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Sheryl E. Landis
Manager, Contracts and Intellectual Property
Business and Operations

Enclosure

SEL/llh

c: Mildred Perry, FETC
FINAL TOPICAL REPORT FOR NOVEL SYSTEMS
SEQUESTERING AND UTILIZATION OF CO₂

DOE Contract Agreement No. DE-AC21-98FT40415; Fund 4519

Final Topical Report – Phase I

(For the period of July 15, 1998 through April 15, 1999)

Prepared for:

Federal Energy Technology Center
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NOVEL SYSTEMS FOR SEQUESTERING AND UTILIZING CO$_2$

EXECUTIVE SUMMARY

A sequestering and utilization system for mitigation of CO$_2$ emissions requires a low-cost conversion coupled with a large-volume application. We proposed a concept based on copolymerization of CO$_2$ from stack gases or from a concentrated CO$_2$ stream coupled with use of the water-soluble products in enhanced oil recovery (EOR). The low cost results from the use of formaldehyde and other carbonyl compounds rather than epoxides as the comonomers. The project has demonstrated that catalytic conversion of CO$_2$ to copolymers can be accomplished. The copolycarbonate products obtained from formaldehyde precursors are in fact water-soluble. In addressing the decision points forecasted for the Phase I work, the following results are called out for the component technologies in the proposed system:

- **The CO$_2$ copolymerization with aldehydes give products with a potential for large-volume utilization.**

  The products from the reactions of paraformaldehyde and formaldehyde were stable water-soluble copolycarbonates with molecular weights of about 20,000. Mixing in 25% of a comonomer spacer (ethylene glycol) gave polymer with twice the molecular weight. Although the solubility properties were excellent, this size is not suitable for conferring high viscosities to the aqueous solution. Thus, it is necessary to cross-link the polymers at the chain ends, or possibly other places, to reach the desired molecular weights of 1–10,000,000 for application in waterflooding EOR. Preliminary experiments with borate indicate that this is feasible. Attaching a nonpolar group to the end(s) makes, alternative applications in detergent flooding EOR feasible.

- **Amine-trapped forms of CO$_2$ have potential for copolymerization to give useful copolymers.**

  Reactions using tertiary amines were successful in producing polymers. This means that these nonvolatile amines could be used to trap CO$_2$ from a flue gas and subsequently reacted with aldehydes, the tertiary amine acting as the catalyst for the copolymerization. On the other hand, reactions with primary amines such as ethanolamine were not successful. Thus, the conventional trapping with ethanolamine has little promise.

- **Concentrated CO$_2$ streams from advanced energy conversions or fermentation have the potential for copolymerization to give useful copolymers.**

  Lewis acid catalysts resulted in the formation of a stable copolycarbonate from the reaction of CO$_2$ with formaldehyde. Utilizing the Lewis acid catalysts on a solid support will provide a convenient reaction system where the CO$_2$ stream and formaldehyde streams are reacted on the solid catalyst.
• Nanostructured photoreactors may have potential for performing photoreductions of CO$_2$

Our earlier work provided novel sol-gel routes to nanostructured catalytic surfaces. No additional experiments have been performed to date. Literature sources indicated that nanostructured photoreactors offer large advantages in efficiency of photoconversions.
1.0 INTRODUCTION

Atmospheric CO$_2$ concentrations are increasing by about 0.5% each year, and there is serious concern that this will cause adverse climate change via the “greenhouse effect.” The principal sources of the increase are the utilization of fossil fuels and the deforestation of land.

The capture of CO$_2$ from flue gas or process streams has been demonstrated using chemical absorption with an ethanolamine solvent. However, the cost of releasing the CO$_2$ by thermal stripping and recovering the solvent is very high, resulting in an energy penalty of 27% to 37%, depending on the type of power plant (1). Alternatives that would result in energy penalties of 15% have been investigated.

Sequestering schemes for CO$_2$ produced from fossil fuels conversion to energy in utility plants could instead yield useful polymer products. Relatively concentrated CO$_2$ byproduct streams from fermentation of cellulose to fuel ethanol will also be available for conversion to useful polymers. As shown in Figure 1, this project offers two opportunities for mitigating the emission of CO$_2$ to the atmosphere, depending on the source configuration and economic feasibility of the proposed processes: CO$_2$ in a conventional utility-produced flue gas could be sequestered to form a reactive monomer using an amine (such as ethanolamine) that reacts with an aldehyde to form an amine intermediate, which subsequently copolymerizes with the CO$_2$ to give a copolyurethane. Using a tertiary amine to trap the CO$_2$ is also proposed. In this case the tertiary ammonium carbonate is reacted with the aldehyde to form the copolycarbonate, regenerating the tertiary amine. In an alternate scheme, a concentrated CO$_2$ stream from an advanced energy system could be directly polymerized with aldehyde and catalyst to Polymer 2 (see Figure 1). Sources of concentrated CO$_2$ include the water–gas shift reaction in an IGCC (integrated gasification combined-cycle) device, fermentation, a fuel cell anode gas, or oxygen-fired combustion.

Significant sequestration of CO$_2$ would be accomplished if large amounts could be efficiently and economically converted to stable and useful products that would pay for the processing. If the CO$_2$ is stored rather than converted to a useful product, the cost of sequestering must be extremely low. If CO$_2$ is to be utilized as a chemical feedstock, the allowable process cost can be higher, but only high-volume commodity chemical products could sequester a significant amount of CO$_2$. Large volumes of inexpensive CO$_2$-derived polymers could be utilized for enhanced oil recovery, structural thermoplastic resins, and ion-exchange applications.

Economic success is better achieved with the availability of a very inexpensive aldehyde or derivative mine. To provide this component inexpensively, a novel photosystem is proposed such that CO$_2$ is also converted to the desired copolymer feedstock.

2.0 PHASE I OBJECTIVES

The proposed work will develop a novel low-cost CO$_2$ sequestering and utilization system based on copolymerization of CO$_2$ from stack gases or from a concentrated CO$_2$ stream. The
technical and economic feasibility of the three components of the proposed system will be assessed. The objectives are to 1) evaluate the formation of a stabilized copolymer of CO\textsubscript{2} with an aldehyde and the corresponding mine form, from both concentrated and stack gas CO\textsubscript{2}, 2) determine the properties of the copolymers so that the utilization can be assessed, and 3) evaluate the potential for photoreactions that produce useful aldehyde intermediates and photoreduce CO\textsubscript{2}. Phase I involves preliminary bench-scale experiments and assessments. Phase II involves laboratory verification and systems engineering evaluation to show proof of concept. Phase III involves scaleup of experimental studies to pilot-scale polymer production and utilization and photoreactor operation.

3.0 ACCOMPLISHMENTS

3.1 Acetal Copolycarbonate Synthesis

The polymers prepared from sequestered CO\textsubscript{2} are those of the acetal copolymer type (Figure 2). The polymer formed from an aldehyde as a comonomer represents the smallest possible polycarbonate structure, since the “diol” is generated at a single carbon (geminal diol). Although polycarbonates and also acetal copolymers are commercial products, there is only one reference to the acetal copolycarbonate in the literature (2). Utilization of this type of copolymer remains to be explored.
In the Phase I work, preparation of acetal copolycarbonates was accomplished by reaction of formaldehyde with CO$_2$ with a series of basic (2) and Lewis acid catalysts. Formaldehyde is a very reactive species and readily polymerizes with itself in the neat liquid or in solution. The self-polymerization and the corresponding depolymerization are catalyzed by acids and bases, so it was logical to use these catalysts for the copolymerization with CO$_2$. Several solvents were utilized, and a matrix of several combinations of temperatures and reaction times were studied to evaluate the conditions needed for effective polymerization.

Three forms of formaldehyde were investigated, the aqueous formalin solution, the polymeric paraformaldehyde form, and the trimer trioxane form. The 37% aqueous solution is actually mainly methanediol or methylene glycol, that is, the addition product of water to the formaldehyde. The paraformaldehyde was not appreciably soluble in either water or solvents at ambient temperatures. The trioxane was soluble, but is a much more stable form than the other two.

Reactions were conducted in a 300-mL pressurized Parr autoclave with generally 16 g of CO$_2$ and an equimolar amount of aldehyde equivalent with 5% by weight of catalyst. Products were worked up differently depending on the solvent for the reaction.

Phase I testing to evaluate the applicability of the series of polymers for EOR included the following:

- Determine molecular weights by gel permeation chromatography (GPC)
- Determine water solubilities
- Determine solution viscosities

Aqueous solutions of the polymeric products were analyzed with high-pressure GPC on a TSK30 gel column with water eluent and UV detection at 210 nm, and dioxane solutions were analyzed with a mixed pore size PL gel column in tetrahydrofuran (THF) solvent. Molecular
weights ($M_w$) were calibrated using retention times of proteins and polymer standards with narrow $M_w$ distributions.

Reaction yields were also determined on the GPC column. The copolycarbonate peak area was calibrated using a known concentration of a standard consisting of a purified copolycarbonate sample.

**Base Catalysis**

A comparison of the catalytic effects of a series of organic bases was conducted on the reactions of carbon dioxide with aqueous formaldehyde to form the acetal copolycarbonate ester. The reactions were performed in a pressurized autoclave at 120°C using organic bases, triethylamine (TEA), dimethylaminopyridine (DMAP), and diazabicyclooctane (DABCO) as catalysts for the reactions (see Table 1). TEA was used in the Chinese work (2). The DMAP and DABCO are much more basic and were expected to exert a better catalytic effect.

A mixture of aqueous formaldehyde (37%), catalyst, and dry ice was placed in a 300-ml Parr reactor. The reactor was sealed under nitrogen and heated at desired temperature for the desired time period. At the end of the reaction, the reactor was degassed and opened. An orange solution was produced. The reaction products were soluble in the water solvent used for the reaction. Extraction of the aqueous product mixture with ether recovered about 70% of the base catalyst. The amount of acetal copolycarbonate in the aqueous solution was determined by GPC. For this determination, one mL of this solution was diluted to 50 mL by adding deionized water. The solution (50 μL) was injected on the TSK30 column and eluted with water. Polymer peaks

**TABLE 1**

Reactions of Formaldehyde

<table>
<thead>
<tr>
<th>Aldehyde</th>
<th>Catalyst</th>
<th>Solvent</th>
<th>Temp., °C</th>
<th>Time, hrs.</th>
<th>Polymer Solubility</th>
<th>$M_w$ (Yield)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCHO (37%, 40 mL)</td>
<td>TEA (2 g)</td>
<td>Water</td>
<td>120</td>
<td>100</td>
<td>Very viscous oil (4.01 g)</td>
<td>Somewhat soluble in water</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>20,000 (17%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>16,000 (19%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>12,000 (8%)</td>
</tr>
<tr>
<td>HCHO (37%, 40 mL)</td>
<td>DMAP (2.3 g)</td>
<td>Water</td>
<td>120</td>
<td>100</td>
<td>Very viscous oil (6.2 g)</td>
<td>Somewhat soluble in water</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>14,000 (27%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>11,500 (15%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1000 (20%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>&lt;1000 (rest)</td>
</tr>
<tr>
<td>HCHO (37%, 40 mL)</td>
<td>DABCO (2.24 g)</td>
<td>Water</td>
<td>120</td>
<td>100</td>
<td>Very viscous oil (5.1 g)</td>
<td>Somewhat soluble in water</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1000 (17%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>&lt;1000 (rest)</td>
</tr>
</tbody>
</table>

* HCHO = formaldehyde
elated early, and molecular weights and amounts were determined from retention times and peak areas. Low-molecular-weight oligomers were also present in the products, as evidenced by the presence of a late GPC peak. This peak was not quantitated, nor was methanediol (formaldehyde monomer), owing to its lack of UV response.

Higher yields of polymer were obtained from the reaction using the more powerful base DMAP. TEA gave the lowest yield and is the most volatile. The GPC results showed multiple peaks, indicating a polydispersed product. The reason for this is unknown. Assuming the tertiary amines can be recovered and recycled, the higher cost of DMAP may be offset by higher yields. In some experiments, ether extraction recovered 70% of the DMAP. More work is needed to determine the optimum recovery methods or to use a heterogeneous or supported catalyst.

In addition to GPC analysis, water was removed from the reaction products by low vacuum distillation. The impure reaction products were tacky solids with good water and ethanol solubility, but poor solubility in THF and dioxane. Infrared spectroscopy of the products indicated that substantial amounts of aliphatic ester carbonyl groups were present, verifying that the desired incorporation of \( \text{CO}_2 \) to form the polycarbonate ester had occurred. Unreacted formaldehyde monomer (methanediol) or oligomeric products were also present, as evidenced by the large hydroxyl bands in the IR.

A comparison of the reaction conditions was also performed with the reaction of \( \text{CO}_2 \) in aqueous formaldehyde using the basic catalyst, DMAP, for all the reactions. This reaction matrix varied temperature (120°C to 200°C) and the reaction time (12 versus 24 hr). Initially, the reactions were run at 120°C and 100 hr. Relevant data are given in Table 2. At higher reaction temperatures, some of the polymeric product was insoluble in water. The amount of the insoluble polymer increased with temperature.

For the 12-hr series of runs, polycarbonate yields increased with temperature as follows: 120°C, 4%; 150°C, 5%; 175°C, 9%; 200°C, 11%. Increasing the reaction time to 24 hours at 150°C increased the yield from 5% to 7%. The molecular weight of the polymer products was about 20,000 daltons for most of the reactions but was 40,000 for the reaction at 175°C.

**Recovery of Catalysts**

The ether extract obtained from ether extraction of the reaction product was diluted to known volume. An aliquot of this solution was mixed with internal standard (o-chlorobenzene) and analyzed by gas chromatography.

Two disadvantages of the aqueous formaldehyde became obvious during these initial studies: 1) The product polymers are not easily separated from the reactant formaldehyde and oligomers, owing to similarity in solubility and difficulty in distilling the formaldehyde off without decomposition. 2) The aqueous formaldehyde contains methanol (normally 5%–15% present in commercial formalin solution) that could cap the ends of the chains as an acetal linkage. Methanol and formic acid are also formed as byproducts in the reaction via the Cannizarro reaction of
aldehydes in base. Although it is displaceable from the end formaldehyde unit, it would inhibit the reaction and prevent the reaction with the CO₂.

**Paraformaldehyde Reactions**

Paraformaldehyde is a pure homopolymeric form of formaldehyde. The homopolymer can be depolymerized readily at elevated temperatures in the presence of a catalyst. It was not soluble in water or dioxane. However, it was reacted with CO₂ as a slurry in dioxane at 120°C using the DABCO catalyst. The reaction products had limited solubility in dioxane, so were easily separated as a viscous liquid by decantation of the solvent. This product exhibited high water and ethanol solubility. IR confirmed its polycarbonate structure.

An investigation of the reactions of paraformaldehyde with CO₂ was conducted in ether and ester solvents at 120°C (see Table 3). The products were compared for reactions with two basic catalysts, DMAP and DABCO in two solvents, methyl tertiary butyl ether (MTBE) and dioxane. The molecular weights of the products were determined by high-pressure GPC. In MTBE solvent, the
stronger of the base catalysts, DMAP, resulted in the highest yields of polycarbonate, but the molecular weight of the product (12,000) was lower than that obtained with DABCO (19,000 and 23,000 two peaks). Yields in dioxane were similar for the two bases. Reactions in the ester solvent (ethyl acetate) gave no polymer product.

Higher-temperature reactions of paraformaldehyde were also investigated. Reactions of paraformaldehyde with CO$_2$ in dioxane solvent (DMAP catalyst) at 175°C for 12 hr gave a 33% yield compared with a yield of 21% for the reaction at 120°C for 48 hr. The molecular weights were similar for the two reactions (23,000). Thus temperature has a very significant effect in increasing the reaction yields, but does not significantly affect the molecular weights.

Paraformaldehyde gave higher yields of polymer than aqueous formaldehyde. The reaction of paraformaldehyde required the catalyzed depolymerization to the reactive monomer in situ. When paraformaldehyde was heated in dioxane at 120°C for 24 hr, no formaldehyde was formed. However, when paraformaldehyde was heated in dioxane in the presence of 4-dimethylaminopyridine, a significant amount of formaldehyde was formed. Quantitative analyses was not performed. Trioxane does not decompose to formaldehyde in base and therefore did not react to form polymer.

**Reactions of Trioxane**

Trioxane, the trimer of formaldehyde, is easily formed from formaldehyde and represents a soluble form. One reaction of trioxane was attempted with CO$_2$ with the DMAP catalyst at

<table>
<thead>
<tr>
<th>TABLE 3</th>
<th>Reactions of Paraformaldehyde</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Aldehyde</strong></td>
<td><strong>Catalyst</strong></td>
</tr>
<tr>
<td>Paraformaldehyde (15 g) + Dry Ice (16 g)</td>
<td>DMAP (2.37g)</td>
</tr>
<tr>
<td>Paraformaldehyde (15 g) + Dry Ice (16 g)</td>
<td>DMAP (2.37g)</td>
</tr>
<tr>
<td>Paraformaldehyde (15 g) + Dry Ice (16 g)</td>
<td>DABCO (3.58g)</td>
</tr>
<tr>
<td>Paraformaldehyde (15 g) + Dry Ice (16 g)</td>
<td>DMAP (2.3g)</td>
</tr>
<tr>
<td>Paraformaldehyde (22 g) + Dry Ice (24 g)</td>
<td>None</td>
</tr>
<tr>
<td>Paraformaldehyde (15 g) + Ethanol-amine (30.5 g) + Dry Ice (16 g)</td>
<td>DABCO (2.3g)</td>
</tr>
</tbody>
</table>
150°C. No polymer formed in the reaction. The basic catalyst was not effective in breaking down the trioxane to formaldehyde for the copolymerization.

Reactions with Glycol Comonomer

Incorporation of ethylene glycol as a comonomer was attempted to determine if additional stability would result from the presence of the glycol or 1,2-dioxy unit in the chain. This unit would be expected to be more stable than the vicinal acetal or 1,1-dioxy unit that results from polymerization of the aldehydes. Thus, the polymerization of CO₂ with paraformaldehyde and 25% ethylene glycol in a dioxane solvent and DABCO catalyst was carried out. The ethylene glycol unit was also expected to modify the crystallinity of the chains by acting as a “spacer” group.

The copolymer products obtained with ethylene glycol contained 58% of a significantly higher-molecular-weight polymer (42,500 daltons) in addition to the normal 20,000-dalton polymer. The products were still soluble in water. Further reactions with epoxide and other comonomer mixtures is needed to understand and optimize the copolymerization reaction chemistry.

Copolymerization of Other Aldehydes

The scope of the acetal copolycarbonate reaction was expanded to include other aldehydes. Reactions of acetaldehyde were conducted with carbon dioxide in dioxane (DMAP catalyst) at 150°C (see Table 4). A low yield of polymer was obtained. The condensation product, crotonaldehyde, and low-molecular-weight oligomers were present. A repetition at this temperature gave similar results. A reaction temperature of 175°C gave higher yields than the reactions at 150°C. In contrast to the formaldehyde copolycarbonates, the polymer products from the acetaldehyde polymerization were not water-soluble. The acetaldehyde copolycarbonate is in fact soluble in dioxane and THF. The molecular weight of the product from the higher temperature reaction (19,000) was similar to that from the 150°C reaction. With the basic catalyst, the major products result from condensation rather than copolymerization. The reactions of acetaldehyde with an Lewis acid catalyst have not yet been investigated. Because of the poor water solubility of the acetaldehyde copolycarbonate, the usefulness of this polymer is not likely to be in EOR. The resinous product may find use in other resin applications, however.

TABLE 4
Reactions of Acetaldehyde

<table>
<thead>
<tr>
<th>Aldehyde</th>
<th>Catalyst</th>
<th>Solvent</th>
<th>Temp., °C</th>
<th>Time, hr</th>
<th>Polymer</th>
<th>Soluble</th>
<th>Mₜ (Yield)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetaldehyde (22 g) + Dry Ice (16 g)</td>
<td>DMAP (2.37 g)</td>
<td>Dioxane (40 mL)</td>
<td>150</td>
<td>12</td>
<td>(0.73 g)*</td>
<td>Dioxane</td>
<td>86,000 (35%)</td>
</tr>
<tr>
<td>Acetaldehyde (22) + Dry Ice (16 g)</td>
<td>DMAP (2.3 g)</td>
<td>Dioxane (40 mL)</td>
<td>175</td>
<td>12</td>
<td>(5.73 g)*</td>
<td>Dioxane</td>
<td>19,000 (100%)</td>
</tr>
</tbody>
</table>

* Yield based on GPC data.
Reactions of a second aldehyde (furfuraldehyde) with CO\textsubscript{2} were also investigated at 120°C. The product was, however, only partially soluble and appeared to have been converted to a pitch under the reaction conditions.

**Lewis Acid Catalysis**

A large number of Lewis acid catalysts have been tested in other laboratories for the related copolymerization of epoxides with CO\textsubscript{2} (3). A literature survey of Lewis acid catalysts that may be appropriate for the aldehyde CO\textsubscript{2} copolymerizations was conducted. The list of potential Lewis acid catalysts that are expected to have promise includes those used by the following authors:

- Inoue (4): ZnEt\textsubscript{2} + H\textsubscript{2}O
- Soga (5): Zn carboxylates
- L. Chen (6): ZnEt\textsubscript{2} with polymer acid; (iPrOZnO)\textsubscript{2}AlOiPr; zinc ferrocynide complexes.
- Kuran and Listos (7): ZnEt\textsubscript{2} + phenols
- Kricheldorf (8): BX\textsubscript{3}
- X. Chen (9): Rare-earth phosphate + Al(iBu)\textsubscript{3} + ROH
- Koinuma and Hirai (10): AlR\textsubscript{3}
- Darensbourg and Holtcamp (11): bulky Zn phenoxides
- Cheng (12): bulky Zn bisanil complex

The Phase I work tested only one of these that was recently shown to be highly effective for the epoxides reactions (12). The zinc bisanil catalyst was prepared for the reactions of CO\textsubscript{2} with paraformaldehyde and acetaldehyde. The function of the acid catalyst is to break down the paraformaldehyde or trioxane, as well as catalyze the copolymerization. Most acids will catalyze the breakdown.

Several forms of the Zn bisanil catalyst have been investigated briefly in the Phase I work. A mixture of paraformaldehyde, catalyst, and dry ice were placed in a 300-mL Parr reactor. The reactor was sealed under nitrogen, and heated at desired temperature for the desired time period. At the end of the reaction, the reactor was degassed and opened. A white polymeric film was formed on top of a orange solution. The polymeric film was separated by filtration. The white film was air-dried and weighed. The orange solution was evaporated to remove solvent. Upon removal of solvent, a highly viscous orange oil was formed. The oil was completely soluble in water. A 1% solution of the polymer in water was formed and analyzed by GPC. Molecular weight determination of the product was carried out by injecting 0.5-mL of the dilute solution. Multiple peaks were obtained for these polymer products. Molecular weight of this polymer was determined using a calibration curve obtained from polymers of known molecular weights. Area of the peaks were used to determine the weights of the polymers using area of polymer obtained from the known weight of paraformaldehyde polymer. Relevant data are given in Table 5.

The methoxide form of the catalyst gave the most product, but only a portion of it was the 21,000 dalton polymer. Most was the oligomers. The chloride form gave the least product, and since it was not soluble in water, it has not yet been analyzed in the GPC system. The trichloroacetate form
TABLE 5

Zinc bisanil Complex Catalyzed Reactions of Paraformaldehyde and CO₂

<table>
<thead>
<tr>
<th>Aldehyde</th>
<th>Catalyst</th>
<th>Solvent</th>
<th>Temp., °</th>
<th>Time, hr</th>
<th>Polymer</th>
<th>Soluble</th>
<th>Mₘ (Yield)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paraformaldehyde (15 g)</td>
<td>Bis anil + NaOMe +ZnCl₂ (1.08 g)</td>
<td>Dioxane (40 mL)</td>
<td>150</td>
<td>20</td>
<td>Orange oil (8.71 g)</td>
<td>White solid</td>
<td>Water</td>
</tr>
<tr>
<td>Paraformaldehyde (15 g)</td>
<td>Bisanil ZnCl₂ (3.54 g)</td>
<td>Dioxane (40 mL)</td>
<td>150</td>
<td>12</td>
<td>Orange oil (4.62 g)</td>
<td>Water</td>
<td>85,000 (1.5%) 24,000 (3%) 21,000 (36%) 17,000 (24%) 13,000 (7%)</td>
</tr>
<tr>
<td>Paraformaldehyde (15 g)</td>
<td>Bisanil ZnTCA (0.5 g)</td>
<td>Dioxane (40 mL)</td>
<td>150</td>
<td>12</td>
<td>Orange oil (6.26 g)</td>
<td>Water</td>
<td>85,000 (1.5%) 24,000 (3%) 21,000 (36%) 17,000 (24%) 13,000 (7%)</td>
</tr>
</tbody>
</table>

was reasonably successful in producing the 17,000- to 21,000-dalton product. Further modifications of this catalyst are in progress and will be continued in the Phase I and II work.

3.2 Copolyurethane Synthesis

For direct sequestering of CO₂ from a conventional dilute flue gas, the CO₂ could be captured by a suitable basic comonomer and the monomer–CO₂ adduct subsequently polymerized (Figure 3). The project investigated the use of imines for the adduct formation and copolymerization. Aldehydes react readily with primary amines to form the imine. Formaldehyde imine is extremely reactive and self-condenses to form hexamethylenetetramine. This base would trap CO₂ but not polymerize. But imines of acetaldehyde and various other aldehydes and ketones could adduct CO₂ and form the polymer. The resulting polymers will be acetal copolyurethanes (Figure 3). Alternatively, the primary amine would react with CO₂ in the flue gas to form an alkylammonium carbonate and subsequently with aldehyde to form the copolyurethane. The primary amine should be nonvolatile, as is the case with ethanolamine in current scheme. With appropriate end-capping groups and spaces, the stability of the copolyurethane should be acceptable and the water solubility increased.

A reaction of paraformaldehyde was carried out with ethanolamine and carbon dioxide in dioxane. Ethanolamine can be used to effectively absorb CO₂ from flue gas. It was expected that the both the nitrogen and the carbonyl would be incorporated into the polymer product as a polyurethane linkage. However only 2% yield of polymer was obtained.

Reactions of aldehydes were also conducted using ammonium carbonate, but very low yields of polyurethane were obtained. Further reactions involving primary amines were abandoned. It is possible that the tertiary amine is needed for effective formation of the polymer.
Since reaction of aldehydes with CO$_2$ with tertiary amine catalysts was successful, the most feasible sequestering scheme would be to trap CO$_2$ from a flue gas stream with a low-volatility tertiary amine such as DABCO and subsequently react formaldehyde with the tertiary-ammonium carbonates. This intermediate furnishes both the catalyst and carbonate needed for the reaction.

**Viscosity measurements:**

Viscosity measurements of the polymers were carried out using two different viscometers, namely, Brookfield Synchro-Lectric viscometer and an-all glass Cannon-Fenske Reverse Flow Kinematic Viscometer. Solutions of the polymers were prepared by dissolving 1 wt% of the polymers in 24 g of deionized water.

The Cannon-Fenske Reverse flow viscometer requires a minimum of 12-mL of liquid and is rated for measurements between 0.8 and 4 centistokes. Viscosity was determined by recording the time in seconds required for the solution to travel through a fixed distance of the viscometer. The time in seconds was multiplied by a factor of 0.004 to get viscosity in centistokes (Table 6).

The polymer was also mixed with 10 wt% of boric acid and thoroughly mixed. The paste was allowed to stand for 30 mins. It was then dissolved in deionized water to prepare 1 wt% solution. The solution was filtered to remove insoluble material, and the viscosity of the solution was determined. The viscosity data are given in Table 6.
TABLE 6

Viscosity Data of the Polymers by Cannon-Fenske Viscometer

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Time, sec</th>
<th>Viscosity, centistokes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>276</td>
<td>1.1</td>
</tr>
<tr>
<td>Polyacrylamide</td>
<td>304</td>
<td>1.22</td>
</tr>
<tr>
<td>PF + DABCO + Dry ice + Dioxane (solvent)/120°C/100 hr</td>
<td>287</td>
<td>1.15</td>
</tr>
<tr>
<td>PF + EG + DABCO + Dry ice + Dioxane (solvent)/120°C/48 hr</td>
<td>290</td>
<td>1.16</td>
</tr>
<tr>
<td>PF + EG + DABCO + Dry ice + Dioxane (solvent)/120°C/48 hr/10 wt% Boric acid</td>
<td>325</td>
<td>1.30</td>
</tr>
<tr>
<td>PF + DMAP + Dry ice + Dioxane (solvent)/175°C/12 hr</td>
<td>285</td>
<td>1.14</td>
</tr>
<tr>
<td>PF + DMAP + Dry ice + Dioxane (solvent)/175°C/12 hr/10 wt% Boric acid</td>
<td>330</td>
<td>1.32</td>
</tr>
</tbody>
</table>

The measured viscosities of 1% solutions of both the copolycarbonate and the polyacrylamide standard were low, as expected for the low molecular weights. Reaction of the polymers with borate improved the viscosity by a small factor. Further cross-linking reactions to improve the molecular weight and viscosity are in progress.

For the measurements of viscosities using Brookfields Synchro-Lectric viscometer, a solution of the polymers were prepared by dissolving 1 wt% of the desired polymer in deionized water. The appropriate spindle No. 1 and 60-rpm speed were used. The spindle was spun in the solution before taking measurements. Owing to the lower sensitivity of this instrument, solution viscosities were not distinguishable from pure water. Thus this instrument will be used when high-molecular-weight polymers are attained and viscosities are significantly higher.

3.3 Utilization of CO$_2$-Derived Copolymers

Viscosifier for Waterflooding EOR

The Phase I work demonstrated that water-soluble copolymers can be formed from sequestered CO$_2$. The CO$_2$-derived copolymers are desired for increasing oil production in waterflooding EOR. Water-soluble polymers are added during waterflooding to increase the viscosity of the water, so water does not “finger” into the oil and get pumped out with the oil. The principal polymer used for increasing viscosity is polyacrylamide, costing about $2–3/lb. Since large amounts of polymers are utilized, less expensive CO$_2$-derived polymers from a sequestering process could lower the cost of EOR technology and thus pay for the sequestering process.

To achieve the high viscosities required for waterflooding EOR, high-molecular-weight polymers (10,000,000 daltons) are required. The viscosities are exponentially related to the molecular
weight. Neither the water-soluble copolycarbonates (M\textsubscript{w} = 20,000 daltons) produced in Phase I nor commercial polyacrylamides of the same molecular weight exhibit a significant effect on viscosity at low concentrations (0.1 %). Because the copolycarbonates are not branched and do not have extensive functionality along the chain, it will be relatively easy to achieve the desired molecular weight polymers by linking the chain ends. Thus, the viscosity can be increased without forming a gel or insoluble resin. Preliminary experiments linking with boric acid were successful in raising the viscosity. Further experiments in Phase II are needed to optimize the molecular weight by this means and are proposed in Volume II.

Further Phase II work is also proposed in to optimize the formation of polymers by increasing the yields and molecular weights of the products. This will be investigated by testing additional catalysts and solvents for the reactions, and by conducting a matrix of reactions under a variety of pressures, temperatures and reaction times. Catalyst recovery and recycle will also be investigated.

**Surfactants**

Surfactants are also required in EOR for lowering surface forces that prevent migration of the oil. The nonionic surfactants consist of a nonpolar hydrocarbon-binding end attached to a very polar water-binding end, such as polyethylene glycol. The water-soluble copolycarbonates prepared in the Phase I project are ideal for the water-binding end and can be converted to the desired surfactant structures by covalently attaching a fatty alkyl or acyl group. This application will be proposed for Phase II work.

### 3.4 Photocells

An important part of the proposed sequester system is a method for obtaining inexpensive aldehyde intermediates for the copolymers. Solar energy conversion could provide such synthetic intermediates, as in living photosynthetic systems. The type of photoreactor proposed is based on sol-gel construction from ruthenium, manganese, and other metal oxotitanates. This approach will connect the photosensitizer sites containing ruthenium more intimately with the titanium dioxide semiconductor base that results from the hydrolysis of the soluble precursor oxotitanates. Incorporation of these into CO\textsubscript{2} photoreduction sites is proposed. It further offers the potential for construction of unique polymetal cluster oxidation sites also linked to the semiconductor base that result from the corresponding polymetal (e.g., Mn\textsubscript{4}) oxotitanates. Thus the oxidation potential of the photocell hole is used for alcohol oxidation to aldehyde.

The sol-gel methods needed for construction of the photoreactor systems are based on our earlier work with alumina- and titania-supported catalysts. The approach in the proposed work is prepare metal oxotitanates that could be converted by sol-gel techniques to nanocrystalline or supramolecular photoreactors. The Phase I and Phase II work will investigate the feasibility of constructing a suitable photooxidation site for alcohols using a sol-gel technology that we developed earlier at the Energy & Environmental Research Center (EERC) and UFDA (Universal Fuel Development Associates) (13,14).

A review of the literature concerning CO\textsubscript{2} photoreduction and other photoreactors was carried out. Certain relevant aspects of the literature study are incorporated into Volume II of the Phase II
proposal, as they pertain to the ideas that we wish to pursue. The ideas in Volume II are essentially similar to those we originally proposed, but some modification of the Ru photocenter is being considered. We do not present a complete review here because the existing published reviews generally suffice. Systems for photochemical conversions of CO₂ are discussed in recent monographs (15, 16). The approach of using sensitized nanocrystalline TiO₂ photoanodes has been recently investigated (17). The concept of building supramolecular systems for photoreactions from nanocrystalline materials has been developed and discussed by Bignozzi, Schoonover, and Scandola (18). Supramolecular systems offer advantages in the charge separation efficiencies, increasing light absorption cross sections, and suppressing charge recombination.

Further synthetic work toward these systems is planned in Phase I but has not yet been accomplished. Based on a reported oxometallate synthesis (19), our prior work (13, 14) involved the construction of a soluble complex containing a divalent metal atom bound via two oxygen atoms to two titanium trialkoxide groups. The precursors of the metal oxotitanates and oxoaluminate were generally the metal acetates and either titanium isopropoxide (or ethoxide) or aluminum isoproxide. This metal oxotitanate complex was converted to a colloidal semiconducting material by hydrolysis or heating under nitrogen, which decomposed the alkoxide groups. Similarly, the soluble metal oxoaluminate complexes were prepared and decomposed to the colloidal gels. Thus the divalent metal was contained in a matrix of titania (TiO₂) or alumina and was active for hydrogen transfer reactions when activated with CO. A similar sol-gel technique was used for a triiron acetate cluster to prepare the cluster dispersed in an alumina matrix. While being too expensive for coal liquefaction catalysts, these materials offer promise for other applications where the nanocrystalline nature can exert a positive effect on the efficiency of electron as well as mass transfer.

The proposed work will examine the Ru oxotitania semiconductor produced from the hydrolysis of the soluble Ru oxotitanates. The basic hypothesis is that the ruthenium or other metal is incorporated into the photoreactive semiconducting units. Further extensions of this idea are discussed in Volume II.

4.0 CONCLUSIONS

Several options for producing copolymers from flue gas CO₂ were initially considered, and the Phase I work served to narrow the focus as intended at the point of decision. Phase I work established that the copolymerization reaction with aldehydes is feasible. Two types of catalysts gave water-soluble copolycarbonates. In contrast, the Phase I studies showed that the use of imine intermediates as CO₂ acceptors and comonomers failed to produce the desired polyurethane copolymers, eliminating this option. Thus, the following two schemes for utilizing CO₂ from stack gas or another source are potentially commercially viable.

1. A concentrated CO₂ stream (80%) produced by membrane separation of flue gas can be reacted with paraformaldehyde or formaldehyde in a suitable solvent and with a catalyst, such as zinc bisanil or a tertiary amine, to produce a water-soluble copolymer. Cross-linking of the polymer will give a high-molecular-weight polymer with appropriately high viscosity.
suitable for applications in EOR. This scheme provides a novel end use for the inexpensively separated CO\textsubscript{2} stream or from fermentation byproduct streams.

2. Tertiary amines that are actually the catalysts for the subsequent copolymerization reaction would be used to trap CO\textsubscript{2} from flue gas. The tertiary amine carbonates would be reacted with formaldehyde to produce the copolymer. The catalytic tertiary amines would be recovered and recycled to the flue gas-cleaning unit. This is significantly novel compared with amine sequestering currently used in and thus would create a large energy savings in not having to thermally regenerate the amine.

5.0 REFERENCES


