ABSTRACT

The absorption of nitric oxide from gas streams with cumene hydroperoxide (CHP) in n-hexadecane (cetane) as the scrubbing solution was investigated. The efficiency of the scrubbing solution to remove nitric oxide was evaluated over the temperature range of 90 to 110°C, concentration range of 0.1 to 0.5M, and residence time of 12 to 80 seconds. The products were analyzed by gas chromatography (GC), Fourier transform infrared spectroscopy (FTIR), and ion chromatography (IC). The goal of this research was to determine the NO removing efficiency of cumene hydroperoxide solution, a relatively inexpensive tertiary organic hydroperoxide. Also, a possible reaction mechanism for the scrubbing reactions was postulated based on all by-products of the reaction. To achieve more reproducible results, the scrubbing device was redesigned to prevent possible gas leaking and to better control the temperature of the scrubbing solution. The NO removal ability of cumene hydroperoxide was found to be 70% at 100°C, 0.5M CHP concentration, and 80 seconds residence time. Experiments showed the cumene hydroperoxide solution was stable up to 120°C, but the CHP concentration decreased with NO presence by 0.18M. The products from NO oxidation remained in the scrubbing solution. The solution was then hydrolyzed with an aqueous ammonia solution. All nitrogen containing compounds in the scrubbing solution formed inorganic nitrate and nitrite ions. Important reaction by-products such as cumyl alcohol and α-methylstyrene were found by GC-FTIR and their concentrations were determined by comparing with standard solutions. The distribution of reactants and products was obtained and a possible mechanism of the NO with CHP reaction was proposed based on the information found this research.

NITRIC OXIDE ABSORPTION FROM FLUE GAS WITH CUMENE HYDROPEROXIDE SOLUTION

by
Chung-Der Chen

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CHAPTER I

INTRODUCTION

Nitrogen containing compounds, both organic and inorganic, play an important role in the chemistry of the atmosphere. The major polluting nitrogen compounds are called oxides of nitrogen (NO_X). Oxides of nitrogen are mixtures of compounds of nitrogen and oxygen generally found in effluents from combustion sources. The predominant NO_X compounds are NO and NO_2. They are formed as a result of the reactions of atmospheric nitrogen with atmospheric oxygen at high temperatures. Also, large quantities of NO_X are formed from the oxidation of nitrogen compounds found in fuels, or in wastes being incinerated. More than 90% of the NO_X emitted from stationary combustion sources consists of NO which is relatively insoluble in aqueous solutions. Acidic deposition is related primarily to the emissions of sulfur dioxide (SO_2) and nitrogen oxides (NO_X). In 1985, anthropogenic sources in the United States contributed 19 Tg of NO_X emissions. Emissions of NO_X are estimated to have increased steadily during the period between 1900 and 1970. The increase in NO_X emissions resulted from the rise in fuel consumption, particularly in power plants and motor vehicles (Irving, 1991). The object of this research is to find ways to remove NO from effluent gases using essentially unexplored methods such as organic oxidizing agents.

1.1 NO_X Formation and Sources

Nitrogen oxides are emitted primarily as nitric oxide (NO) from a variety of combustion or high temperature sources. The estimated emissions of NO_X have large uncertainties associated with them. About 70-90% atmospheric NO_X emission are from anthropogenic sources in the world (Singh, 1987).

1.1.1 Lightning

The major natural source of NO_x is due to the effect of atmospheric lightning on atmospheric nitrogen and oxygen. The temperature of a column of air exposed to atmospheric lightning is a function of energy deposition of the lightning. For a typical energy deposition of about 10^5J/m, the column of air immediately surrounding the charge is heated to the temperature on the order of 30,000K. At temperatures above 2,300K, NO is in thermodynamic equilibrium with N_2 and O_2. As the temperature of the heated air drops below 2,000K, NO then cools down rapidly and doesn't revert back to oxygen and nitrogen.

The total global production of NO due to atmospheric lightning is the product of two terms. First, the yield of NO per energy input or lightning (J), or the NO per lightning flash. Second, the total energy deposited by lightening or the lightning flash frequency (Levine, et al., 1984). This is a major natural source of NO_x and accounts for 1/3 of natural NO_x (Bolin, et al., 1983).

1.1.2 Microbial activity in soils

It has been found from field flux measurements and laboratory experiments that soil microorganisms also produce appreciable amounts of NO. To quantify the rate of NO production, a series of laboratory experiments were performed using two of the most common bacteria found in soils named Nitrosomonas Europaea and Alcaligenes Faecalis. The result indicates that nitrification is an aerobic process in which ammonium cations are oxidized to inorganic nitrite and nitrate ions. NO and N_2O are direct or indirect intermediates of this mechanism (Levine, et al., 1984). Soil accounts for about 2/3 of natural NOx (Bolin, et al., 1983).

1.1.3 Fuel combustion

Nitrogen oxides (NO_x) are produced in combustion processes that use air as the oxidizer. At flame temperatures, the combustion of atmospheric nitrogen and oxygen results in the formation of nitric oxide (NO). The NO formation mechanism from nitrogen and oxygen follows the chain reaction sequence first postulated by Zeldovich (1946) for the H_2-O_2-N_2 reaction system and confirmed by shock tube studies on N_2-O_2 mixtures (Glich, et al., 1957). The chain reaction sequence is shown in Equations (1) through (3),

$$O_2 + M \longrightarrow 2O + M \quad (1)$$

$$O + N_2 \longrightarrow NO + N \quad (2)$$

$$N + O_2 \longrightarrow NO + O \quad (3)$$

where M is a third body.

1.2 Effects of Nitrogen Oxides

Nitrogen oxides (NO_x) cause a lot of serious environmental problems, such as tropospheric ozone formation, depletion of stratospheric ozone, acid precipitation, respiratory diseases, etc. These problems will be discussed later in this section.

1.2.1 Tropospheric ozone formation

Air pollution alerts due to ozone (O_3) and peroxyacetyl nitrate (PAN) may increase the rate of O_3 formation by releasing NO_2. PAN is thermally unstable and may contribute to O_3 formation downwind of urban areas by transporting NO_x, and then decomposing into peroxyacetyl radicals and NO_2 as shown in Figure 1, which is similar to diurnal cycle (Finlayson-Pitts, 1986). Thus, NO_2 is important because it is the precursor to ozone formation. Ozone adversely affects the health of the elderly and the very young through its impact on the respiratory system.

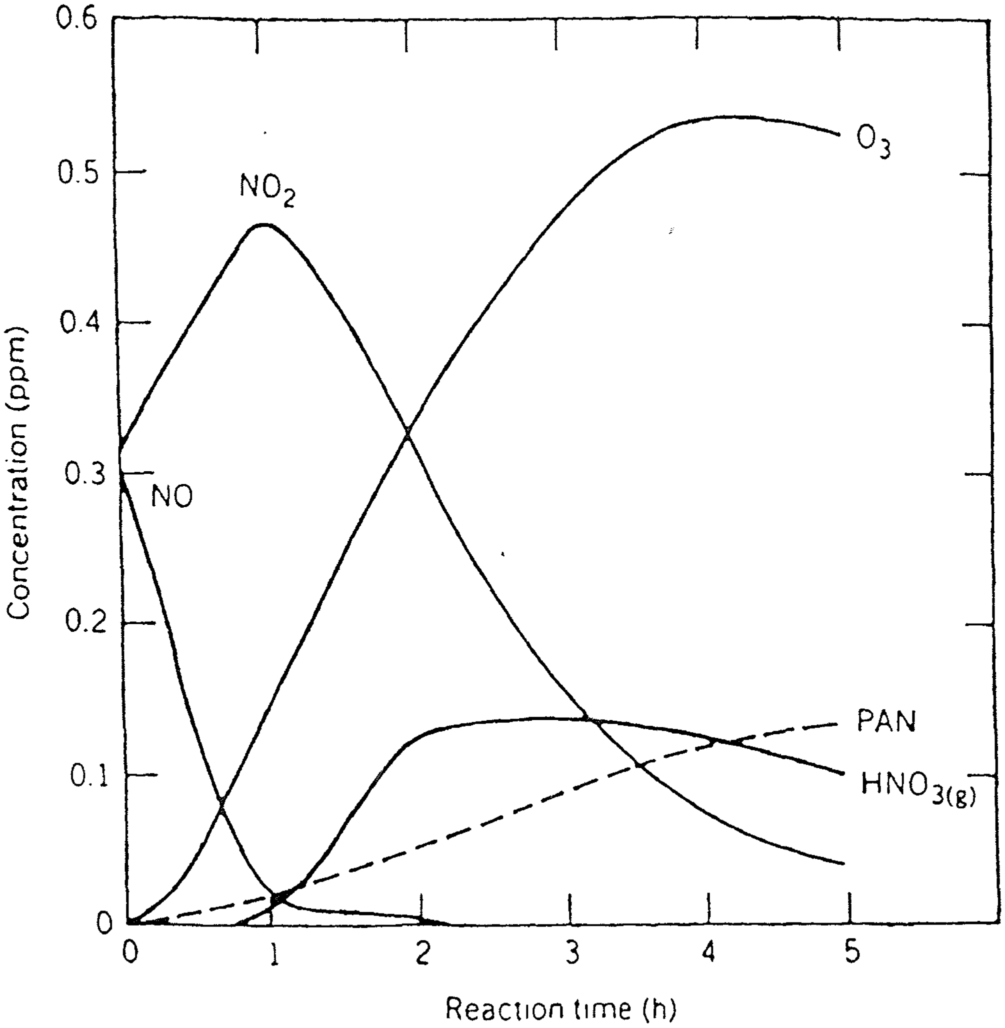


Figure 1 Profiles of Selected Reactants and Products for a Typical Smog Chamber Run

The reason that NO_2 is used as a standard rather than NO for health effect studies is because all NO is oxidized to NO_2 in the atmosphere. The reaction rate between nitric oxide and oxygen is very slow (equation 4), but all NO will become NO_2 in the atmosphere if there is enough time.

$$2NO + O_2 \longrightarrow 2NO_2 \qquad (4)$$

1.2.2 Acid precipitation

The increasing acidity in poorly buffered soils (Bridgeman, 1990) is having a serious influence on vegetation, surface water, biological systems, and structures of the earth. The U.S. National Acid Precipitation Assessment Program (NAPAP) was implemented in 1980 to conduct research and assess the complex causes and effects of acid deposition. There were two major goals for NAPAP: First, it sought to fill many gaps in the scientific understanding of acid deposition. Second, the program developed methods and evaluated the consequences of alternative acid deposition control strategies (Isom, et al., 1984).

1.2.3 Health effect

Nitrogen oxides are not very active biologically. At exposures well above a few ppm, NO_2 causes lung damage of various types, including bronchial damage reminiscent of that from SO_2, through less severe, and acute pulmonary edema, an effect characteristic of ozone. Since atmospheric level only rarely reaches a half ppm ($1000\mu g/m^3$), there has historically been little concern over the direct health effects of NO_2. This view has been questioned by the findings from a major observational study conducted in Chattanooga. It was found that certain portions of the population had decreased ventilatory function and increased respiratory illness in neighborhoods near a factory that manufactured TNT. This unusual situation provided a test area with very low NO_2 levels ranging from 0.06 to 0.109ppm ($113\text{-}205\mu g/m^3$). These NO_2 levels are of the same general magnitude as the higher ambient concentrations experienced in many cities. Consequently, if further pursuit of these observations confirms the results, we need to consider NO_2 in a new manner (Lynn, 1976).

1.3 NO_x Control Technologies

NO_x emissions should be controlled in order to prevent their environmental problems, and to comply with federal and local regulations. In the past few years, a variety of processes for NO_x control have been developed. These processes can be divided into two types: combustion modification and add-on devices for flue gas cleaning. Table 1 summarizes these NO_x control techniques (Yang, 1990).

Table 1. Comparison of several NO_x emission control techniques

METHOD	EFFICIENCY	RELATIVE COST
Combustion modification:		
Low NOx Burners (LNBs)	50~60%	
Staged Gas Combustion (SGC)	10~50+%	Medium to low
Flue Gas Recirculation (FGR)		
Flue gas cleaning:		
Selective Non-catalytic Reduction (SNR)	30~80%	Medium
Selective Catalytic Reduction (SCR)	50~90%	High
Scrubbing System	>90%	High*

* The cost may be reduced by obtaining salable products.

1.3.1 Combustion modification

[*a*] Low NO_x Furnaces (LNFs): Various furnace designs have been proposed to lower NO_x emissions such as the tangentially fired boiler. Traditional cyclone furnaces produced high concentrations of NO_x in flue gas. Because the temperature of heat sinks of tangential fired furnace is almost equal to the temperature of furnace flame, it reduces thermal NO_x formation by 50 to 60%. (Maulbetsch, 1981).

[*b*] Flue Gas Recirculation (FGR): Flue gas recirculation is an effective way to reduce thermal NO_X. The recirculated flue gas lowers the flame temperature and the oxygen content in combustion. It was reported that the thermal NO_X formation was reduced by 20-30% (Jahnig and Shaw, 1981).

[*c*] Staged Gas Combustion (SGC): Thermal NO_X formation can be reduced by operating the incinerator in a fuel rich mode, followed by interstaged cooling and burn out of the uncombusted compounds with excess air. Incomplete combustion in the first stage lowers thermal NO_X formation. The second stage uses excess air to complete the combustion, reduces the combustion temperature and lowers the thermal NO_X formation (Bienstock, 1972). Alternatively, another method of interstage cooling can be used in order to avoid a large excess of stoichiometic air.

1.3.2 Add-on devices for flue gas cleaning

[*a*] Selective Non-catalytic Reduction (SNC): NO_X can be reduced to nitrogen and water by adding NH_3 into the effluent gas from a combustor at 930 to 990^oC. The major disadvantages of this process are the narrow temperature range, the need for well mixed NH_3 and the possibility that NH_3 may breakthrough.

[*b*] Selective Catalytic Reduction (SCR): This is a similar process to the thermal process that we just mentioned above except a catalyst is used. Because of the catalyst, the reactions occur at a much lower temperature of 300 to 400^oC. The commercial catalysts containing noble metals or vanadium/titanium that can reduce NO_X by 90% for the former and 80% for the later. Current research is concerned with using zeolites to catalyze the reaction of NO_X with NH_3 (Makansi, 1988).

[*c*] Scrubbing System: A number of scrubbing processes have been proposed to remove NO from gas stream. Research on NO_X scrubbing processes has shown that these processes require expensive oxidation reagents and may present disposal problems. However, a scrubbing systems are less expensive than competing add-on device

technologies, and has the advantage that the same scrubber could be used for acid gas and particulate control.

Various aqueous inorganic solutions have shown high capacity for NO_2 absorption, but NO is absorbed with difficulty. In these processes, solvents are used to scrub NO from flue gas. But due to the low solubility of NO in aqueous phase, adsorbents which will react with NO should be added in the solvent to remove NO from gas phase. Thus, a method to oxidize NO to NO_2 or an equivalent oxidized state of nitrogen is required to substantially reduce NO_x emissions. Aqueous solutions of a number of oxidizing agents have been studied to determine their effectiveness in removing NO_x and SO_x from flue gas, including processes using acidic H_2O_2, alkaline solutions of $NaClO_2$ and peracids.

The objective of this research was the detailed analysis of cumene hydroperoxide reaction with nitric oxide including complete product analysis, nitrogen balance and complete material balances.

CHAPTER II

LITERATURE REVIEW

This chapter presents the background literature pertinent to the research conducted for this thesis.

2.1 Free Radical Reaction

Most of the reactions that have been considered to date have involved the participation of polar reactions and intermediates, that is, carbonium ions and carbanions, or related highly polarized intermediates, involving the heterolytic fission and formation, of covalent bonds:

$$R_3C^- + X^+ \longrightarrow R_3C-X \qquad (5)$$

But homolytic fission can also generate intermediates containing an unpaired electron or free radical, e.g., (a) and (b):

$$R_3C-X \longrightarrow \underset{(a)}{R_3C\cdot} + \underset{(b)}{\cdot X} \qquad (6)$$

Reactions involving radicals occur widely in the gas phase. The combustion of organic compounds is nearly always a free radical process. The oxidation of alkanes in internal combustion engines is one of the most widiy used chemical reactions. Radical reactions also occur in solutions especially if carried out in non-polar solvents, if stimulated by light or some other method of producing free radicals. Radicals are generally less selective in their attack on other solution compounds, or in undergoing rearrangements than are carbonium ions or carbanions.

Another characteristic of many radical reactions is that, once initiated, they often proceed with great rapidity owing to the establishment of a chain reactions.

Much of the known chemistry of NO_X in the presence of R-OOH is the result of photo-oxidative reactions of R-OO· free radical in the atmosphere which are listed in equations (7)-(10):

$$\mathrm{R\text{-}OO\cdot + NO \longrightarrow R\text{-}O\cdot + NO_2} \qquad (7)$$

$$\mathrm{R\text{-}OO\cdot + NO \longrightarrow (R\text{-}OONO)^* \longrightarrow R\text{-}ONO_2} \qquad (8)$$

$$\mathrm{R\text{-}OO\cdot + NO_2 \longrightarrow RO_2NO_2} \qquad (9)$$

$$\mathrm{R\text{-}O\cdot + NO_2 \longrightarrow R\text{-}ONO_2} \qquad (10)$$

In the study of the reactions of NO with liquid tertiary organic hydroperoxides, Shelton and Kapczewski (1967) reported that the reaction of NO with t-butyl hydroperoxide in benzene gave t-butyl nitrate and t-butyl nitrite via a four-step NO-induced free radical reaction sequence.

$$t\text{-}\mathrm{BuOOH + NO \longrightarrow} \; t\text{-}\mathrm{BuO\cdot + HONO} \qquad (11)$$

$$t\text{-}\mathrm{BuO\cdot} + t\text{-}\mathrm{BuOOH \longrightarrow} \; t\text{-}\mathrm{BuOH} + t\text{-}\mathrm{BuOO\cdot} \qquad (12)$$

$$t\text{-}\mathrm{BuOO\cdot + NO \longrightarrow} \; [t\text{-}\mathrm{BuOONO}]^* \longrightarrow t\text{-}\mathrm{BuONO_2} \qquad (13)$$

$$t\text{-}\mathrm{BuOH + HONO \longrightarrow} \; t\text{-}\mathrm{BuONO + H_2O} \qquad (14)$$

The net reaction (equation 15) can be obtained by adding equations (11) through equation (14):

$$2\, t\text{-}\mathrm{BuOOH + 2\, NO \longrightarrow} \; t\text{-}\mathrm{BuONO} + t\text{-}\mathrm{BuONO_2 + H_2O} \qquad (15)$$

2.2 Absorption of NO Followed by Oxidation

Nitric oxide oxidation is the most important step in the NO scrubbing process. Oxidation of NO to NO_2 induced by atmospheric oxygen is very slow, and becomes the rate determining step in most approaches. The rapid oxidation of NO is necessary when it is in a dilute phase. The general agents for this application are: ozone, sodium chlorite, hydrogen peroxide, peracid solution, organic hydroperoxide, etc.

[*a*] Ozone (O_3): The reaction of NO with ozone is given by following equation:

$$NO + O_3 \longrightarrow NO_2 + O_2 \qquad (16)$$

The resulting NO_2 can be easily scrubbed in caustic solutions even at concentration as low as a few ppm. The mechanism of reaction (16) has been studied by Harcourt (1972), and Bhatia and Hall (1980). The kinetics of this reaction have been studied by Borders (1982). The main disadvantage of this ozone method is the large power requirement that must be available in a stand-by system (Shaw, 1976).

[*b*] Sodium chlorite ($NaClO_2$): The absorption of NO in aqueous mixed solutions of $NaClO_2$ and NaOH has been studied by Sada, et al., (1979). Oxidation of NO with $NaClO_2$ in the presence of NaOH can be expressed as:

$$4NO + 3ClO_2^- \longrightarrow 4NO_3^- + 3Cl^- + 2H_2O \qquad (17)$$

The results indicated that the rate constant decreases with an increase in NaOH concentration.

Yang (1990) showed that the products of the reaction of NO and $NaClO_2$ in the absence of NaOH are still Cl^- and NO_3^- with a 1:1 NO to ClO_2^- ratio rather than 4:3.

[*c*] Hydrogen peroxide: Shaw (1976) reported that dilute hydrogen peroxide does not actually oxidize NO to NO_2, but large excess quantities of H_2O_2 are required to obtain a high NO conversion. Takahashi, et al., (1979) also carried out gas phase NO oxidation using hydrogen peroxide. Nitric oxide and hydrogen peroxide were taken in the ratio of 1:13 at a temperature greater than 400°C and using 100ppm of NO. The NO conversion was reported more than 95%. The absorption experiments were carried out by using 101.5mm ID stirred cell by Ladhabhoy and Sharma (1969). The reaction between NO and H_2O_2 is shown as following equation:

$$NO + H_2O_2 \longrightarrow NO_2 + H_2O \qquad (18)$$

Absorption of NO is accompanied by a fast pseudo-first order reaction. The value of reaction rate constant at 30°C was found to be $8.42 * 10^2 m^3$/kg-mole-s with an activation energy of 13,700kcal/kg-mole (Shaw, 1976).

[*d*] Peracid solution: The treatment of water soluble carboxylic acids with concentrated hydrogen peroxide generates solutions of peracids. These compounds can oxidize NO_X to the respective oxides. This property makes the peracid solution useful in flue gas cleaning.

The reactions involved in the scrubbing process are shown in equation (19) and (20):

$$RCOOOH + NO \longrightarrow NO_2 + RCOOH \qquad (19)$$

$$RCOOOH + 2NO_2 + H_2O \longrightarrow 2NO_3^- + RCOOH + 2H^+ \qquad (20)$$

[*e*] Organic hydroperoxide: Much of the known NO_X chemistry in the presence of ROOH is considered to be free radical reactions. In all but the remote troposphere, the alkylperoxyl radicals formed from the alkyl radicals, react with NO. It is believed that the significant pathway for the alkyl radicals is the oxidation of NO to NO_2 and the formation of alkoxy radicals:

$$R\text{-}OO\cdot + NO \longrightarrow R\text{-}O\cdot + NO_2 \qquad (21)$$

Only in the past few years have techniques for measuring rate constants for these reactions been reported. However, the sparse data available indicate that the rate constants for above reaction are not sensitive to the nature of the alkyl group. As a result, until additional data become available, a value of $7.6*10^{-12}cm^3/$ molecule-s is recommended by Atkinson and Lloyd (1984) for the NO-alkylperoxy radical reaction.

Finlayson-Pitts (1986) reported that essentially all of the $CH_3O_2\cdot$ reacts with NO according to equation (21). For larger alkyl radicals, another reaction mechanism becomes significant according to Darnall, et al., (1976). This is the addition of NO to the alkyl group and the formation of stable products, alkyl nitrate:

$$R\text{-}OO\cdot + NO \longrightarrow R\text{-}ONO_2 \qquad (22)$$

Carlsson, et al., (1988) repeated that concentrated hydroperoxide compounds react with NO to give alkyl nitrate as the dominant products with only trace amounts (< 5%) of alkyl nitrites. Rather than the NO induced O-O bond cleavage (equation 11) proposed by

Shelton and Kapczewski (1967), Carlsson proposed that the hydrogen was abstracted by NO (equation 23-24). A greenish yellow gas was observed in these experiments, that could possibly be HNO.

$$\text{R-OOH} + \text{NO} \longrightarrow \text{R-OO}\cdot + \text{HNO} \tag{23}$$

$$\text{R-OO}\cdot + \text{NO} \longrightarrow (\text{R-OONO})^{*} \longrightarrow \text{R-ONO}_2 \tag{24}$$

Both Shelton's and Carlsson's experiments were not carried out under typical flue gas conditions. Their NO concentrations were much larger than those found in typical flue gases such as 1000ppm to perhaps 5ppm. Furthermore, highly concentrated R-OOH solutions would be too expensive for flue gas scrubbing.

Perlmutter, et al., (1993) reported the feasibility of a total organic scrubbing system for NO removal under simulated flue gas conditions. The NO absorption was conducted in a scrubber which was filled with tertiary organic hydroperoxides in n-hexadecane. It was found that the NO reacted with the hydroperoxides to produce alkyl nitrates. These are easily hydrolyzed with ammonium hydroxide to ammonium nitrate and the alcohol. The highest rates of NO removal were obtained at the highest temperatures, concentrations and residence times.

CHAPTER III

EXPERIMENTAL

This chapter describes the experimental equipment, sources of materials, and analytical procedures.

3.1 Materials

3.1.1 Organic scrubbing solution

The organic scrubbing solution was made by adding a measured amount of cumene hydroperoxide (CHP) (1) into n-hexadecane (cetane). Both of these chemicals were purchased from Aldrich Chemical Co. and were used without further purification.

3.1.2 Alkaline aqueous scrubbing solution

The secondary scrubber contained 1M sodium hydroxide solution. It was made by dissolving 8g of sodium hydroxide in 200ml of deionized water. The sodium hydroxide was purchased from Aldrich Chemical Co. and was used without further purification.

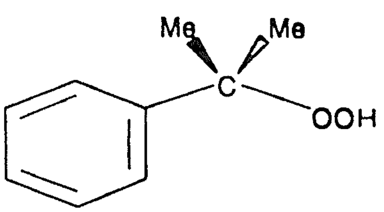
3.1.3 Gases

Gas cylinders containing 1200ppm NO and the balance helium were purchased with analysis from Matheson Gas Co. and used directly without further purification. The cylinders contained a small quantity of NO_2 which was less than 60ppm. Cylinders containing 99.99 percent pure helium were also supplied from Matheson Gas Co..

3.1.4 Standard compounds used to calibrate analytical instruments

Acetophenone (2), isobutyl nitrate (3), t-butyl nitrite (4), α-methylstyrene (AMS) (5) and cumyl alcohol (2-phenyl-2-propanol) (6) were used as quantative standards to measure

Structure Sheet



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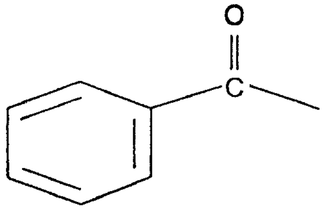


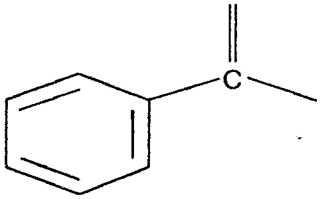
(2)

$(CH_3)_2CH\text{-}CH_2ONO_2$

(3)

$(CH_3)_3C\text{-}ONO$

(4)



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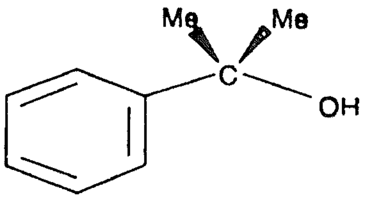

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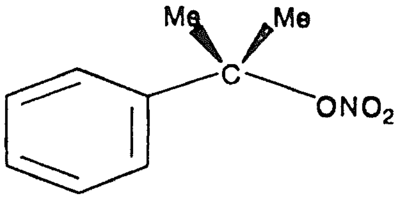

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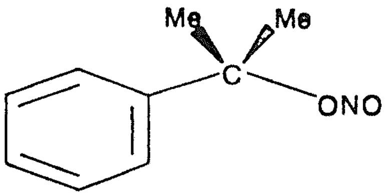

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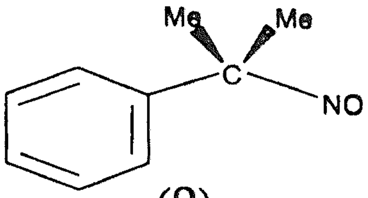


(9)

product concentrations in the organic scrubbing solution. These four organic compounds were purchased from Aldrich Chemical Co. and were used without further purification.

3.1.5 Compounds for iodometric titration

Isopropyl alcohol (IPA), sodium iodide (NaI) and sodium thiosulfate ($Na_2S_2O_3$) were used in iodometric titration to determine the concentration of cumene hydroperoxide in the organic scrubbing solution. These three compounds were purchased from Aldrich Chemical Co. and were used without further purification.

3.2 Apparatus

All nitric oxide scrubbing experiments were carried out in a laboratory-scale scrubbing system depicted in Figure 2. Both the organic scrubber and aqueous scrubber were made out of pyrex of 40 cm in length and 4 cm in diameter. The organic scrubber was equipped with a 200kw heating tape to control the reactor's temperature. The temperature of the organic scrubbing solution was monitored with a Chromel-Alumel thermocouple which was immersed in the solution. A gas-liquid separator was used to prevent organic carry over from flowing into the downstream system's tubing. The alkaline aqueous scrubber was added to absorb any possible nitrogen dioxide or nitric acid generated in the organic scrubber. To avoid water vapor carry over to the GC from the aqueous scrubbing solution, a glass U-tube immersed in ice water, was used as a cold trap.

3.3 Experimental Procedure

3.3.1 Thermal stability of cumene hydroperoxide solution

Two hundred ml of cumene hydroperoxide solution were placed in the organic scrubber and purged with helium. Reactor temperature and purge gas flow rate were controlled as the same operating conditions that were planned for NO scrubbing experiments. Two ml

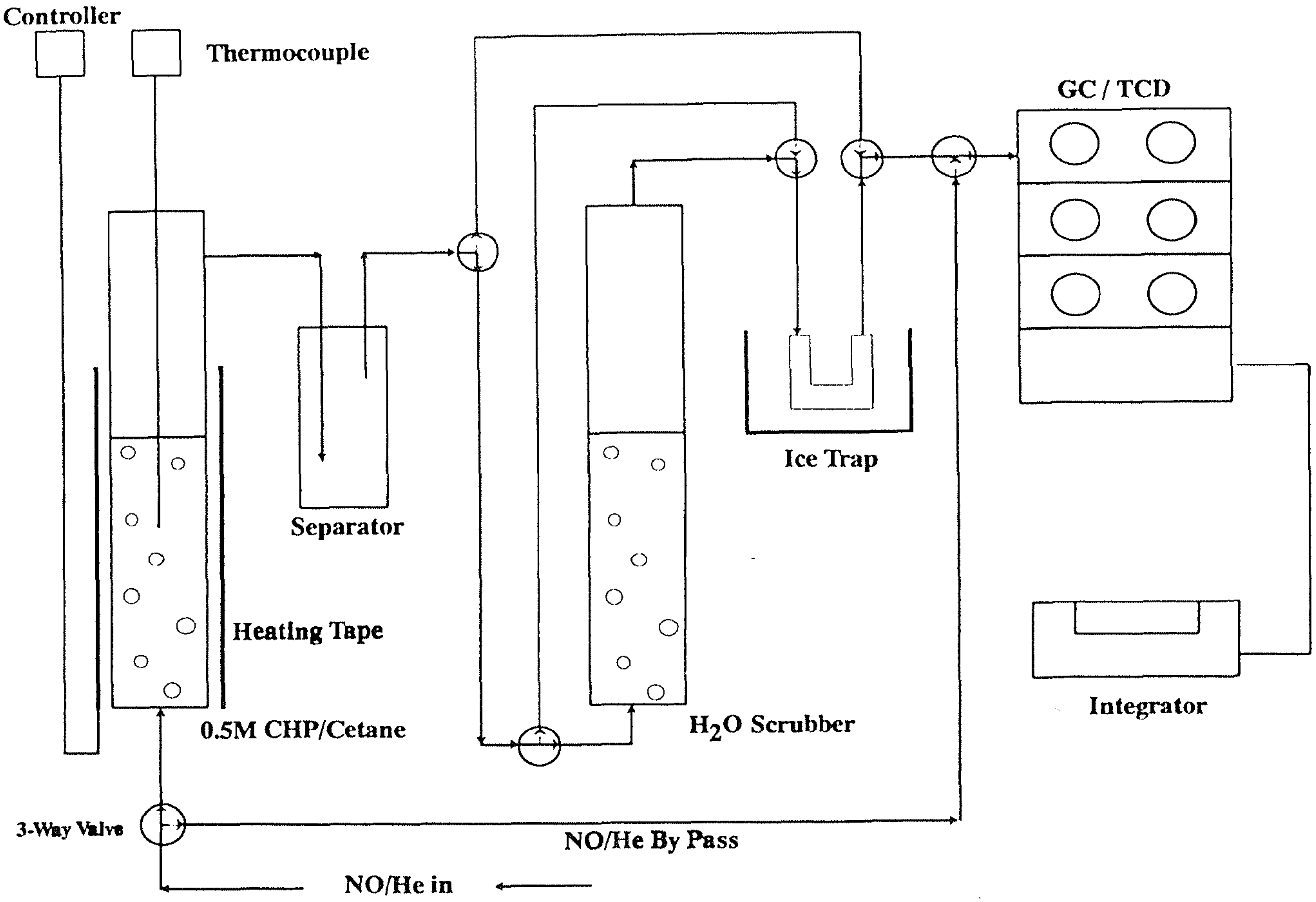


Figure 2 Nitric oxide scrubbing apparatus

samples of the scrubbing solution were taken out before heating, and every one or two hours after heating to experimental conditions. The CHP concentration of each sample was determined by iodometric titration. The half life for the thermal decomposition of the scrubbing solution was thus estimated.

3.3.2 Nitric oxide scrubbing

A known volume of cumene hydroperoxide solution and 200ml of 1M sodium hydroxide solution were placed in the organic scrubber and in the aqueous scrubber respectively. Before heating the organic scrubbing solution, 3ml of the CHP solution were taken out from the scrubber and the initial CHP concentration was determined by iodometric titration. While heating the organic scrubbing solution, the system was purged with pure helium and the gas flow rate was adjusted to the required level. When the temperature reached steady state, the three-way valve was turned to introduce the nitric oxide mixture (1200ppm) into the scrubbing system. The effluent gas was analyzed with a GOW-MAC gas chromatograph using thermal conductivity detector (TCD). Part of the flue gas was collected in a gas cell before entering the secondary aqueous scrubber and was analyzed using a BIO-RAD Fourier transform infrared spectrometer (FTIR). The inlet gas concentration was checked during the experiment by allowing the gas stream to by-pass the reactor into the GC. The outlet gas was vented into a hood. Three ml of the organic scrubbing solution was collected every hour in the first 9 hours during the experiment and every two hours after that. To quantitatively determine unreacted cumene hydroperoxide and reaction products, the collected samples were analyzed by iodometric titration and GC-FTIR analysis.

3.3.3 Denitration

Four ml of the reacted organic scrubbing solution were mixed with 20ml of 10% ammonium hydroxide solution in a round-bottom flask equipped with a reflux condenser.

The mixture was continuously stirred and the temperature was maintained at 70°C over night. After reaction, the aqueous layer was separated from the organic layer. The organic layer was dried with granular sodium sulfate and was analyzed by FTIR. The aqueous layer was analyzed by ion chromatograph (IC) to quantify the nitrate and nitrite ions.

3.4 Analytical Techniques

Analytical techniques were a very important part of this research. All the analytical techniques that were used in this study are summarized in Table 2 and will be discussed briefly later in this section.

Table 2 Analytical techniques used in NO scrubbing study.

Compound	Method
Cumene Hydroperoxide (1)	Iodometric Titration
Acetophenone (2)	FTIR
α-Methylstyrene (5)	FTIR, GC
Cumyl Alcohol (6)	GC
Cumene Nitrate (7)	FTIR
Cumene Nitrite (8)	FTIR
Nitroso Compound (9)	FTIR
Nitric Oxide	GC
Inorganic Nitrate / Nitrite	IC

3.4.1 Gas chromatography

The outlet effluent gas entered an on-line GOW-MAC gas chromatograph after passing through the U-tube. The GOW-MAC GC was equipped with a thermal conductivity detector (TCD) to measure the concentration of nitric oxide in the flue gas. The column used was a 1/8 inch in diameter by 12 feet in length stainless steel column packed with poropak-Q. To obtain a good separation of NO and O_2 peaks, this poropak-Q column was extended from the oven and was immersed in an ice bath to keep the column temperature at $0^{o}C$. A Hewlett Packard 3396 integrator was connected to the GC to quantify the peak area of the chromatogram.

The GC operating conditions are listed as following:

- Injection port temperature = $150^{o}C$
- Detector temperature = $200^{o}C$
- Poropak-Q column temperature = $0^{o}C$
- Detector current = 200mA
- Carrier gas flow rate = 24.7ml/min
- Reference gas flow rate = 24.7ml/min

The main purpose of using this GOW-MAC GC was to measure the NO-removal efficiency of the scrubbing system. The efficiency can be expressed as the capability of the scrubbing system to remove NO from flue gas; that is, the amount of NO removed from the feed gas. For convenience, "% NO conversion" was defined to represent the nitric oxide removing ability of the scrubbing solution, and it was obtained by the following equation:

$$\% \text{ NO conversion} = [1 - (A/B)]*100\% \qquad (25)$$

where A = NO content in the effluent from the scrubber

B = NO content in the unreacted flue gas

3.4.2 Fourier transform infrared spectrometer (FTIR)

A Bio-Rad Fourier transform infrared spectrometer was employed to analyze the organic compounds in the organic scrubbing solution. There are two major applications of FTIR. One is to obtain the absorbance spectra of the organic scrubbing solution; and the other, is to use it as a detector for a GC. The major organic compounds found in the organic scrubbing solution and their characteristic absorbance are listed in Table 3. Due to the high sensitivity of the FTIR, organic compounds with particular absorbances at known wave number of intereste can be qualitatively and quantitatively determined with FTIR.

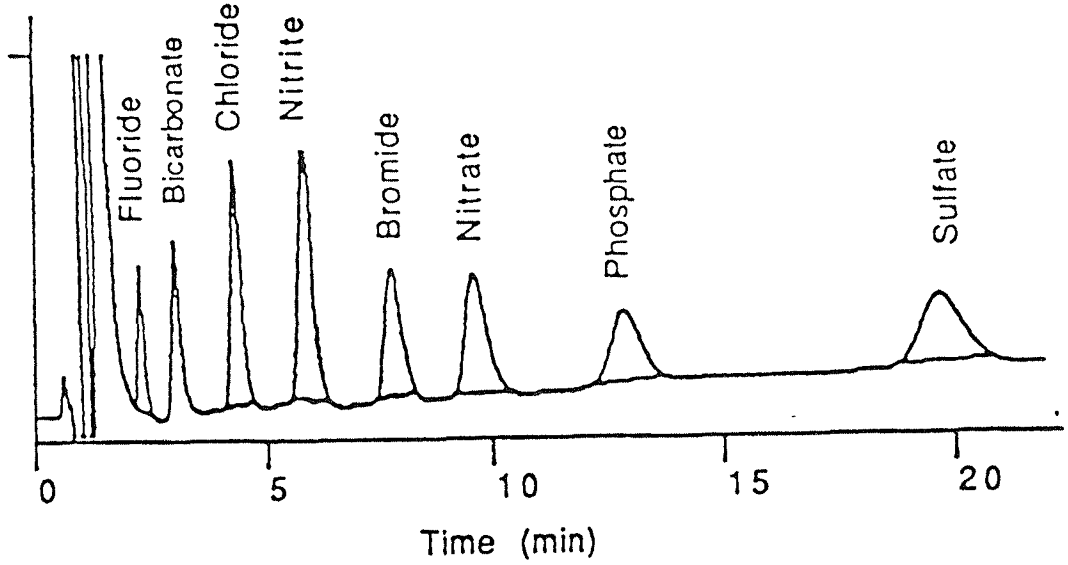
The major absorbance represents the IR absorption peak of each compounds. When two compounds have the same major absorbance, like cumene nitrate and cumene nitrite, the other IR absorbances were chosen as the auxiliary absorbances to identify these compounds.

Table 3 Characteristic absorbance of the organic compounds found in the NO treated organic scrubbing solution.

Compound	Major Absorbance	Auxiliary Absorbance
Acetophenone (2)	1689 cm^{-1}	
Cumene Nitrate (7)	1630 cm^{-1}	860 cm^{-1}
Cumene Nitrite (8)	1630 cm^{-1}	778 cm^{-1}
Nitroso Compound (9)	1566 cm^{-1}	
α-Methylstyrene (5)	890 cm^{-1}	

3.4.3 Ion chromatography

A Waters ion chromatograph was used to detect the inorganic nitrate and nitrite ions after hydrolysis with ammoina solution. This is actually a high performance liquid chromatograph (HPLC) equipped with an ion exchange column. After injection, the sample passed through an ion exchange column and was detected by UV detectors at the end of the flow stream. Ion exchange chromatograph is used to separate ionic compounds. Ion exchange packing is prepared by bonding ionic functional groups to silica gel or to a porous polymer support. Packings with negatively charged group are called cation exchangers and packings with positive charged functional groups are called anion exchangers. Ion exchange eluents are usually aqueous buffers that may contain organic solvents. Eluent strength increases with the ionic strength of the buffer. pH and organic content of the eluent also affect retention. A typical ion chromatography of inorganic anions on an anion exchange packing with aqueous buffer eluent is shown on Figure 3.



Working Standard	
Fluoride	1 ppm
Chloride	2 ppm
Nitrite	4 ppm
Bromide	4 ppm
Nitrate	4 ppm
Phosphate	6 ppm
Sulfate	4 ppm

Figure 3 Typical IC chromatogram

3.4.4 Iodometric titration

Thirty ml of isopropyl alcohol (IPA) were mixed with 2ml of acetic acid and 1ml sample in a 200ml round-bottom flask. Pure nitrogen gas was purged into the flask. While purging with nitrogen, 10ml of IPA (contained 2g of sodium iodide) was added into the solution. The mixture was refluxed under nitrogen for 5 minutes. The solution was titrated under nitrogen by 0.01N $Na_2S_2O_3$ solution immediately after reflux.

CHAPTER IV

RESULTS

This section presents the research results for the reactions of cumene hydroperoxide with nitric oxide.

4.1 Thermal Stability of Cumene Hydroperoxide Solution

It is important to determine if cumene hydroperoxide is thermally stable at flue gas treatment temperature. This allows us to ascertain if the products are a result of thermal decomposition or NO induced reactions. Figure 4 shows the concentration change of cumene hydroperoxide solution as a function of time. It was found that there is a minor decrease of CHP concentration after heating at 100°C for 19 hours. The thermal stability of cumene hydroperoxide solution can be expressed as the half life ($t_{1/2}$) of cumene hydroperoxide, that is, the time required to decompose half of the solute concentration at the operating conditions. The half-life was estimated as follows:

The decomposition rate of cumene hydroperoxide can be expressed as:

$$-\frac{d[R-OOH]}{dt} = k_1[R-OOH] \qquad (26)$$

where k_1 is the decomposition rate constant of cumene hydroperoxide.

$$\therefore -\frac{d[R-OOH]}{[R-OOH]} = k_1 dt \qquad (27)$$

$$\int_{M}^{M/2} -\frac{d[R-OOH]}{[R-OOH]} = \int_{0}^{t_{1/2}} k_1 dt \qquad (28)$$

$$-\ln[M] \Big|_{M}^{M/2} = k_1 t_{1/2} \qquad (29)$$

$$\ln[M]-\ln[M/2] = k_1 t_{1/2} \qquad (30)$$

$$\ln 2 = k_1 t_{1/2} \qquad (31)$$

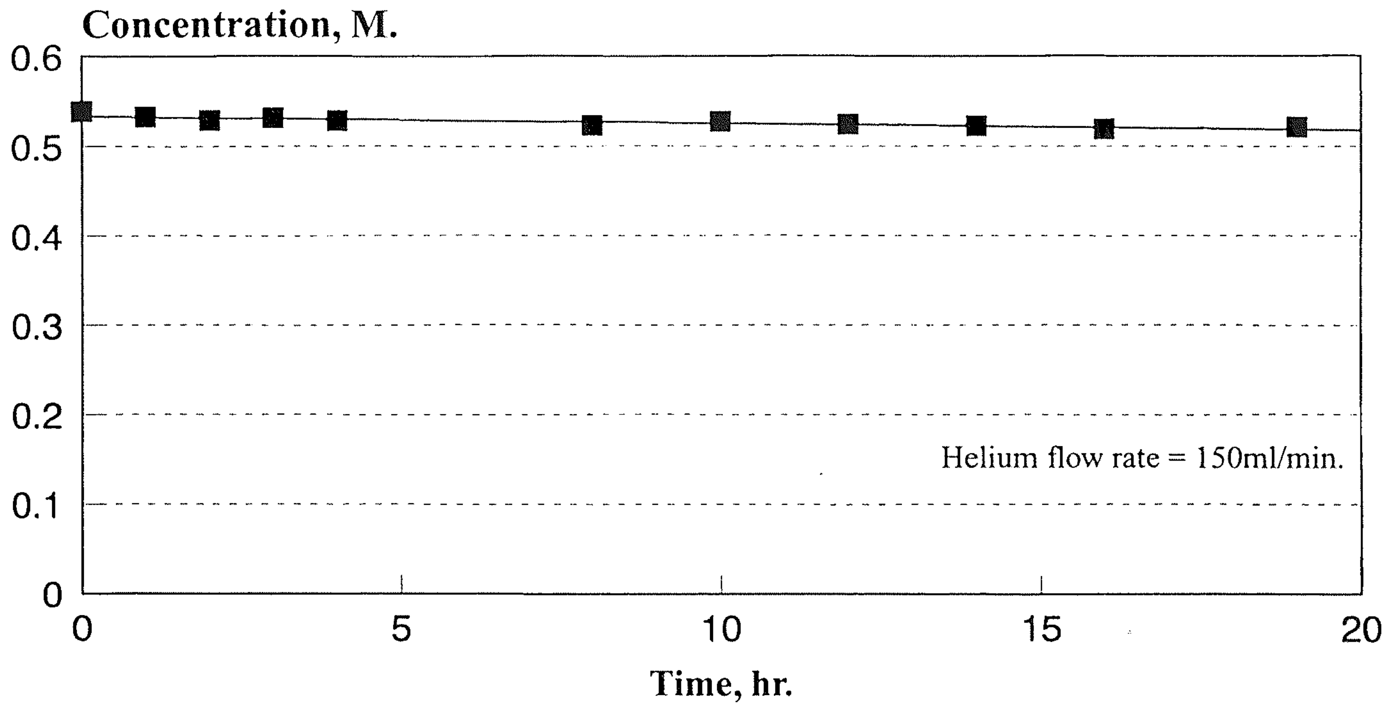


Figure 4 Concentration change of cumene hydroperoxide solution at 100^{O}C

$$\therefore t_{1/2} = \frac{\ln 2}{k_1} \qquad (32)$$

The decomposition constant k_1 is the slope of ln(M/M') against time plot, where M is the initial CHP concentration and M' is the concentration after time t. From the plot, k_1 is equal to $1.48*10^{-3}$. Thus, the half life of cumene hydroperoxide solution was estimated from equation (32) and was equal to 467 hours at 100°C. These results are in agreement with H. Szamant (1989) who reported $t_{1/2} > 500$ hours at 120°C.

4.2 Nitric Oxide Scrubbing

The results showing the effectiveness of NO removal by cumene hydroperoxide are described in this section.

4.2.1 NO scrubbing efficiency

As mentioned previously, the scrubbing efficiency of the organic scrubbing solution was expressed as "% NO conversion". Figure 5 shows a plot of "% NO conversion" against reaction time. NO conversion averaged about 70% during 15 hours of scrubbing at 100°C.

4.2.2 Decrease of concentration of cumene hydroperoxide solution

The concentration change of the cumene hydroperoxide solution as a function of reaction time during scrubbing is shown in Figure 6. The observation that there was a major decrease in concentration of CHP due to reaction with nitric oxide was unexpected. The CHP concentration decreased from 0.53M to 0.35M after reacting with NO at 100°C for 15 hours. The moles of CHP that were consumed in this scrubbing experiment were 36mmol, while the moles of nitric oxide that had reacted were just 4.8mmol. This

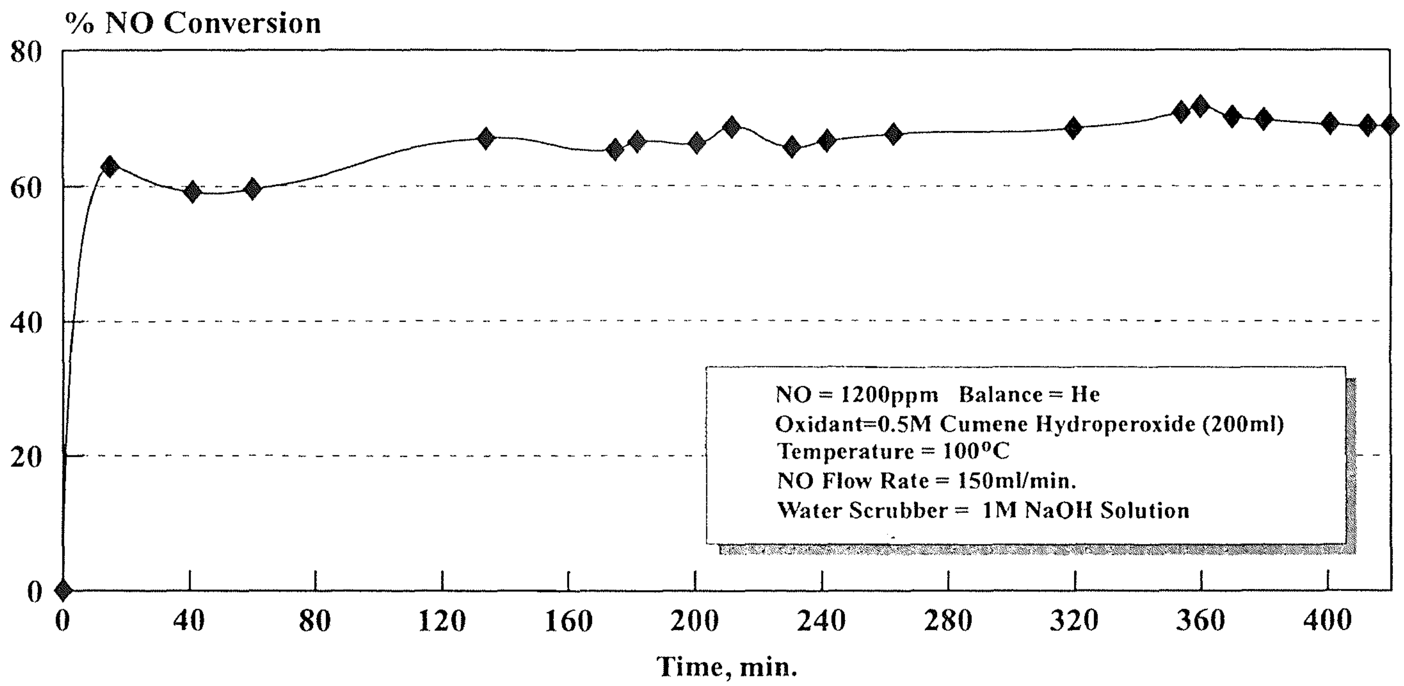
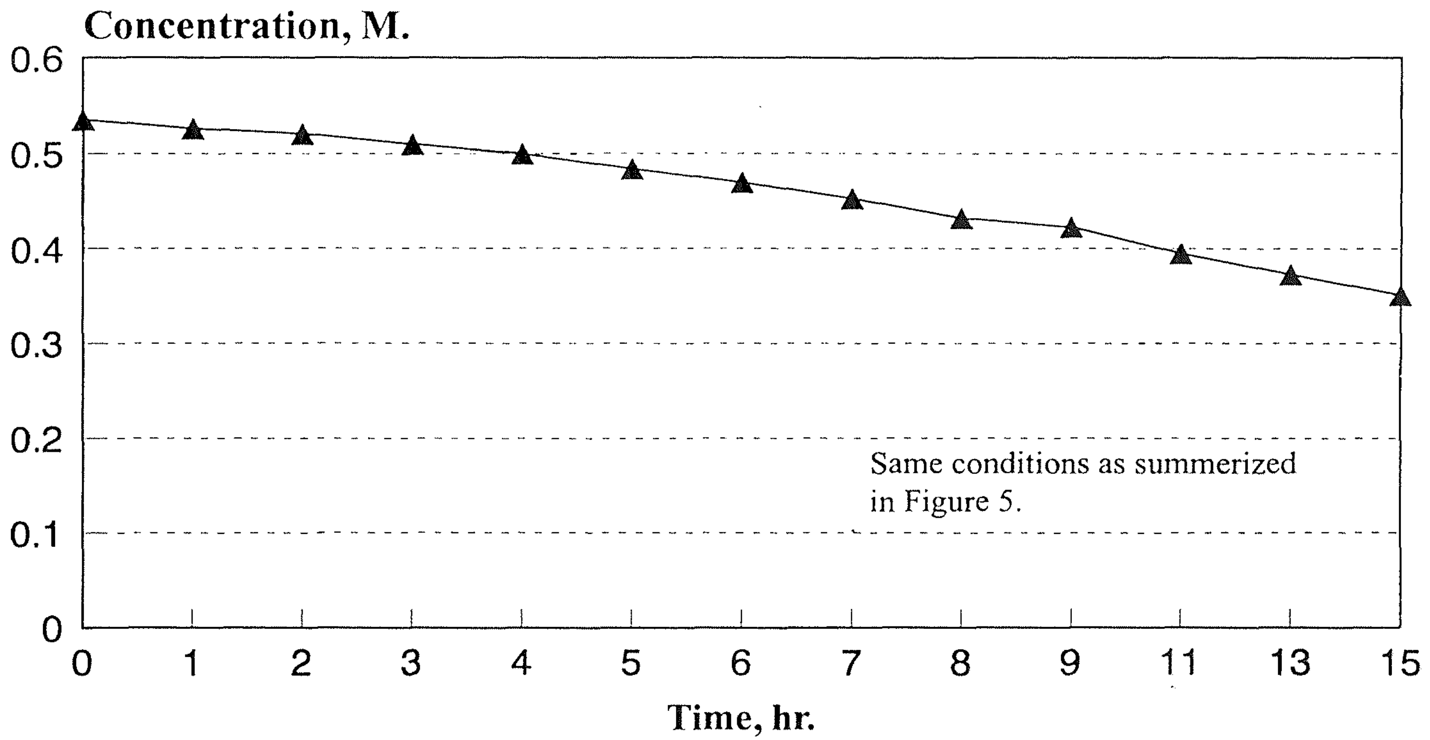


Figure 5 NO conversion as a function of time



Same conditions as summerized in Figure 5.

Figure 6 Concentration change of cumene hydroperoxide during NO scrubbing indicated that the reaction of CHP with NO is a 36:4.8 ratio but not 1:1 as had been assumed by Perlmutter, et al., (1993).

4.2.3 Nitrogen balance

Nitrogen balance is the way to account for all the nitrogen containing compounds in this scrubbing system. The fate of nitrogen is summerized in the following scheme:

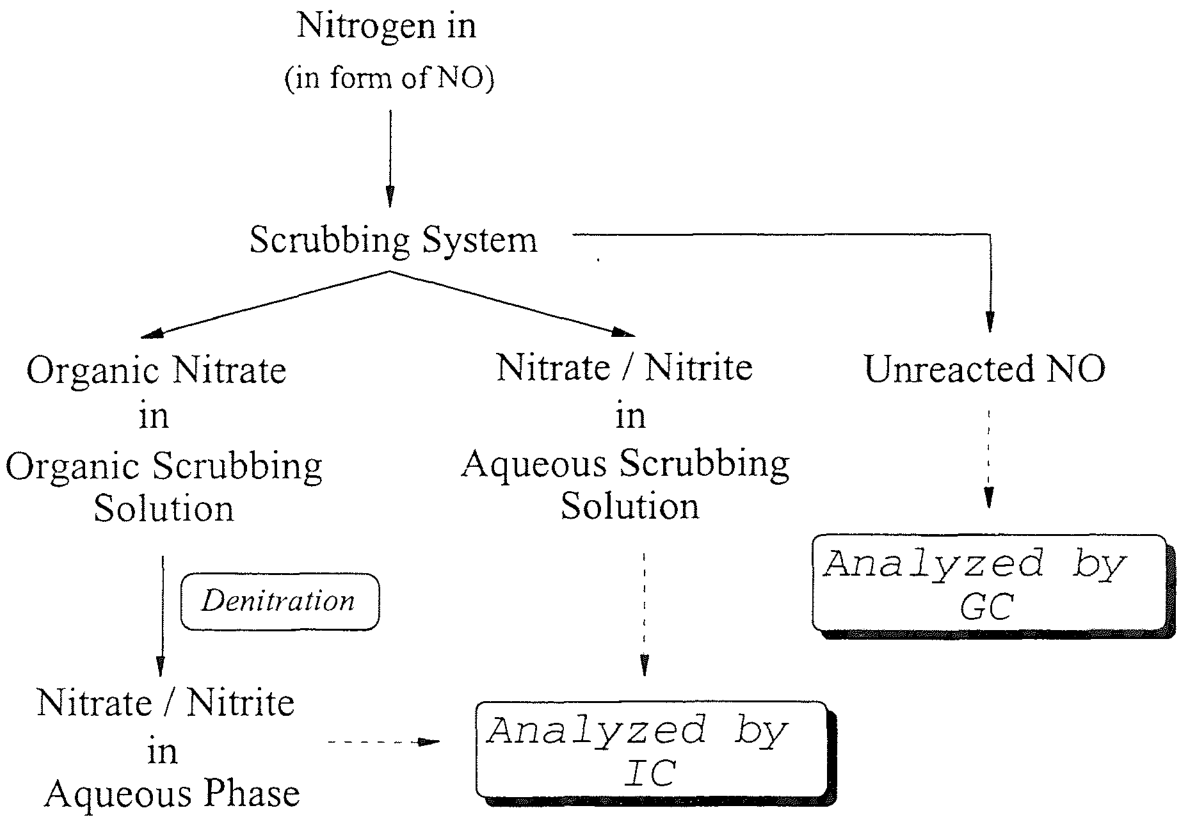


Figure 7 The fate of nitrogen.

As shown in the previous section, 70% of the inlet NO was oxidized by the scrubbing solution and was retained in the scrubbing system. The amount of nitrogen fed to the scrubber consisted of 6.88mmols of nitrogen which can be obtained from the following calculation:

$$\frac{1249.2 \text{ moles of NO} + \text{NO}_2}{10^6 \text{ moles Gas}} \times 155\frac{\text{cm}^3}{1 \text{ min}} \times 15 \text{ hrs} \times 60\frac{\text{min}}{\text{hr}} \times \frac{1 \text{ mole Gas}}{25,400\,\text{cm}^3} = 6.86\text{mmols}$$

The rest of the NO passed through the scrubbing system unreacted and was analyzed by the on-line GC. The nitrogen that stayed in the scrubbing system was found in both organic and aqueous scrubbing solutions. The organic nitrogen in the organic scrubbing solution was transferred into the 10% ammonia solution by denitration. All the nitrate and nitrite in aqueous phase were analyzed by ion chromatography. The result for nitrogen balance was shown in Table 4.

Table 4 Nitrogen balance.

Nitrogen distribution	**Moles of nitrogen**
Organic Scrubbing Soln'	4.02 mmol
Aqueous Scrubbing Soln'	0.74 mmol
Exiting Gases (GC)	2.07 mmol
Sum.	6.83 mmol
Total	6.86 mmol
Balance = Sum/Total	99.6%

4.3 Material Balance

4.3.1 Organic products analysis

To analyze the organic products of the scrubbing reaction quantitatively, standard solutions of acetophenone (2), isobutyl nitrate (3), and tertiary butyl nitrite (4) were used to calibrate the instrument for the specific functional group concentrations, viz., ketone, nitrate and nitrite. Three calibration curves with respect to these organic groups are shown in Figure 8 (acetophenone), 9 (nitrate), and 10 (nitrite). It was assumed that both of these low molecular weight nitrate and nitrite represent quantitatively the same absorbance as the nitrates and nitrites that were produced from cumene hydroperoxide. The spectrum of the thermally treated CHP was essentially identical to that of the fresh solution and is not presented here. The FTIR spectrum of the organic scrubbing solution

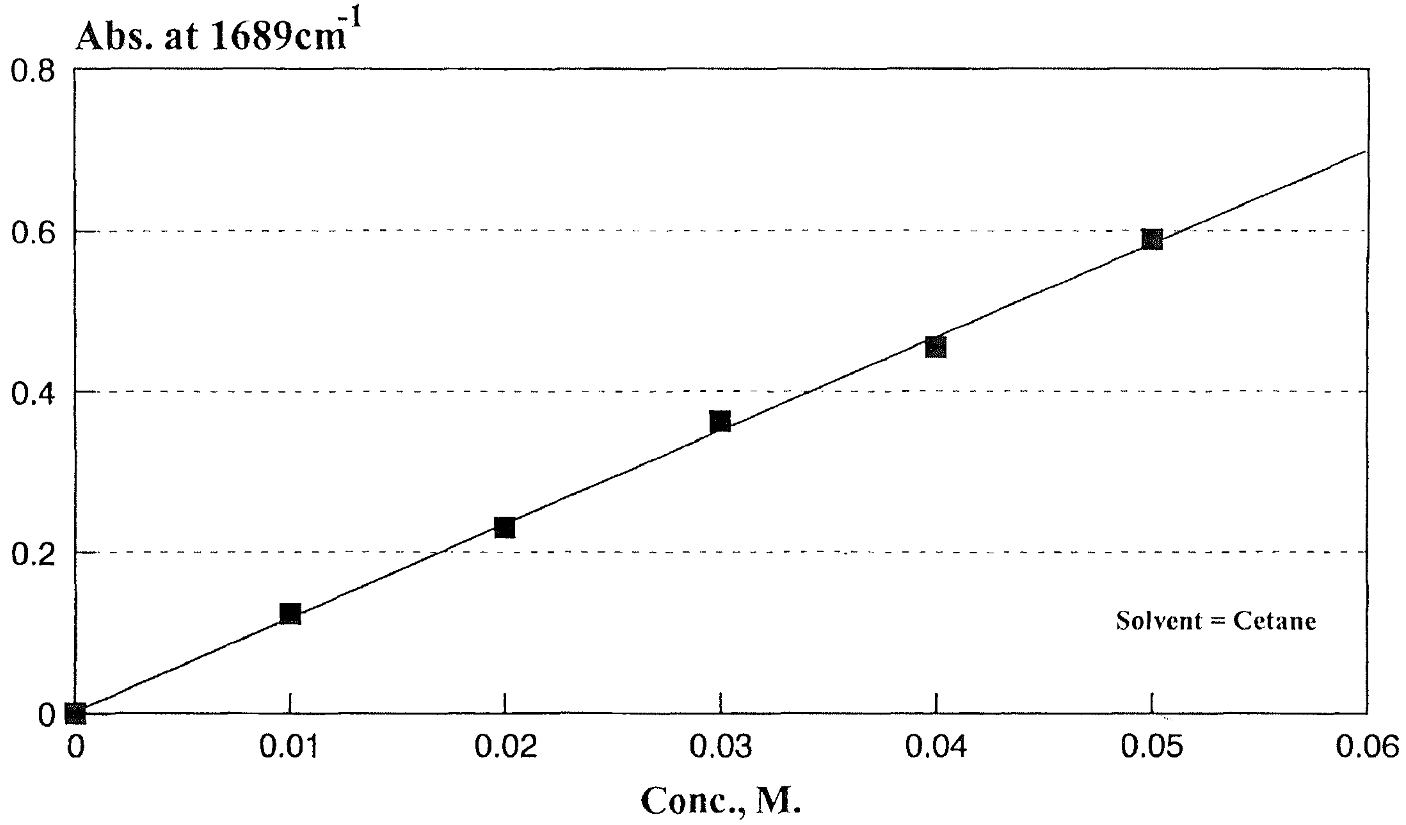


Figure 8 Acetophenone calibration curve

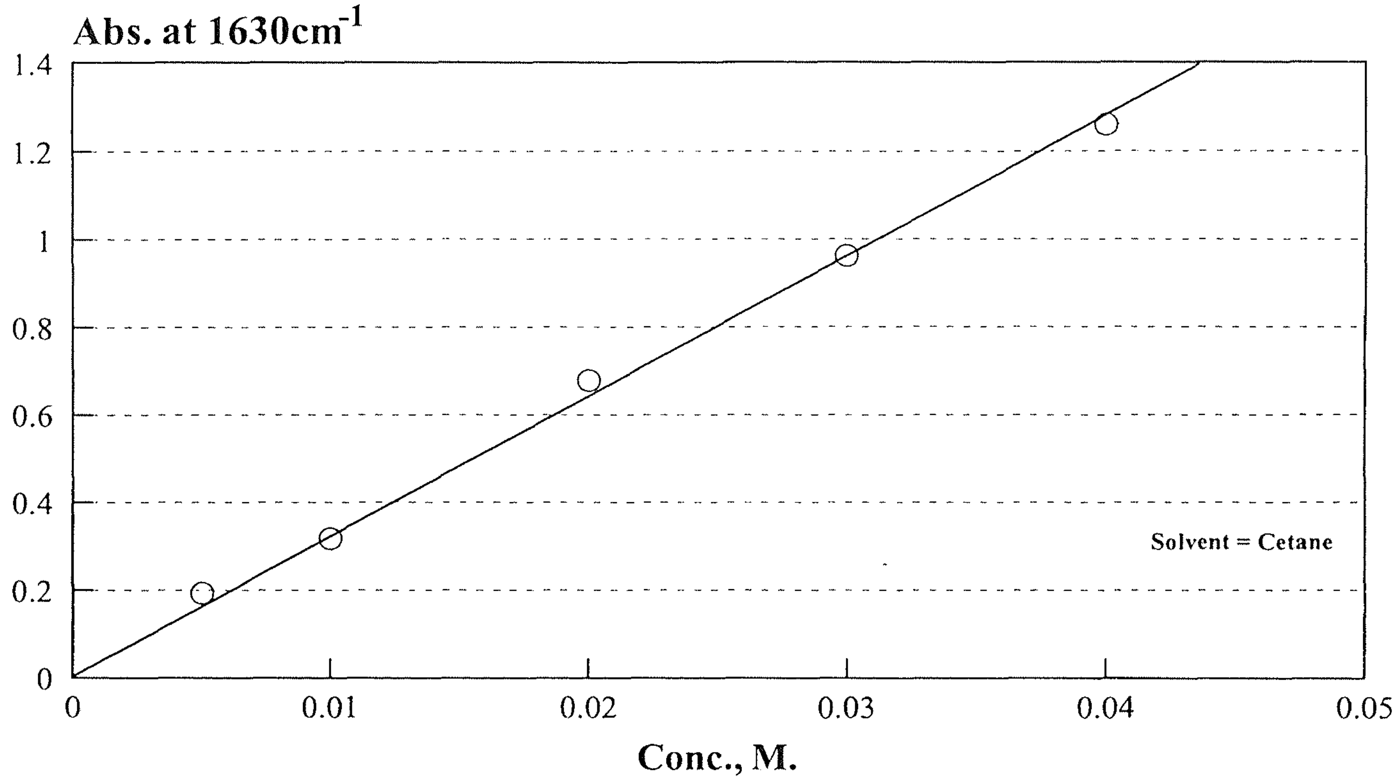


Figure 9 Nitrate calibration curve

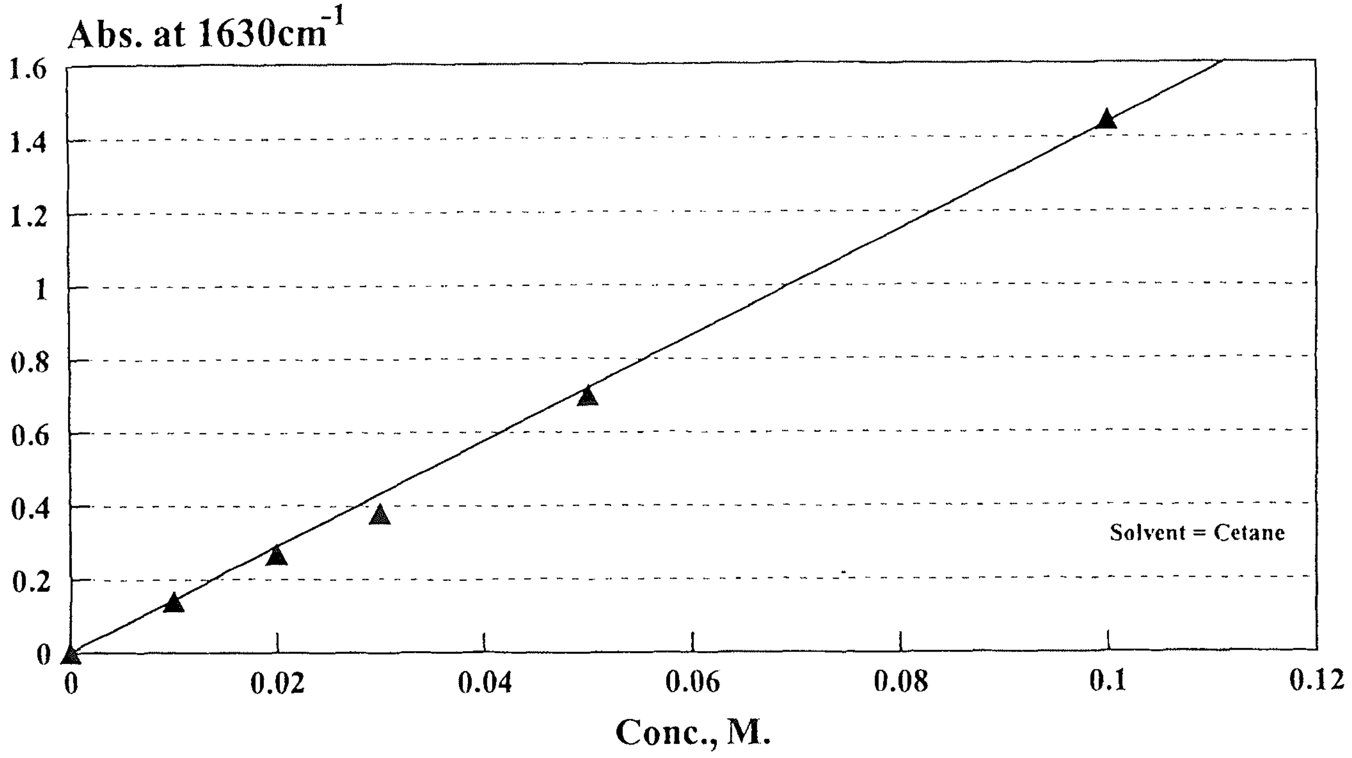


Figure 10 Tertiary nitrite calibration curve

was taken after reacting with NO for 15 hours, and is shown in Figure 11. The characteristic absorbance of each organic compound was compared to each standard calibration curve. A careful examination of Figure 11 shows that there is no increase in absorbance at both 778cm^{-1} or 1562cm^{-1}. This shows that there was no cumene nitrite (8) nor the nitroso compound (9) in the final scrubbing solution. The peaks at 1689cm^{-1} and 1630cm^{-1} represent acetophenone (2) and cumene nitrate (7), respectively. The concentrations of these organic compounds were calculated from the standard calibration curves.

The organic scrubbing solution was also analyzed with a Hewlett Packard 5890A gas chromatograph. The operating conditions are as follows:

- Column: DB-Wax capillary column
- Detector: flame ionization detector (FID)
- Injection port temperature = 180^{o}C
- Detector temperature = 220^{o}C
- Oven temperature = 140^{o}C

Gas flow rate:

- Carrier gas in column = 6.12ml/min
- Carrier gas + makeup gas = 31.0ml/min
- H2 + carrier gas + makeup gas = 61.0ml/min
- Air + carrier gas + makeup gas = 450ml/min

The typical GC chromatogram was shown in Figure 12. The peaks at 1.821 and 7.379 minutes represented α-methylstyrene (5) and cumyl alcohol (6). Both peaks were checked by spiking the injection solution, and were also identified by GC-FTIR. Figure 13 and 14 showed the GC calibration curves that were obtained with standard compounds. By comparing these two calibration curves with the sample's peak area, the amount of α-methylstyrene (5) and cumyl alcohol (6) were calculated. Table 5 shows the result of the organic product analysis:

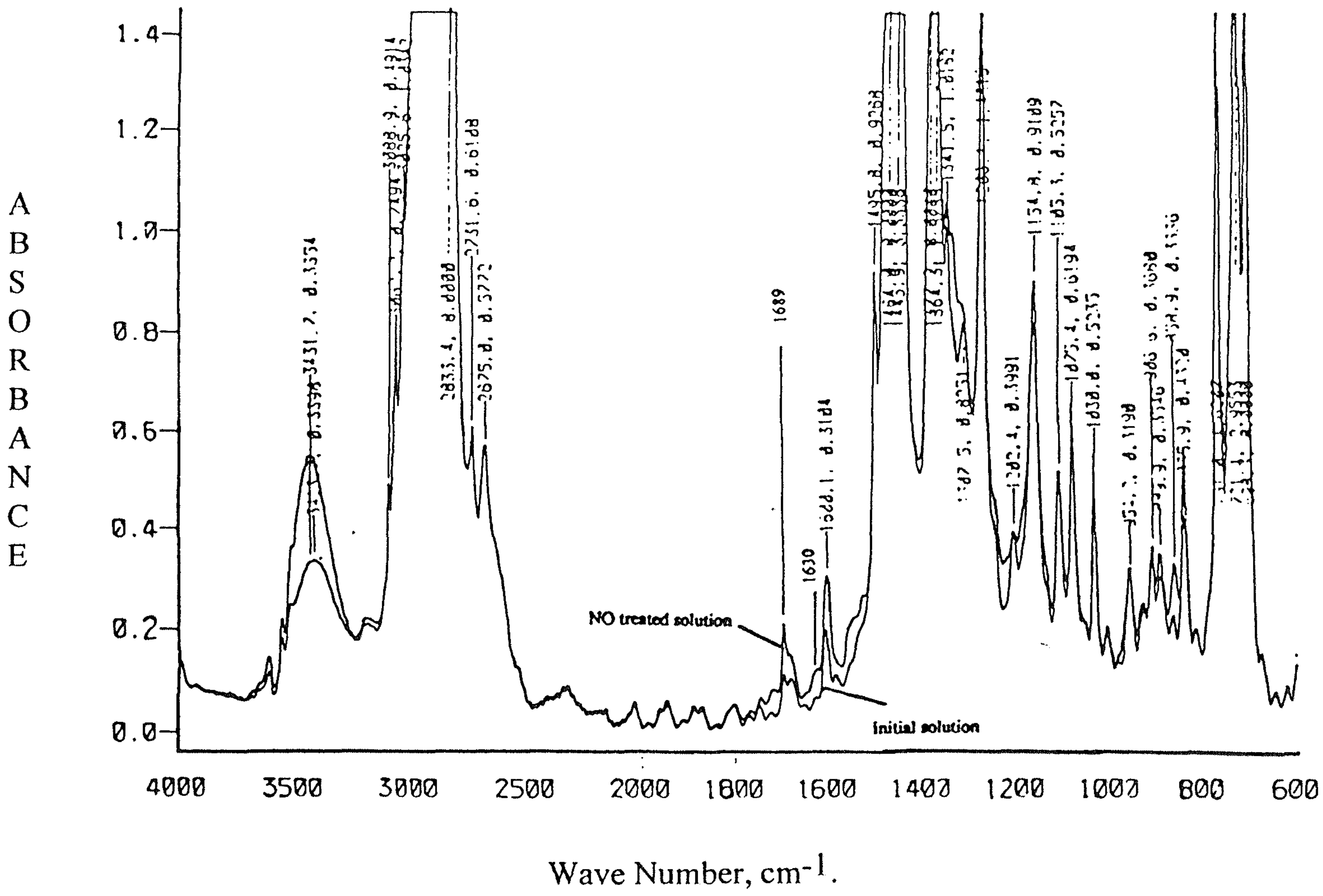


Figure 11 Typical FTIR spectra of the NO treated organic scrubbing solution

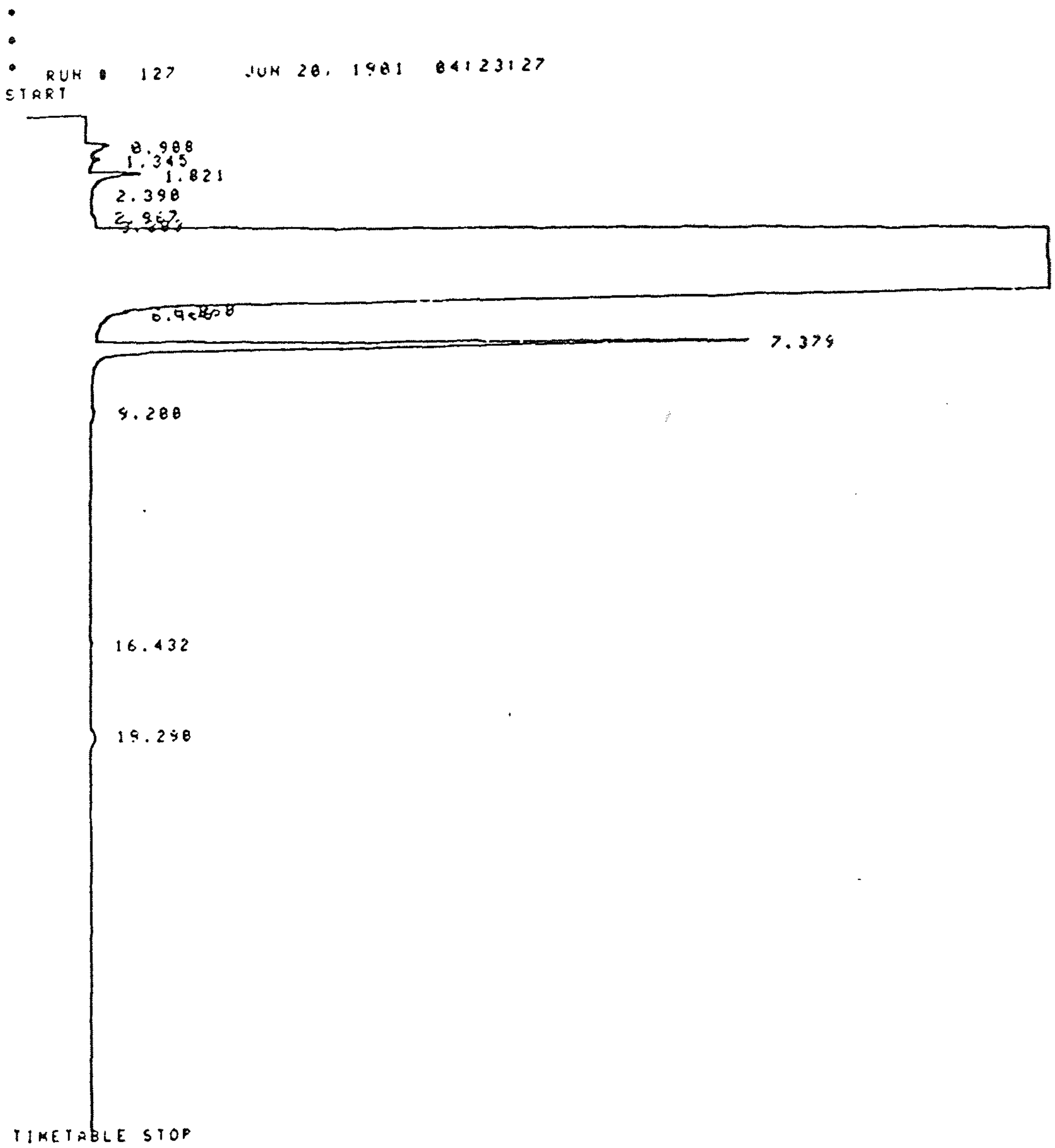


Figure 12 Typical GC chromatogram of the NO treated organic scrubbing solution

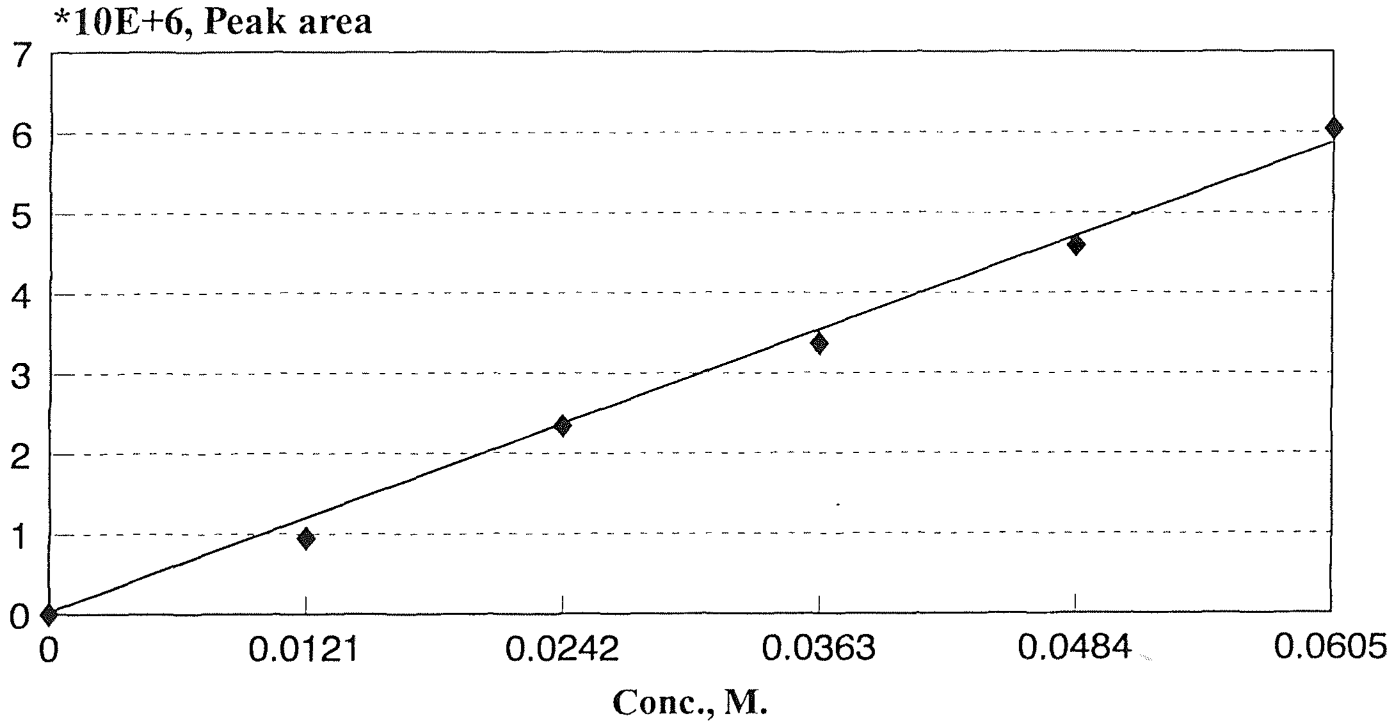


Figure 13 α-Methylstyrene calibration curve

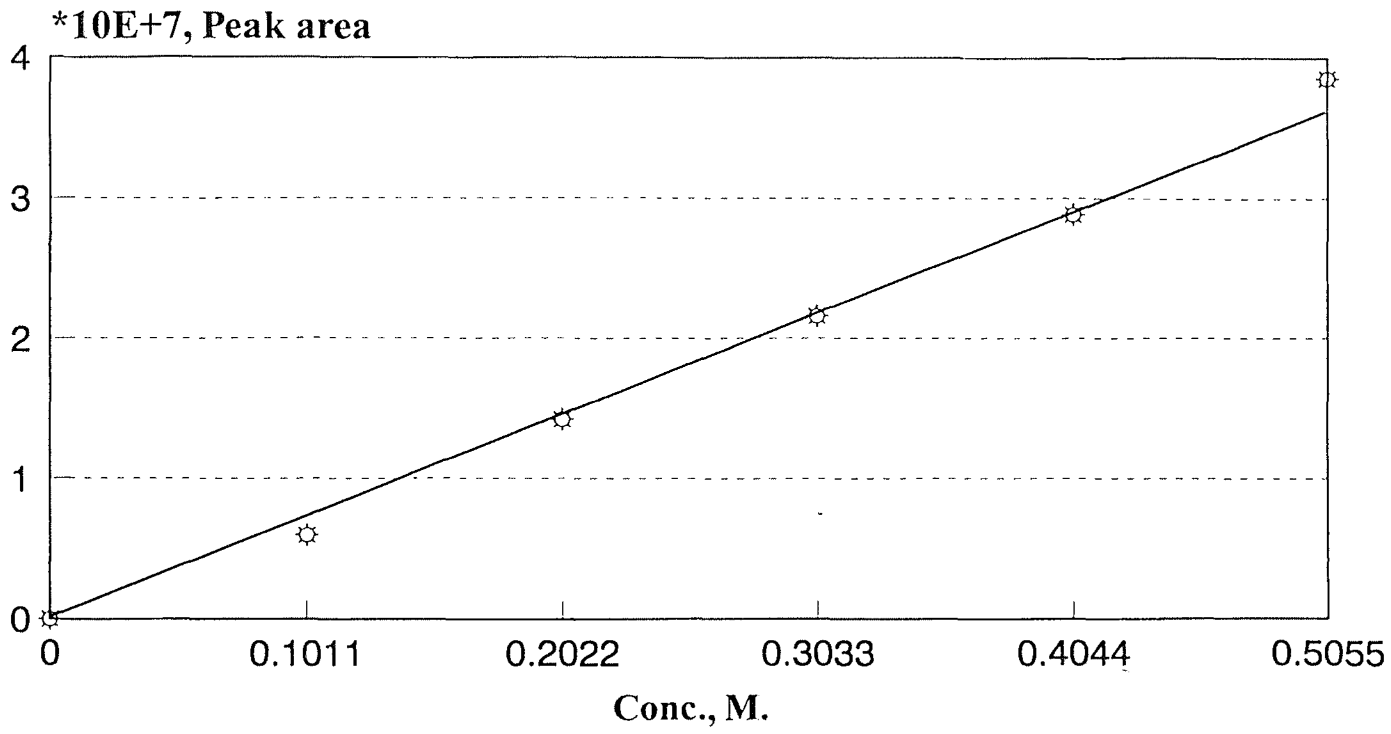


Figure 14 Cumyl alcohol calibration curve

Table 5 Products in the reacted organic scrubbing solution.

Product	**Amount, mmol.**
Cumyl Alcohol (6)	24.0
Acetophenone (2)	1.53
Cumene Nitrate (7)	0.34
Cumene Nitrite (8)	0
Nitroso Compound (9)	0
α-Methylstyrene (5)	5.56
Total	31.4

4.3.2 Material balance

Table 6 summarizes the quantitative analysis of the scrubbing reaction. Most of the cumene hydroperoxide that was consumed in this reaction was changed to cumyl alcohol. Most of the reacted nitric oxide showed up as inorganic nitrate and inorganic nitrite. Relatively small amounts of NO were converted to cumene nitrate.

4.3.3 Effects at other operating conditions

Runs were made to determine the trends of NO absorption as a function of temperature, residence time and CHP concentration. Results from these experiments are presented in the Appendix since they were not duplicated and complete material balances were not carried out. The major purpose of these experiments was to determine trends regarding the major variables.

Table 6 Derivation of the scrubbing reaction stoichiometry

Compound	Reactants		Products							Excess moles[1]
	R-OOH	NO	R-OH	R-ONO_2	APO	AMS	HNO_3	O_2	H_2O	
Detected moles	36	4.76	24.0	0.34	1.53	5.56	4.42	N/A	N/A	
Normalization[2]	106	14	70	1	5	16	13	3	104[3,4]	
C balance	953	0	634	9	36	147	0	0	0	127[4]
N balance	0	14	0	1	0	0	13	0	0	0
H balance	1272	0	840	11	40	160	13	0	208	0
O balance	212	14	70	3	5	0	39	6	104	0
Final ratio	106	14	70	1	5	16	13	3	104	

where R-OOH = cumene hydroperoxide
R-OH = cumyl alcohol
R-ONO_2 = cumene nitrate
APO = acetophenone
AMS = α-methylstyrene
N/A = Not analyzed

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[1] The excess moles are obtained by subtracting the total moles of reactants from the total moles of products.

[2] The nomalization step is to divide the numbers in the first row by 0.34 so that the coefficient of R-ONO_2 can be nomalized to 1.

[3] Estimated.

[4] This excess moles of carbon were not found in this study and the total material balance was not 100%.

CHAPTER V

DISCUSSION

1. According to the experiment results, cumene hydroperoxide was stable under the operating conditions (temperature = 100°C, and helium flow rate = 150ml/min) before adding nitric oxide. When nitric oxide was introduced into the solution, a larger than expected consumption of CHP was observed. The CHP to NO ratio in this reaction was 7.47:1. This phenomenon inferred that NO caused a chain decomposition of cumene hydroperoxide. Figure 15 shows the possible scheme of CHP with NO reaction.

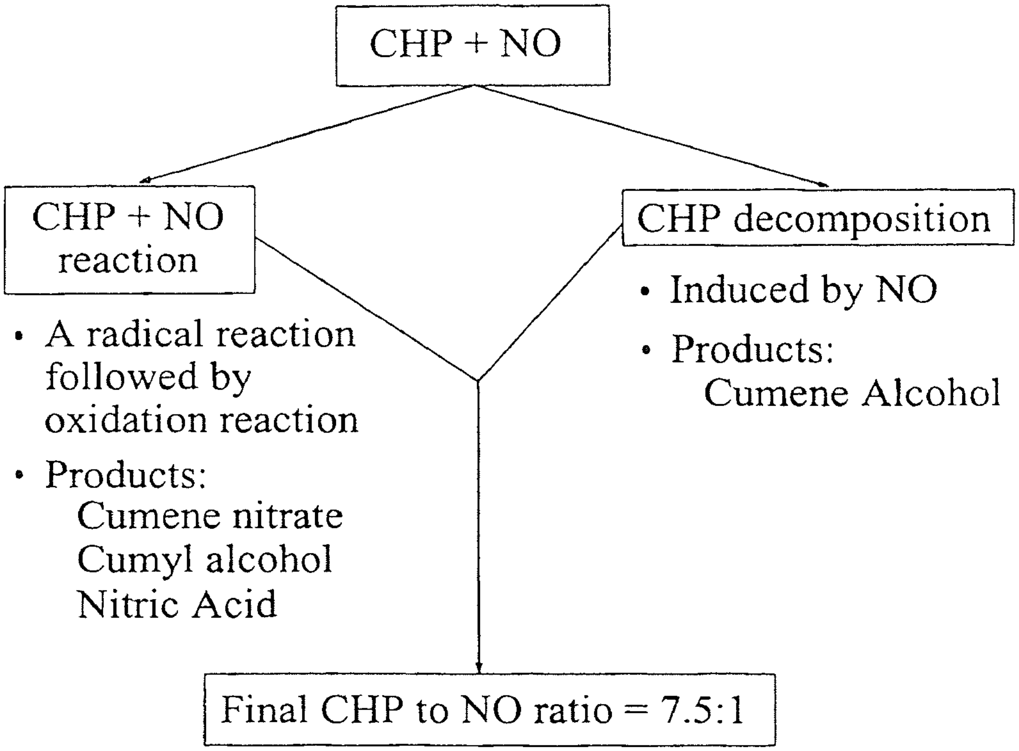

Figure 15 Schematic diagram of cumene hydroperoxide with NO reaction.

2. The result from material balance accounted for the consumption of cumene hydroperoxide. Since cumyl alcohol was the major product from CHP with NO reaction, a possible reaction mechanism was postulated from this result. Shelton and Kopczewski (1967) described that NO with t-butyl hydroperoxide reaction is a free-radical reaction sequence (equation 33-36) induced by nitric oxide:

$$t\text{-BuOOH} + \text{NO} \longrightarrow t\text{-BuO}\cdot + \text{HONO} \qquad (33)$$

$$t\text{-BuO}\cdot + t\text{-BuOOH} \longrightarrow t\text{-BuOH} + t\text{-BuOO}\cdot \qquad (34)$$

$$t\text{-BuOO}\cdot + \text{NO} \longrightarrow [t\text{-BuOONO}]^* \longrightarrow t\text{-BuONO}_2 \qquad (35)$$

$$t\text{-BuOH} + \text{HONO} \longrightarrow t\text{-BuONO} + \text{H}_2\text{O} \qquad (36)$$

The net reaction (equation 37) can be obtained by adding equations (33) through equation (36):

$$2\,t\text{-BuOOH} + 2\,\text{NO} \longrightarrow t\text{-BuONO} + t\text{-BuONO}_2 + \text{H}_2\text{O} \qquad (37)$$

Since our scrubbing reaction has been carried out in presence of excess oxidant, all the nitrogen compounds in the scrubbing solution will reach the maximum oxidation state. Table 7 list four possible oxidation states of the nitrogen compounds:

Table 7 Oxidation states of nitrogen.

Compound	Oxidation number of N
NO	+2
HNO_2, R-ONO	+3
NO_2	+4
HNO_3, R-ONO_2	+5

To account for the major consumption of cumene hydroperoxide, a possible mechanism was proposed to correlate the observed phenomena:

Initiation:

$$\text{R-OOH} \longrightarrow \text{R-O}\cdot + \cdot\text{OH} \qquad (38)$$

$$\text{R-OOH} + \text{NO} \longrightarrow \text{R-O}\cdot + \text{HONO} \qquad (39)$$

Propagation:

$$\text{R-O}\cdot + \text{R-OOH} \longrightarrow \text{R-OH} + \text{R-OO}\cdot \quad (40)$$

$$\text{R-OO}\cdot + \text{NO} \longrightarrow \text{R-O}\cdot + \text{NO}_2 \quad (41)$$

Termination:

$$\text{R-O}\cdot + \text{NO} \longrightarrow \text{R-ONO} \quad (42)$$

$$\text{R-O}\cdot + \text{NO}_2 \longrightarrow \text{R-ONO}_2 \quad (43)$$

$$\text{NO} + \cdot\text{OH} \longrightarrow \text{HONO} \quad (44)$$

$$\text{NO}_2 + \cdot\text{OH} \longrightarrow \text{HONO}_2 \quad (45)$$

$$\text{R-OO}\cdot + \cdot\text{OH} \longrightarrow \text{R-OH} + \text{O}_2 \quad (46)$$

To account for the result that no cumene nitrite nor nitrous acid were found in the NO scrubbing reactions, two global reactions of CHP with cumene nitrite and with HONO were proposed:

$$\text{R-OOH} + \text{R-ONO} \longrightarrow \text{R-OH} + \text{R-ONO}_2 \quad (47)$$

$$\text{R-OOH} + \text{HONO} \longrightarrow \text{R-OH} + \text{HONO}_2 \quad (48)$$

Decomposition of cumene nitrate:

$$\text{R-ONO}_2 \longrightarrow \text{AMS} + \text{HNO}_3 \quad (49)$$

Decomposition of cumyl alcohol:

$$\text{R-OH} \longrightarrow \text{AMS} + \text{H}_2\text{O} \quad (50)$$

where R represents a cumyl group and AMS means α-methylstyrene.

Decomposition of cumene hydroperoxide can be described as a combination of equation (38), (40) and (46), and the net reaction for CHP decomposition can be expressed as equation (51):

$$\text{R-OOH} \longrightarrow \text{R-O}\cdot + \cdot\text{OH} \quad (38)$$

$$\text{R-O}\cdot + \text{R-OOH} \longrightarrow \text{R-OH} + \text{R-OO}\cdot \quad (40)$$

$$\text{R-OO}\cdot + \cdot\text{OH} \longrightarrow \text{R-OH} + \text{O}_2 \quad (46)$$

$$2\text{R-OOH} \longrightarrow 2\text{R-OH} + \text{O}_2 \quad (51)$$

When NO showed up in the scrubbing solution, the amount of R-O· was increased and the decomposition of cumene hydroperoxide was accelerated.

The GC and FTIR analysis showed no nitrogen dioxide present in the flue gas, and the FTIR spectrum of reacted organic scrubbing solution showed no cumene nitrite exists in the solution. These observations lead to two conclusions. First, if NO_2 was produced in the solution, it reacts with the other radicals readily (equation 34 and 36). Second, whenever cumene nitrite was formed in the solution, the excess strong oxidants (CHP) will tend to oxidize them to a higher oxidation state, e.g., cumene nitrate (equation 38).

The amount of cumene nitrate was found to be small in the solution. Combined with the presence of α-methylstyrene, a decomposition of cumene nitrate was proposed (equation 39) as well as decomposition of cumyl alcohol (equation 40).

CHAPTER VI

CONCLUSIONS

Huihong Ao (1991) performed a series of experiments to evaluate the ability of four kinds of tertiary organic hydroperoxide solutions[5] to remove NO from flue gas. According to the conclusions presented in her master's thesis, cumene hydroperoxide exhibits the best ability for nitric oxide removal. This research focused on the study of the cumene hydroperoxide with NO reaction. The thermal stability of cumene hydroperoxide solution was tested first under normal operating conditions (carrier gas flow rate = 150ml/min, solution's temperature = 100°C), then nitric oxide was introduced into the scrubbing solution. The conclusions from this research are listed below:

1. The half life of cumene hydroperoxide was found to be 467 hours at 100°C, which is comparable with manufactures' data ($t_{1/2} > 500$ hours at 120°C). Combined with the commercial unit price from the manufacture (cost = 83 cents/lb), cumene hydroperoxide was found to be the least expensive organic hydroperoxide with the best NO removing ability among the four kinds of tertiary organic hydroperoxides in Huihong Ao's study.

2. It was observed that when temperature is equal or less than room temperature, the NO removing ability of this scrubbing device is almost zero. The "% NO conversion" increased as the organic scrubbing solution's temperature increased. The other operating conditions which can affect the NO conversion are: flow rate of the flue gas (residence time), and concentration of cumene hydroperoxide in the organic scrubbing solution (see

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[5] 3,6-dimethyl-3-octyl hydroperoxide, p-menthane hydroperoxide, piane hydroperoxide and cumene hydroperoxide.

concentration of cumene hydroperoxide in the organic scrubbing solution (see Appendix). NO conversion of 70% was obtained under the following operating conditions:

- Organic scrubbing solution's temperature = 150°C
- Initial concentration of cumene hydroperoxide = 0.53M
- Nitric oxide = 1200ppm (balance = He)
- Flue gas flow rate = 155ml/min

3. Cumene hydroperoxide concentration was checked by iodometric titration during reaction. It was found that 36mmol of cumene hydroperoxide was consumed after 15 hours reaction.

4. Over 99% nitrogen balance was obtained. It indicates the fate of nitrogen can be acconnted for in this scrubbing system. About 59% of nitrogen was retained in the organic scrubbing solution, and was converted to inorganic nitrate and nitrite ions after hydrolysis. About 11% of nitrogen was collected in the aqueous secondary scrubbing solution. The rest of nitrogen did not react and was detected in the exiting gas.

APPENDIX

TRENDS OF NO ABSORPTION AS A FUNCTION OF RESIDENCE TIME, CONCENTRATION, AND TEMPERATURE

Table 8 % NO conversion at different operating conditions of NO scrubbing

Temperature (°C)	Residence Time (sec.)	CHP Concentration (M)	% NO Conversion
90	48	0.1	23.9%
100	48	0.1	42.9%
100	80	0.5	70.0%
110	48	0.1	54.1%
110	48	0.5	68.1%

Table 9 CHP/NO ratio at different operating conditions

Temperature	CHP/NO ratio	
	(Residence time = 48 sec.)	(Residence time = 80 sec.)
110°C	3.63	
100°C	3.30	7.47
90°C	1.87	

Table 8 and Table 9 summarize some important experimental data from nitric oxide scrubbing. Because these data were not double checked in the laboratory, they were not included in the main body of the thesis.

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