The research project has been an assessment of the potential for carbon dioxide capture and storage by chemical reactions between CO₂ and phenolic, polymeric substances of natural origin. The polymers that have been tested are: 1) lignin (a major constituent of hardwoods and, especially, softwoods), one of the most abundant organic polymers found in nature; and 2) humic acid (in the form of tannins), a major constituent of soils.

The principal objective of the research has been to identify one or more processes by which CO₂ can be removed from combustion mixtures by its incorporation into the chemical structure of an abundant, naturally occurring material. The rationale of the project is based on the Kolbe-Schmitt reaction, a classical synthetic method in organic chemistry, in which an aromatic compound bearing hydroxyl groups (a phenol) is treated with CO₂ either as a gas or in the form of bicarbonate/carbonate in aqueous solution. The product of the reaction is a phenolic carboxylic acid. Although with simple phenols, conditions of high temperature and/or pressure are required to bring about the reaction, phenols having two or more hydroxyl (or methoxyl) substituents are appreciably more reactive under milder conditions.

The research objectives were achieved by measuring the uptake of CO₂ under laboratory conditions by the two polymers and selected model compounds. The uptake was assessed by titration of the reaction mixtures and by comparing the intensity of bands in the infrared spectrum characteristic of carboxyl (-COOH) groups. The polymers showing the highest degree of uptake were the condensed tannins, materials found in many seeds and barks, as well as making up part of the humic acid fraction of the soil. Catechin, a model compound related to these tannins, readily reacted with bicarbonate in water to give a red product containing added CO₂ in the form of carboxyl (-COOH) groups.
EXECUTIVE SUMMARY

Carbon capture and storage (CCS) has become a topic of intense interest as concern grows over the massive input of the greenhouse gas, CO\textsubscript{2}, into the earth’s atmosphere and its effects on increasing global temperature. The idea behind CCS is that CO\textsubscript{2} produced by combustion can be trapped, concentrated, and delivered into an area where it is prevented from passing into the atmosphere.

Carbon dioxide is the ultimate product that is formed whenever carbon-containing materials are oxidized. In nature this occurs during respiration by living organisms of reduced carbon compounds such as carbohydrates and lipids. However, for many years the contribution of natural CO\textsubscript{2} has been greatly augmented by human activities such as the burning of petroleum, coal, and wood. The US produces roughly half of its electricity from coal; worldwide, the fraction is nearer to 40%, but this is increasing as China and India open new coal-fired plants nearly every week.

Among the major suggestions for CCS is that CO\textsubscript{2} produced in a high-volume local combustion source, such as a coal-fired power plant, be collected, scrubbed, compressed, and injected into an underground location or into a body of water such as the ocean. Problems with such an approach include the potential for leakage from deep underground and the potential for tectonic earth movements. In addition, the necessity of capturing and processing the emitted CO\textsubscript{2} is energy-intensive; suggestions are that 20-40% more fuel will be required to operate such a plant. Passage of the gas into the ocean is projected to exacerbate the problem of seawater acidification, which has already been recognized as a consequence of the natural atmospheric increase in CO\textsubscript{2}.

Another potentially useful technology is the transfer of coal combustion gases through a pipeline to an oil field, where it could be injected into the petroleum deposit for enhancing oil recovery. One region where this is being tested is western North Dakota, where a coal plant in Beulah, ND, sends its flue gases to Weyburn, Saskatchewan, where there is oil production. However, a possible disadvantage is the fact that recovered oil would subsequently be burned, thus partially reducing the effectiveness of the process.

A less frequently discussed approach is to sequester the CO\textsubscript{2} by chemical reactions; the CO\textsubscript{2} would become incorporated into new inorganic or organic products that would be extremely stable. This approach has been tested in the proposed project. Chemical compounds (phenols) that have been demonstrated to react with CO\textsubscript{2} have been tested in the form of their geochemically abundant polymers, lignin and humic acid (in the form of gallotannins and condensed tannins), as well as model compounds for the polymers. Scattered references in the literature indicate that these substances might be promising acceptors. The compounds have been screened for their reactivity with CO\textsubscript{2} in aqueous solution under controlled conditions in the laboratory. Uptake of CO\textsubscript{2} into their structures, in the form of carboxyl (-COOH) groups have been demonstrated using spectroscopic and titrimetric procedures.
The reaction with resorcinol, (1,3-dihydroxybenzene) a classic Kolbe-Schmitt reaction (Lindsey and Jeskey, 1957), proceeded to afford the product, 3,5-dihydroxybenzoic acid, in 22% yield. Such 1,3-disubstituted (meta-dihydroxybenzene) phenols have been demonstrated to be highly reactive in electrophilic substitution reactions such as chlorination, nitration, and carboxylation. Resorcinol is a model compound for humic substances and has been found among the degradation products of a soil humic acid. The infrared (IR) spectrum clearly showed a new carboxylic acid (-COOH) band at 1690 cm\(^{-1}\).

In a similar fashion, pyrogallol (1,2,3-trihydroxyphenol), a model compound for gallotannins, gave rise to the product, 2,3,4-trihydroxybenzoic acid (in 22% yield) as described by Brown et al. (1992). Although not a meta-dihydroxybenzene, its three -OH substituents make it very electron-rich. Its IR spectrum (methanol on polyethylene card) and thin-layer chromatography (TLC: 1:1 acetic acid: toluene) retention time were identical to that of an authentic specimen provided by T. Paul of the University of Illinois.

Phloroglucinol (1,3,5-trihydroxyphenol), a model compound for condensed tannins, was particularly reactive with bicarbonate solution, either at the boiling point or at room temperature. This compound is not only trisubstituted with -OH groups but also has three equivalent meta positions. In each case the major product was the monocarboxylic acid, 2,4,6-trihydroxybenzoic acid, confirmed by high-performance liquid chromatography (HPLC: Mayer and Melhorn, 1963). In addition, apparent oligomeric products, including intensely red pigments, were produced, especially in room-temperature experiments that were allowed to react for several days.

Catechin, the monomer from which condensed tannins are formed, also reacted readily with bicarbonate solution to produce a dark red polymer that contained -COOH groups as shown by IR and HPLC. Titration of the reaction mixture and comparison to a control indicated that catechin took up 1.6 equivalents of CO\(_2\) per mole of starting material.

2,6-Dimethoxyphenol, a model compound for lignin (similar in structure to pyrogallol), appeared to be unreactive under these conditions. No solid separated when the reaction mixture was treated with aqueous hydrochloric acid. When the residual water from the reaction was extracted with dichloromethane, a small amount of solid material was obtained. Its IR spectrum showed it to be unreacted starting material. Reactions with Kraft lignin from Westvaco were unpromising; no additional -COOH infrared bands appeared.

The results with catechin, resorcinol and phloroglucinol demonstrated that CO\(_2\) can be incorporated into meta-dihydroxyphenyl structures which are present in humic acid and condensed tannins. In fact, naringenin, a flavonol of plant origin also containing a meta-dihydroxyphenyl group, also demonstrated increased absorbance in the 1700 cm\(^{-1}\) region when carboxylated using the standard procedure. Polymeric compounds rich in condensed tannin structures (extracts from grape seed and pine bark) reacted in boiling bicarbonate solution to afford -COOH-containing materials, as shown by IR and Fourier transform infrared spectroscopy (FT-IR).
The results with pyrogallol demonstrate that trihydroxyphenol structures typical of gallotannins (hydrolyzable tannins) may be carboxylated under relatively mild conditions. However, a trihydroxyphenol containing an ester group (propyl gallate), a possible model compound for gallotannins, gave mostly starting material when carboxylated.

The spectra of the material(s) from lignin carboxylation reactions showed little (or no) addition of -COOH groups, which would have given increased absorbance near 1700 cm\(^{-1}\). Several experiments using different conditions with Kraft lignin gave similar results. The reaction with the lignin model compound 2,6-dimethoxyphenol was likewise negative. The experiments suggest that lignin and lignin-like molecules may not be sufficiently reactive under these conditions to undergo a Kolbe-Schmitt reaction.

The modified polymers from condensed tannins may have useful properties, such as improved rubber vulcanizers; substances that may increase the bioavailability of essential trace metals as soil additives; corrosion inhibitors; copolymers, etc.
OBJECTIVES

The principal objective of the research has been to identify one or more processes by which CO₂ can be removed from combustion mixtures by its incorporation into the chemical structure of an abundant, naturally occurring material. The rationale of the project is based on the Kolbe-Schmitt reaction, a classical synthetic method in organic chemistry, in which an aromatic compound bearing hydroxyl groups (a phenol) is treated with CO₂ either as a gas or in the form of bicarbonate/carbonate in aqueous solution. The product of the reaction is a phenolic carboxylic acid resulting from the uptake of one or more molecules of carbon dioxide. Although with simple phenols, conditions of high temperature and/or pressure are required to bring about the reaction, phenols having two or more hydroxyl (or methoxyl) substituents are appreciably more reactive under milder conditions. Several abundant, naturally occurring polymers were selected whose properties and/or references in the literature suggested they might be effective recipients of carbon dioxide or bicarbonate.

The tasks scheduled in the proposal were:

Task 1. Acquisition of lignin and its precursors/model compounds.

Task 2. Acquisition of humic acid and its precursors/model compounds.

Task 3. Reactions of the model compounds and polymers with aqueous bicarbonate.

Task 4. Modifications of the reaction conditions to enhance carboxylations.

INTRODUCTION AND BACKGROUND

The rationale for this avenue of research is explained in the following brief literature review. Organic reactions with CO₂ (carboxylation or carbonation) include the classical Kolbe-Schmitt reaction, the conversion of phenolic compounds to phenolic acids. In the simplest of these reactions, phenol is transformed into \( \alpha \)-hydroxybenzoic (salicylic) acid. This particular reaction requires high temperatures and/or pressures, as well as organic solvents, and is not likely to be useful for industrial-scale carbon capture. Phenols that are more electron-rich, that is, those bearing electron-donating substituents such as –OH or –OCH₃, are much more reactive toward carboxylation. Thus, for example, resorcinol, which has 2 –OH substituents, reacts with an excess of sodium or potassium bicarbonate with brief heating in water to afford a mixture of \( \beta \)- and \( \gamma \)-resorcylic acids (Hale et al., 1952). Numerous other phenols with two or more hydroxy and/or methoxy substituents have been subjected to Kolbe-Schmitt reaction conditions and have given moderate- to good yields of carboxylic acid derivatives (Baine et al., 1954; Deineko et al., 1977; Brown et al., 1992).

Two of the three precursors of lignin are phenols having one or more methoxyl groups, and are accordingly electron-rich. As a consequence, it might be expected that lignin could be readily carboxylated by CO₂. A few references suggest this possibility. For example, spruce
wood was heated with sodium bicarbonate at temperatures up to 190°C for short periods (Kwasniakova et al., 1996). Carboxyl groups were assumed to be present in the treated wood due to swelling and tensile strength decreases. In another study, dry ice (solid CO₂) was added to spruce sawdust during the pulping stage, leading to increased delignification, which was attributed to the incorporation of CO₂ into the lignin fraction of the wood (Deineko et al., 1982). Finally, CO₂ was shown to be incorporated into alkaline kraft lignin at pH 8 and a temperature of 140-150°C. The lignin product had increased infrared absorbance at 1720 cm⁻¹, which is characteristic of carboxyl groups (Ivanenko, 1967).

Another complex and abundant polymer, humic acid (HA), a major constituent of soils, is believed to contain at least some phenolic groups on the assumption that degraded lignin makes up a portion of its structure. A single reference on the treatment of a peat HA with gaseous CO₂ at moderate temperatures (20-60°C) indicated that the carboxyl content of the HA increased from 2.73 meq/g to 3.35-4.12 meq/g (22-51%; Lebedeva et al., 2005).

The work undertaken was a one-year screening study that has indicated what types of organic polymers will react efficiently with CO₂ (in aqueous solution as bicarbonate/carbonate). Off-gases from Illinois coal combustion will be more complex (although most would not interfere with the reactions under study), and will include sulfur oxides, which may possibly complicate the reactions observed. We have simulated this potential effect by adding a small amount of sodium bisulfite to promising reactions.

**EXPERIMENTAL PROCEDURES**

Lignin was obtained from Mead Westvaco (Richmond, VA). Technically a “kraft lignin,” was prepared from spruce wood by alkaline pulping. It was purified to remove existing salts through washing with water followed by filtration and drying. This was repeated several times till salts had been removed and the water added remained clear. The infrared (IR) spectrum was determined by a hexane mull on a KBr plate and resembled that of an authentic material (Sarkanen and Ludwig, 1971).

Humic acid was obtained from Aldrich. Humic model polyphenolic compounds included resorcinol, pyrogallol (1,2,3-trihydroxybenzene), naringenin (a flavonoid of plant origin), and propyl gallate (3,4,5-trihydroxybenzoic acid propyl ester). The previous compounds were acquired from Sigma-Aldrich, as was tannic acid, a humic acid-like polymer from plant galls or oak bark. A pine bark extract and a grapeseed extract were obtained from PureBulk Nutrition (Myrtle Point, OR). HPLC analysis confirmed that both contained high levels of polymeric condensed tannins, though there were minor differences in their smaller-molecule content.

High purity solvents (methanol, acetonitrile), reagent grade solvents (acetone, ethanol) and reagent grade hydrochloric acid (37%) were from Fisher Chemical (Pittsburgh, PA). Reagent grade reverse osmosis water was in-house facility supplied. Reagent grade inorganic chemicals: sodium bicarbonate, potassium carbonate, and potassium bicarbonate were from
Fisher Chemical. CO₂ was standard laboratory grade, 99% purity delivered from a high pressure gas tank (S.J. Smith Co., Davenport, IA).

Carboxylation reactions were, in general, carried out as follows. Resorcinol or other compound (2 g), potassium hydrogen carbonate (10 g), and deionized water (20 mL) were stirred and heated to boiling over 30 minutes in a 100 mL round flask with a condenser attached. With continual stirring the mixture was boiled for another hour. The hot mixture was then poured into a beaker containing 40 mL of 6 M HCl to acidify. The mixture was allowed to cool to room temperature then placed in an ice bath allowing crystals to form. The crystals were then removed through vacuum filtration, washed with deionized water, and dried using a desiccator (Hale et al., 1952). In other cases, gaseous CO₂ was also bubbled into the reaction mixture (Brown et al., 1992).

Infrared and FTIR spectra were obtained using a 727B infrared spectrometer (Perkin Elmer, Norwalk, CT) and a Model 2000 Fourier-transform infrared spectrometer (Midac Corp., Costa Mesa, CA) spectrometer, respectively. Polyethylene IR sample cards were from International Crystal, Garfield NJ. Ultraviolet-visible (UV-vis) spectra were determined with a DU 7400 photodiode array scanning spectrophotometer (Beckman Coulter, Fullerton, CA).

High performance liquid chromatography (HPLC) with ultraviolet absorbance detection was used in some analyses to assess changes in the starting material. Solvent delivery was from a Perkin Elmer 250 binary HPLC pump (Perkin Elmer Corp, Norwalk, CT) with single wavelength detection at 220 nm (Spectroflow 757 detector, ABI Analytical, Kratos Subdivision, Ramsey, NJ) with output to a recording integrator (ChromJet, Spectra Physics Analytical, San Jose, CA); and multi-wavelength detection for recording complete absorbance spectrums were made using a photodiode array detector (PF-1 20/20, Groton Technology, Acton, MA).

Using reverse-phase chromatography, the polar aqueous phase was passed through a C_{18} column (4.6 x 150 mm Prontosil™ ace-EPS column, Mac-Mod Analytical, Inc., Chadds Ford, PA) with a flow rate of 1 mL/min. A 10 μL portion of the dissolved sample was injected and separated with a gradient elution programmed with an initial hold of 5 min at 90% A, followed by a linear change to 80% A in 5 min, hold at 80% for 20 min, then a linear change to 0% A in 10 min; hold at 0% for 10 min, ending with a return to 90% A in 10 min and equilibration for 10 min. Mobile phase A was a mixed combination of 95% 5 mM HCl (pH 2.5) with 5% acetonitrile and mobile phase B was 100% acetonitrile. Under these conditions, the RT of catechin was 19.8 min and the main polymeric product peak was at 42 min. This method has also been demonstrated to separate the monomers and dimers through hexamers of complex proanthocyanidin mixtures (unpublished results).

Carbon-13 nuclear magnetic resonance (NMR) spectra were performed by Dr. Feng Lin at the University’s Chemistry department.
RESULTS AND DISCUSSION

Task 1. Lignin and model compounds. Lignin was obtained from Mead Westvaco (Richmond, VA). Technically a “kraft lignin,” was prepared from spruce wood by alkaline pulping. It was purified to remove existing salts through washing with water followed by filtration and drying. This was repeated several times till salts had been removed and the water added remained clear. The infrared (IR) spectrum was determined by a hexane mull on a KBr plate and resembled that of an authentic material (Sarkanen and Ludwig, 1971).

Task 2. Humic acid and model compounds. Humic acid was obtained from Aldrich. Humic model polyphenolic compounds included resorcinol, pyrogallol (1,2,3-trihydroxybenzene), naringenin (a flavonoid of plant origin), and propyl gallate (3,4,5-trihydroxybenzoic acid propyl ester). The previous compounds were acquired from Sigma-Aldrich, as was tannic acid, a humic acid-like polymer from plant galls or oak bark. A pine bark extract and a grapeseed extract were obtained from PureBulk Nutrition (Myrtle Point, OR). HPLC analysis confirmed that both contained high levels of polymeric condensed tannins, though there were minor differences in their smaller-molecule content.

Task 3. Reactions with aqueous bicarbonate. For the general technique, resorcinol or another compound (2 g), potassium hydrogen carbonate (10 g), and deionized water (20 mL) were stirred and heated to boiling over 30 minutes in a 100 mL round flask with a condenser attached. With continual stirring the mixture was boiled for another hour. The hot mixture was then poured into a beaker containing 40 mL of 6 M HCl to acidify. The mixture was allowed to cool to room temperature then placed in an ice bath allowing crystals to form. The crystals were then removed through vacuum filtration, washed with deionized water, and dried using a desiccator (Hale et al., 1952).

Specific reactions:

The reaction with resorcinol (1,3-dihydroxybenzene), a classic Kolbe-Schmitt reaction (Lindsey and Jeskey, 1957), proceeded to afford the product, 3,5-dihydroxybenzoic acid, in 22% yield. The IR spectrum clearly showed a new carboxylic acid (-COOH) band at 1690 cm⁻¹.
In a similar fashion, pyrogallol (1,2,3-trihydroxybenzene) gave rise to the product, 2,3,4-trihydroxybenzoic acid (in 22% yield) as described by Brown et al. (1992). Its IR spectrum (methanol on polyethylene card) and TLC (1:1 acetic acid: toluene) retention time were identical to that of an authentic specimen provided by T. Paul of the University of Illinois.

Propyl gallate (left-hand structure), a closer model for gallotannins (right-hand structure), however, was unreactive under our conditions. Apparently the addition of an electron-withdrawing ester group makes the nucleus electronically or sterically unreactive to carboxylation.

2,6-Dimethoxyphenol, a model compound for lignin, appeared to be unreactive under these conditions. No solid separated when the reaction mixture was treated with aqueous hydrochloric acid. When the residual water from the reaction was extracted with dichloromethane, a small amount of solid material was obtained. Its IR spectrum showed it to be unreacted starting material.

Kraft lignin (0.5g, generalized structure below), potassium hydrogen carbonate (10g), and 20 mL of deionized water were stirred and slowly heated to a boil for 1 hour in a 100 mL flask with condenser. The mixture was kept at a boil for 2 hours under constant stirring. The hot mixture was poured into 40 mL of 6 M HCl. The product precipitated quickly, and an ice bath was used to collect additional material. The products were analyzed by IR
(hexadecane on KBr plates). The IR spectrum of the precipitates showed no bands in the carboxyl region and very few changes from that of the original lignin.

Naringenin, a flavonol of plant origin containing a meta-dihydroxyphenyl group, demonstrated increased absorbance in the 1700 cm$^{-1}$ region when carboxylated using the standard procedure.
Phloroglucinol: in the literature, this compound is claimed to be extremely reactive toward carboxylation. This might be expected given its structure which features three equivalent 1,3-dihydroxybenzene sites. In our hands, 2 g of phloroglucinol, 10 g KHCO₃ (potassium bicarbonate), and 20mL of distilled water were stirred at room temperature for up to 5 days. 10 mL of 6 M HCl were added and the solution was analyzed by UV and HPLC. The major product was the monocarboxylic acid, 2,4,6-trihydroxybenzoic acid, confirmed by HPLC of an authentic standard (Mayer and Melhorn, 1963). In addition, apparent oligomeric products, including intensely red pigments, were produced, especially in experiments that were allowed to react for several days.

Catechin is a polyphenol of interest because it is a precursor of the condensed tannins, constituents of certain humic materials which are abundant in some seeds and barks. In addition, it resembles a trisubstituted phenol such as phloroglucinol, and should be highly reactive with bicarbonate. This turned out to be the case; 1 g of catechin with 5 g of KHCO₃ in 10 ml of water was stirred at room temperature for 5 days. The solution gradually deepened in color. Gaseous CO₂ was bubbled in to lower the pH to 7.4. Dark red (nearly black) crystals separated. The FTIR spectrum of the product showed incorporation of CO₂, seemingly in several locations, and the HPLC trace indicated that the monomer had completely disappeared, and an apparent polymeric material eluted much later in the run (around 43 min).
HPLC chromatogram of catechin carboxylation product. Catechin (which would have eluted at ~19 min) is shown to be completely gone.

Infrared (FT-IR) spectrum of carboxylated catechin showing several new bands in the ~1700 cm\(^{-1}\) (-COOH) region.
Catechin was submitted for a $^{13}$C-NMR spectrum which turned out to be very similar to one reported in the literature (Davis et al., 1998), but attempts to determine a similar spectrum for the product were unsuccessful due to its insolubility in the solvents tried. This was unfortunate, since the appearance of a new peak at around 170 ppm would have been diagnostic for the incorporation of -COOH groups and the peak height would have given quantitative information.

Titration of the catechin carboxylation mixture (Snoeyink and Jenkins, 1980) and a control reaction without catechin revealed that bicarbonate was removed from the catechin-containing solution and was presumably taken up by the catechin. Calculation indicated that...
about 1.6 equivalents of bicarbonate were removed per mole of catechin.

Titration of the catechin carboxylation

Condensed tannins: These materials are polymers of catechin. Their type structure is shown at left. Grape seed extract, a condensed tannin-rich material similar to humic substances (especially those from highly colored waters; Lawrence, 1989; 2g), potassium hydrogen carbonate (10g), and 20 mL of deionized water was stirred and slowly heated to boiling for 2 hr and poured while still hot into 40 mL 6 M HCl solution. The solution was cooled on ice and vacuum filtered. After water washing the precipitate was dried in a desiccator to give 1.5g of product. The IR spectrum of the product showed increased absorbance in the 1700 cm\(^{-1}\) region. Very similar results were observed with pine bark extract.
Task 4. Modification of the reaction conditions.

We conducted the carboxylation reaction of catechin in the presence of sodium bisulfite, which would be the reaction product if flue gas containing both CO₂ and SO₂ was passed into water. Catechin (2 g) K₂CO₃ (8 g), 20 mL of distilled water, and 0.6 g NaHSO₃ were stirred in a 100mL round-bottomed flask at just under boiling temperature. Three experiments were performed: one under 1 hour, one under 2 hours and one under 3 hours. The solutions were cooled and poured into a mixture of 40 mL of 6 M HCl. After further cooling in an ice bath, the precipitate was filtered off under vacuum. In each case the product was virtually identical to the material formed in the absence of bisulfite, as shown by IR spectroscopy.

CONCLUSIONS AND RECOMMENDATIONS

The results with resorcinol demonstrate that CO₂ can be incorporated into meta-dihydroxyphenyl structures which are present in humic acid and condensed tannins (Pomes et al., 1999; Smolander et al., 2005). In fact, naringenin, a flavonol of plant origin containing a meta-dihydroxyphenyl group, also demonstrated increased absorbance in the 1700 cm⁻¹ region when carboxylated using the standard procedure.

The IR spectra of the material(s) from the lignin carboxylation reaction showed little or no apparent addition of carboxyl groups, which would have given increased absorbance around 1700 cm⁻¹. Additional experiments under different conditions with Kraft lignin gave similar results. The reaction with the lignin model compound 2,6-dimethoxyphenol was likewise negative. The experiments suggest that lignin and lignin-like molecules may not be sufficiently reactive under these conditions to undergo a Kolbe-Schmitt reaction.
The results with pyrogallol demonstrate that trihydroxyphenol structures typical of gallotannins (hydrolyzable tannins; Robinson, 1991) may be carboxylated under relatively mild conditions. However, a trihydroxyphenol containing an ester group (propyl gallate), a possible model compound for gallotannins, gave mostly starting material when carboxylated.

Trihydroxybenzenes such as phloroglucinol, as well as catechin, the monomer related to condensed tannins, were shown to be extremely reactive with bicarbonate, even at ambient temperatures. Preliminary results with catechin and bisulfite appeared to show that the presence of SO$_2$ in an emitted gas might have little or no effect on the bicarbonate reaction.

The IR spectra of the condensed tannin-containing grapeseed or pine bark extract reaction products (hexadecane-KBr) clearly showed a new band at 1700 cm$^{-1}$. This result is highly promising; together with the naringenin, phloroglucinol, and resorcinol results, it appears likely that polyphenols related to humic materials and having a 1,3-dihydroxy nucleus are especially susceptible to carboxylation under relatively mild conditions. Although grapeseed extract is available in large quantities, pine bark contains similar condensed tannins and is presumably less expensive. Future experiments should focus on optimizing the conditions for reactions with pine bark and its constituents.

REFERENCES


This report was prepared by Richard Larson, University of Illinois at Urbana-Champaign, with support, in part, by grants made possible by the Illinois Department of Commerce and Economic Opportunity through the Office of Coal Development and the Illinois Clean Coal Institute. Neither Richard Larson, University of Illinois at Urbana-Champaign, nor any of its subcontractors, nor the Illinois Department of Commerce and Economic Opportunity, Office of Coal Development, the Illinois Clean Coal Institute, nor any person acting on behalf of either:

(A) Make any warranty of representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately-owned rights; or

(B) Assumes any liabilities with respect to the use of, or for damages resulting from the use of, any information, apparatus, method or process disclosed in this report.

Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring; nor do the views and opinions of authors expressed herein necessarily state or reflect those of the Illinois Department of Commerce and Economic Opportunity, Office of Coal Development, or the Illinois Clean Coal Institute.

Notice to Journalists and Publishers: If you borrow information from any part of this report, you must include a statement about the state of Illinois' support of the project.