the UVA and B regions (280-400 nm wavelength) and the other from UVP for the UVC (100-280 nm) region. Carbon dioxide gas tanks were delivered from Airgas, and the gas was circulated with a quadhead liquid/gas pump made by Boxer®. A constant, precise flow of carbon dioxide was controlled by a C100 mass flow controller purchased from Sierra Instruments.

UV Lamp Light Intensity

The light intensities of both the UVA (365 nm wavelength) and UVC (254 nm wavelength penrays were determined using UV intensity meters with peak sensitivity at each respective wavelength. The intensities were measured from the vertical center of each lamp at a distance of 11/16" away from the penray surface. This was the distance measured from the surface of the penray to the inside surface of the coated filter. The intensities were measured to be 24.5 and 42.75 W/m^2 for the UVA and UVC penrays, respectively. It should be noted that when the intensity sensors for both penrays were moved to the outside diameter of the filter, no light was detected. This indicates that any photons not absorbed by the catalysts were absorbed by the filter or support and converted to thermal energy. The UVA penray was expected to have the weaker intensity. This is because the photon source is the same in both penrays, while the shorter wavelength photons are filtered out by a cobalt-based coating on the UVA penray. This

loss in emitted photons lessens the intensity. Having the options of two different wavelengths and intensities in the same setup enhances the flexibility of the reactor setup. It allow future work to be completed for gaining a better understanding of wavelength's and light intensity's effects on the carbon dioxide conversion and selectivity for methanol.

Task 2 Catalyst Preparation and Filter Coating

Xray diffraction was used to confirm the anatase mineral form of TiO_2 that was prepared in Task 2. Because there are difficulties when examining the filters in the XRD, the powders of γ-Al_2O_3 and TiO_2 were used instead. The XRD results for the prepared TiO_2 powder are shown in Figure 5. The peaks correspond to the anatase mineral form.
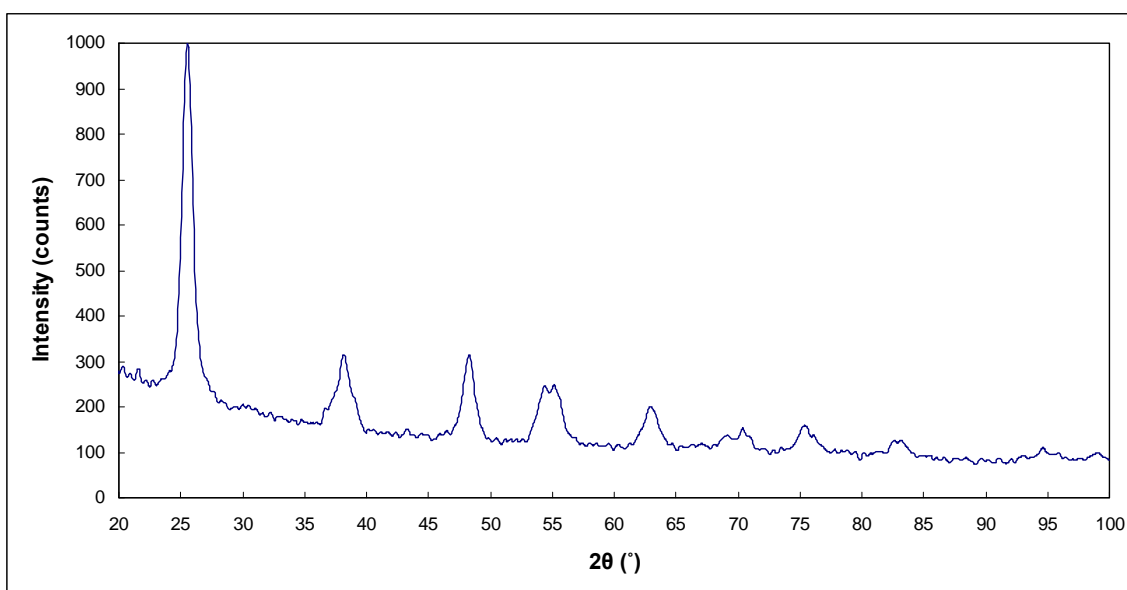
Figure 5 - XRD results of the prepared TiO_2 powder, showing anatase

Task 3 Verification of Photocatalytically Active Catalyst

Upon confirmation of the anatase form from the x-ray diffractograms, the powder was tested in different aqueous solutions to verify its photocatalytic activity under UVC (254 nm) irradiation emitted from a penray. In each of the three experiments (H_2O, 0.2 N NaOH, and 1 M propanol solutions), trace amounts of formaldehyde were found. The formaldehyde formation reaction is an intermediate reaction in the reduction steps from carbon dioxide to methanol, indicating that the reaction did not proceed to completion. This could be attributed to several parameters of the experiment. The CO_2 flow rate could have been too high resulting in a shorter contact time between the reactants and catalyst to proceed to methanol formation as well as the fact that the low partial pressure of the intermediates and products (due to the high CO_2 partial pressure) could result in premature desorption of the intermediates. Lastly, the light intensity of the penray (42.75

W/m^2) may be too low and the present catalyst was not supplied adequate energy for the complete conversion of CO_2 to the desired product, methanol.

<u>Task 4 Conversion of Carbon Dioxide to Methanol with Photocatalytic Filters</u>

A dry run with nitrogen passing through the impregnated filter with the penray illuminated, as well as, a run with CO_2 and steam passing through an uncoated filter with the penray illuminated, were conducted on the system to identify any problems and to obtain data regarding baseline information. In both experiments, no reaction was found to occur. Then, the carbon dioxide reduction experiments were conducted using a twice γ-Al_2O_3 washcoated, eight times TiO_2 impregnated tube filter. The CO_2 at the entry of the reactor had a flow rate of 30 ml/min. The products, upon exiting the reactor, were passed through a water trap for separation of the liquid samples and the remaining gases were analyzed with a gas chromatograph utilizing a thermal conductivity detector and a Hayesep Q column. The results of these "blank" runs indicated that no reactions were occurring without either a catalyst or reactant gases.

After confirming no leaks were present and collecting the "blank" experiment data, a twice-washcoated, eight times impregnated filter was placed inside the reactor. The reactor and tubing were completely purged with the CO_2/H_2O mixture to remove any air from the system. This step was performed with the lamp turned off to prevent any reaction. The initial composition in this experiment was 85 mol% CO_2 and 15 mol% H_2O. After verification of the reactant composition, the 254 nm UV penray was switched on. The experiment was conducted for a duration of 1 week. Liquid product samples were collected from inside the reactor and analyzed using gas chromatography/mass spectrometry. As with the results from Task 3, only formaldehyde was found in the product sample. In this experiment using the impregnated photocatalytic filter, in addition to the issues discussed in Task 3 results, the formaldehyde formation could be a result of insufficient catalytic surface (anatase) available on the coated filter.

CONCLUSIONS AND RECOMMENDATIONS

The following conclusions were made:

The method of preparing the TiO_2 catalyst in this work was effective in achieving the anatase form, which has been shown to be the most photocatalytically active mineral form of TiO_2.

A condition-flexible photocatalytic reactor was made which enables the CO_2 flow rate, CO_2:H_2O ratio, UV wavelength, intensity, temperature, pressure, and recycle amount to easily be studied.

The flow through catalytic filter reactor, although not effective for the conversion of CO_2 to methanol in the experiments that were conducted, has promise in that the probability of reactant-catalyst contact is higher than in previously reported reactor designs.

The exploratory research resulted in the development of a protocol for preparation of catalysts, the design of a flexible reactor system as well as for evaluation of such systems for future improvements.

The following recommendations were made based on the results:

Doping the anatase TiO_2 semi-conductor catalyst with a suitable CO_2 reducing catalyst (such as copper) should be attempted with the current setup.

Although this filter coating procedure was effective for the destruction of volatile organic compounds in previous work, the photocatalytic conversion of CO_2 to methanol may require a greater catalyst loading, and methods with the ability to load more TiO_2 to the filter should be explored.

Obtaining UV penrays with higher intensities may help the full utilization of the present catalyst.

REFERENCES

1. Bakardjieva, S.; Subrt, J.; Stengl, V.; Vecernikova, E.; and Bezdicka, P. 2003. "Comparison of Photocatalytical Properties of Anatase and Rutile TiO_2 in Degradation of 4-Chorophenol in Aqueous Solution." <u>Solid State Phenomena</u>. 90-91:7-12.

2. Wu, C. S.; Lin, H.; and Lai, C. 2005. "Photo Reduction of CO_2 to Methanol Using Optical-Fiber Photoreactor." <u>Applied Catalysis A: General</u>. 296:194-200.

3. Anpo, M.; Yamashita, H.; Ichihashi, Y.; and Ehara, S. 1995. "Photocatalytic Reduction of CO_2 with H_2O on Various Titanium Oxide Catalysts." <u>J. Electroanaly. Chem</u>. 396:21-26.

4. Matthews, R. W. and McEvoy, S. R. 1992. "A Comparison of 254 and 350 nm Excitation of TiO_2 in Simple Photocatalytic Reactors. <u>J. Photochem. Photobiol. A: Chem</u>. 66:355-366.

5. Koci, K.; Obalova, L.; and Lacny, Z. 2007. "Photocatalytic Reduction of CO_2 over TiO_2 Based Catalysts." <u>Chemical Papers</u>. 62(1):1-9.

6. Usubharatana, P.; McMartin, D.; Veawab, A.; and Tontiwachwuthikul, P. 2006. "Photocatalytic Process for CO_2 Emission Reduction from Industrial Flue Gas Streams." <u>Ind. Eng. Chem. Res</u>. 45:2558-2568.

7. Tseng, I.; Chang, W.; and Wu, C.S. 2002. "Photoreduction of CO_2 Using Sol-Gel Derived Titania and Titania-Supported Copper Catalysts." <u>Applied Catalysis B: Environmental</u>. 37:37-48.

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