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**A Novel Method of Converting Sulfur Dioxide in Coal Utilization Process
to Marketable Sulphones – Faculty/Student Development**

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Shuming Zheng, Ph.D., Principal Investigator
Associate Professor of Chemical Engineering
Tel: (757) 727-5069, Fax: (727) 727-5189

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Department of Chemical Engineering, School of Engineering & Technology
Hampton University, Hampton, VA 23668

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ABSTRACT

The main objective of this study was to develop a Faculty/Student Exploratory Activity in Environmental Engineering. This activity was carried out by using low-cost organic compounds to convert pollutants in coal utilization process to marketable sulphones. Although the research of sulphones in organic synthesis is only about 20 years young and has never been introduced to the application of industrial pollution researches, the products sulphones have enormous value in many of the most demanding organic synthesis [1] and the use of sulphones in organic synthesis has increased dramatically in recent years [2]. Sulfones are easily prepared by a range of mild and high-yielding routes, and are a robust group and frequently confer useful properties such as crystallinity [3]. Sulfones can be prepared by simply oxidation of sulfides [4], alkylation of sulfinic acid salts (e.g., RSO_2Na), reactions of sulfonic acid derivatives (e.g., RSO_2X), and the addition of carbon-centered radicals to SO_2 [5,6]. Many organic compounds, in which they all contain carbon, have vast numbers of substances, both natural and synthetic. It is not farfetched to say that we are living in the Age of Carbon. The number of compounds that contain carbon is thousands times greater than the number of compounds that do not contain carbon. Due to the low-cost and ease of preparation, organic materials are crucial to our economy as the source of countless manufactured products that essential to our comfort and well being. Therefore, the introduction of low-cost organic compounds to remove the pollutants in coal utilization is feasible.

In this novel method, the sulfone preparation was administrated involving the passage of the SO_2 gas through a solution of benzoyl peroxide in diphenylmethane. The liquid

product diphenylmethyl phenyl sulfone was isolated from the gases phase. Feasibility studies including the design of four teaching labs were performed to evaluate the pollution control system. The results from this study have shown a promising success for industrial scale-up.

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INTRODUCTION

Sulfur dioxide is a colorless, toxic gas, its presence in polluted air from the burning of fossil fuels and is known to cause respiratory ailments. Fossil fuels are major energy source in the United States, and its combustion results in the emission of pollutants. Petroleum and coal, as the fossil fuels, laid down over millennia and non-renewable. When the sulfur is burned along with the coal, sulfur gases-notably sulfur dioxide is produced as pollutants. The effects of incomplete combustion in air, and combustion of fuels that are not pure hydrocarbons yields the following qualitative description of combustion:

Some of the above pollutants in coal can be removed prior to burning, but the process is expensive and only partially successful, especially with organic sulfur [7]. Alternatively, sulfur gases can be trapped by special devices, "scrubbers", [8,21] in exhaust stacks by using some inorganic compounds (e.g., CaCO_3 , CaO , Na_2SO_3), but the process is not completely efficient.

From the standpoint of environmental quality, then, low-sulfur coal (less or equal 1%) is more desirable fuel than high-sulfur coal. On the other hand, much of the low-sulfur coal in the United States is also lower-grade coal, which means that more of it must be burned to generate the same amount of energy. Many chemical and physical methods have been developed for removing sulfur before combustion. The chemical processes operate at high temperature (100-400°C) and are energy intensive, whereas physical methods such as flotation result in energy loss by removing coal particles containing finely distributed pyrite [9].

During the last 30 years, a number of approaches have been used in the attempt to develop methods which can remove flue gas pollutants effectively and at low cost for scale-up. Included in these approaches is the use of sulfur microorganisms or microbial enzymes. The use of sulfur biocatalysis is as alternative methods to the conventional processing of sulfur pollutants using sulfur microorganisms or microbial enzymes in industry and environment. Microbial removal of inorganic sulfur from coal by microbes of the genus *Thiobacillus* was reported some 30 years ago [10,11].

At present, the reaction has been optimized for desulfurization of acid gas effluent containing hydrogen sulfide, and carbon dioxide [12]. The evaluation of the effect of reactant gas concentrations and photon flux on conversion of H_2S to elemental sulfur without oxidized sulfur compound in fed batch and chemostat reactors was reported by Cork and Kenevan [12]. A microbiological process called the BIO-SR to convert H_2S to S^0 was developed [7,13,14]. Satoh et al. [13] reported the bacterium *Thiobacillus ferrooxidans* oxidizes ferrous sulfate back to ferric sulfate. And some modifications and combinations of typical chemical, physical desulfurization technologies, biconversion of sulfur dioxide to thiosulfate instead of corrosion sulfate have been suggested [15,16,18-23]. However, a detailed kinetic analysis of this process has not been presented [17].

Due to the low-cost and ease of preparation, organic materials are crucial to our economy as the source of countless manufactured products that essential to our comfort and well being. There are two large reservoirs of organic materials from which simple organic compounds are obtained: petroleum and coal. Petroleum and coal, as the fossil fuels, laid down over millennia and non-renewable.

Although the research of sulphones in organic synthesis is only about 20 years young and has never been introduced to the application of industrial pollution researches, our experimental results have indicated that the introduction of low-cost organic compounds to remove the pollutants in coal utilization is feasible.

EXECUTIVE SUMMARY

The research on using low-cost organic compounds to convert SO_2 in coal utilization process to marketable sulphones was carried out since the summer of 1998. Although the research of sulphones in organic synthesis is only about 20 years young and has never been introduced to the application of industrial pollution researches, the products sulphones have enormous value in many of the most demanding organic synthesis and the use of sulphones in organic synthesis has increased dramatically in recent years. Sulfones were prepared by the method described by Simpkins [3]. Due to the low-cost and ease of preparation, organic materials are crucial to our economy as the source of countless manufactured products that essential to our comfort and well being. Therefore, the introduction of low-cost organic compounds to remove the pollutants in coal utilization is feasible.

In this novel method, the sulfone preparation was administrated involving the passage of the SO_2 gas through a solution of benzoyl peroxide in diphenylmethane. The liquid product diphenylmethyl phenyl sulfone was isolated from the gases phase. The experimental design was based on the studies on pollutant SO_2 removal capability by measuring the SO_2 concentration (C_i) of the samples obtained from three different outlet: a) without any absorbent in the compartments ($C_0 = C_i$, $t = 0$ to $t = t_i$) as control I; b) with pure organic solvent diphenylmethane $C_0 \neq C_i$ as control II; and with benzoyl peroxide and diphenylmethane $C_0 \neq C_i$ as samples.

The mechanism of the sulphones formation in organic synthesis has been discussed in detail by Bordwell, the various dipolar ion and diradical mechanism is considered the most consistent with experimental evidence. Though the chemical reactions between the pollutants and the organic compounds involved a number of steps, examples of some relationship resulting in the production of different sulphones is discussed in the Discussion section.

The funding of this project, which was also beneficial, for the principal investigator, to the teaching of the following Chemical Engineering Courses: Industrial Pollution Control (CME 523), Biochemical Engineering (CME 507) and Material Science and Engineering (EGR 303). It is the belief that one way to help achieve basic pollution prevention goals is through the education of our future engineers. The research support from DOE helped in achieving our education goal since pollution abatement and prevention has become one of the most important issues in the chemical process industries. One of the goals of the Chemical Engineering Department is to start some options within the program, like Environmental Engineering. The support from DOE for the proposed study also helped to pave the way to achieve this goal which is very crucial in educating minority students to join the engineering work force on the cutting edge of technology. This project in the Department of Chemical Engineering, the School of Engineering and Technology, at Hampton University which is a historically black institution, was important in the creation of a new Environmental Engineering Program in the Department of Chemical Engineering.

EXPERIMENTAL DESIGN AND TEACHING LAB DEVELOPMENT

Organic compounds have vast numbers of substances, both natural and synthetic. Due to the low-cost and ease of preparation, it is the belief that the use organic compounds to convert the sulfur dioxide from flue gas to marketable sulfones as carried out in this study would receive great attention. This study used low-cost organic compounds, such as benzoyl peroxide and diphenylmethane et al., to convert SO_2 in coal utilization process or some other pollution sources to marketable products - Sulphones.

The experimental design was based on the studies on pollutant SO_2 removal capability by measuring the SO_2 concentration (C_i) of the samples obtained from three different outlet:

- i. without any absorbent in the compartments ($C_0 = C_i$, $t = 0$ to $t = t_i$) as control I;
- ii. with pure organic solvent diphenylmethane $C_0 \neq C_i$ as control II;
- iii. with benzoyl peroxide and diphenylmethane $C_0 \neq C_i$.

The mechanism of the sulphones formation in organic synthesis has been discussed in detail by Bordwell [3], the various dipolar ion and diradical mechanism is considered the most consistent with experimental evidence. Though the chemical reactions between the pollutants and the organic compounds involved a number of steps, examples of some relationship resulting in the production of different sulphones are as shown in the following unbalanced equations:

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The reaction rate for the above reactions was evaluated, and further identification of the target organic reactants and the resulting sulphone products as well as the best efficiency for removal of sulfur dioxide at the fastest reaction rate were investigated.

As discussed before, Sulfones could be prepared in the laboratory with high yield, such as the oxidation of sulfides, alkylation of sulfinate salts (e.g., RSO_2Na), reactions of sulfonic acid derivatives (e.g., RSO_2X), while the addition of carbon-centered radicals to SO_2 to prepare sulphones was a great deal [3]. The sulfone preparation was administrated using the method described by Simpkins [3] and the SO_2 gas was passed through a solution of benzoyl peroxide (B.P.) in diphenylmethane with concentration varying from 1.0-10.0 wt%. The resulting product sulfone was isolated by fractional crystallization and the analysis of the products will be carried out in the near future. Several teaching labs were designed in this study as shown in the following.

Experimental Design:

Lab 1. Pollutant Sulfur Dioxide Preparation:

Objective:

The purpose of this laboratory exercise was to produce one of the main pollutants sulfur dioxide, which is one of the main sources of acid rain and to observe some of its properties.

Materials and Equipment:

Goggles, pH Meters, universal pH paper, 100-mL separatory funnel, Filtering flask, rubber and glass tubings, Fume-hood, Flasks, Clamps, Scoopula, Sodium sulfite, Hydrochloric acid, 100-mL graduated cylinder, and 50-mL beaker.

Procedure:

Sulfur dioxide is a colorless, toxic gas, its presence in polluted air from the burning of fossil fuels and is known to cause respiratory ailments. The pollutant SO_2 was prepared in the lab from the following chemical reaction, and then passed the sulfur dioxide through both sample and control compartments and the sulfur dioxide concentration was measured in three outlet respectively.

Take the above reactants to the fume hood to generate sulfur dioxide, which was used to pass through both the compartments with and without organic compounds filter at the same time. The outlet the sulfur dioxide generator was split and connected to the first compartments with and without organic compounds respectively.

Assignment:

1. Why is sulfur dioxide so damaging to marble statues?
2. How does acid rain formed from sulfur dioxide?
3. Other than damaging marble status, is acid rain a significant worldwide problem? Why? Give two examples to support your conclusion.
4. Draw a diagram for the experiment with relevant balanced chemical equations.
5. Suggest a better procedure and lab-setup for this experiment (if any).

Lab 2. Pollutant Removal Capability Measurement - Qualitative Analysis

Objective:

The purpose of this laboratory exercise was to determine the sulfur dioxide removal capability.

Materials and Equipment:

100-mL Separatory Funnel, Filtering Flask, Rubber and Glass Tubings, Fume-hood, Flasks, Clamps, Scoopula, Sodium Sulfite, Hydrochloric Acid, 100-mL Graduated Cylinder, and 50-mL Beakers (3). Goggles, Glass compartments, pH meter, Clamps.

Procedure:

To qualitatively determine the sulfur dioxide removal capacities, pH meters was used and electrode was immersed to the aqueous solution in the 600-ml beaker. The pollutant SO_2 was passed through both sample and control compartments, and the sulfur dioxide concentration was measured in three outlet respectively. The adsorption rate was estimated from the pH reading.

Assignment:

1. If you want to smell a chemical, what should you do?
2. Give scientific explanation for the experimental set-up.
3. Draw a diagram for the experiment with relevant instruction.
4. Suggest a better procedure and lab-setup for this experiment (if any).

Lab 3. Pollutant Removal Capability Measurement - Quantitative Analysis I

Objectives:

The purpose of this laboratory exercise was to determine the sulfur dioxide removal capability.

Materials and Equipment:

100-mL Separatory Funnel, Filtering Flask, Rubber and Glass Tubings, Fume-hood, Flasks, Clamps, Scoopula, Sodium Sulfite, Hydrochloric Acid, 100-mL Graduated Cylinder, and 50-mL Beakers (3). Goggles, Glass compartments, Benzoyl Peroxide, Diphenylmethane, Tetrachloromercurate (TCM), and Spectrophotometer.

Procedure:

There are numerous methods to measure the concentration of SO_2 quantitatively. The method used in this study was a pararosaniline method. The SO_2 gases before and after the treatment were bubbled through a solution of tetrachloromercurate (TCM) that reacted chemically with the SO_2 being measured to form a colored complex solution. The intensity of the color is proportional to the sulfur dioxide concentration. The resulting solution was measured using a spectrophotometer at wavelength 560 m μ (Fisher Scientific).

Lab 4. Pollutant Removal Capability Measurement - Quantitative Analysis II**Objective:**

The purpose of this laboratory exercise was to determine the sulfur dioxide removal capability.

Materials and Equipment:

Goggles, Glass compartments, Benzoyl Peroxide, Diphenylmethane, Gas Chromatography,

100-mL Separatory Funnel, Filtering Flask, Rubber and Glass Tubings, Fume-hood, Clamps, Scoopula, Sodium Sulfite, Hydrochloric Acid, 100-mL Graduated Cylinder, and 50-mL Beakers (3).

Procedure:

The most current procedures for SO_2 measurement is using Gas Chromatography. The Gas Chromatography was used by introducing the gas sample directly into the gas chromatograph. To analyze the gas sample, results were dependent strongly upon the injection technique of the experiment. The syringe used was rinsed several times when a new sample was to be analyzed. To rinse the syringe, fill it with the sample (gaseous phase) and expel the contents. To inject the sample, center the needle on the septum of the injection, guiding it between the thumb and forefinger to prevent the possibility of bending the needle when it is inserted through the septum.

Assignment for the Students: Develop mathematical models for the pressure drop between the inlet and outlet of the pollutant control system.

EXPERIMENTAL RESULTS AND DISCUSSION

Due to the low-cost and ease of preparation, it is the belief that the use of organic compounds to convert the sulfur dioxide from flue gas to marketable sulfones as carried out in this study would receive great attention.

Studies examining the pollutant SO_2 removal capability by measuring the SO_2 concentration (C_i) of the samples obtained from different outlet:

- i. without any absorbent in the compartments ($C_0 = C_i$, $t = 0$ to $t = t_i$) as a control I;
- ii. with pure organic solvent diphenylmethane $C_0 \neq C_i$ as another control II;
- iii. with benzoyl peroxide and diphenylmethane $C_0 \neq C_i$ (Sample).

Studies on Chemical Reaction Mechanism

The mechanism of the sulphones formation in organic synthesis has been discussed in detail by Bordwell [3], the various dipolar ion and diradical mechanism is considered the most consistent with experimental evidence. The low-cost organic compounds, benzoyl peroxide and diphenylmethane, were used to convert SO_2 pollutant sulphones. Although the mechanism of removing pollutants by organic compounds needs more experimental results, the mechanism may include physical adsorption, ion exchange, and the formation of a complex.

The chemical reactions between the pollutants and the organic compounds involved a number of steps and the production of sulphone can be summarized as shown in the following unbalanced equations:

Experimental Results and Discussion

Experiments have been conducted to evaluate the sulfur dioxide removal and the results are summarized below.

Pollutant Removal Capability Measurement - Qualitative Analysis (pH)

(N > 3, reading $\pm$ 0.15)

TIME (minutes)	CONTROL I (pH)	CONTROL II (pH)	SAMPLE (pH)
0	7.22	7.22	7.22
0 ⁺	3.42	3.50	4.12
10	4.46	4.30	4.61
20	3.25	3.20	4.73
30	2.94	2.82	5.35
40	2.72	2.67	5.27
50	2.51	2.95	4.28
60	2.27	2.80	4.32

As shown above, without any absorbent in the compartments ($C_0 = C_i$, $t = 0$ to $t = t_i$) as a control I, the pH changed from 7.22 which was a deionized water to 2.27 (strong acidic).

The results indicated that the sulfur dioxide generated from sodium sulfite and hydrochloric acid was dissolved in the deionized water perfectly that resulted in the pH change dramatically. The results are considered as control I.

In order to evaluate the effect of the solvent diphenylmethane on the sulfur dioxide removal rate, it was necessary to test the sulfur dioxide solubility in the organic solvent, therefore to find the true pollutants removal efficiency. The pure organic solvent diphenylmethane was used to measure the pH at t_0 to t_i as control II. The pH changed starting from 7.22 to 2.80 (strong acidic). The results indicated that the sulfur dioxide generated from sodium sulfite and hydrochloric acid was partially dissolved in the deionized water that resulted in the pH change dramatically, and with very small amount of sulfur dioxide dissolved in diphenylmethane compared with the above control I.

The experiment with both diphenylmethane and benzoyl peroxide from t_0 to t_i was carried out for the sample measurement. The pure organic solvent diphenylmethane was used to measure the pH at t_0 to t_i as control II. The pH changed starting from 7.22 to 4.12 at 0+, which indicated that a significant amount of sulfur dioxide was reacted/dissolved in the diphenylmethane and benzoyl peroxide system by compared with the results from controls I and II, which resulted in the fact that outlet pH was stabilized from 0+ to 60 minutes.

Pollutant Removal Capability Measurement - Quantitative Analysis

Calibration Curve

# of Sample	Concentration of Sulfur Dioxide (Mg/ml)	Reading (O.D. $\pm$ 0.05)
1	0.000	0.000
2	0.01	0.024
3	0.10	0.243
4	0.20	0.478
5	0.40	0.956
6	0.60	1.452
7	0.80	1.895

Pollutant Removal Capability Measurement - Quantitative Analysis

(% SO₂ removed, n>3, 25°C, B.P. = 5.0wt%)

TIME (minutes)	CONTROL I (%)	CONTROL II (%)	SAMPLE (%)
0 ⁺	0	0.02	2.0
20	0	0.07	10.2
40	0	0.07	27.1
60	0	0.09	32.0

The above results are consistent with the results that obtained from the qualitative

analysis. Since the control I without any reactants in the system, the removal was constantly zero and this outlet was served as a blank control. The control II indicated that the organic solvent also contributed a little bit to the removal rate and was subtracted from the sample measurement. By the consideration from both the controls I and II, as well as the sample measurement, the sulfur dioxide removal rate was obtained as much as 32 percent at 25°C.

Effect of Operation Temperature on Pollutant Removal - Quantitative Analysis

(% SO₂ removed, n>3, B.P. = 5.0wt%)

TEMPERATURE (°C)	SO ₂ REMOVED (%)
25	32.0
20	35.0
10	39.0

As shown above, when the operation temperature decreased, the sulfur dioxide removal rate was increased. When the sulphone was prepared involved the passage of sulfur dioxide through a solution of benzoyl peroxide in diphenylmethane, and the diphenylmethyl phenyl sulphone was isolated from the reaction, the reported yield was only 36% [3]. As Simpkins [3] pointed that such reactions are clearly different to control, with by-products arising from unwanted alkyl radical coupling, and hydrogen atom abstraction by sulphonyl radicals leading to sulphinic acids which is very sensitive to the change of temperature.

Although predicting the temperature of solubility for organic compounds system is very difficult, there is some correlation between the sign of $\Delta H^\circ_{\text{soln}}$ and the variation of solubility with temperature. In general, the solubility of a gas in solvent decreases with increasing temperature for aqueous solution, the above results are also showed the constancy with the organic solution system. This may be caused by the formation of boiler scale in which the decreasing solubility of gases with increased temperature is responsible for, and the change of temperature would definitely change the vapor pressure of the solution, especially for the volatile solution.

Effect of B.P. Concentration on Pollutant Removal - Quantitative Analysis

(% SO₂ removed, n>3, 25°C)

B.P. (wt%)	SO ₂ REMOVED (%)
1.0	3.00
5.0	32.0
10.0	38.0

The experimental results showed that the reaction rate depends on the reactant concentration since the molecules must collide to react. Since we have excess sulfur dioxide in this system, the limiting reagent is B.P. Although the kinetic molecular theory predicts that an increase in temperature raises molecular velocities and so increases the frequency of collisions between molecular, while sulphone radicals RSO₂• are involved in a host of

important sulphone chemistry including the additions of RSO_2X (e.g. $\text{X}=\text{halogen}$, SePh [3]) reagents to multiple bonds, rearrangements of unsaturated sulphones, and the sulfur dioxide extrusions from cyclic sulphones, which resulted in the difficulties of sulphone as major products which resulted in the sulfur dioxide removal efficiency.

More experiments will be conducted in the near future to prepare sulphones such as bis(tetrahydrofuranyl and phenolic sulphone, to determine and evaluate the temperature stability of the sulphone products, the patterns of removal and recovery of both the pollutants from flue gas and the sulphones from the products, the safety of the procedure for industrial scale-up, the identification on both target organic compounds and pollutants, such as CO_2 , CO , NO_x , SO_x , Pb and PM , and to develop new technique and compare this technique with the characteristics obtained by published techniques.

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