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Emission Reduction of Air Pollutants Produced from Chemical Plants

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Abstract

This study identified emission sources and emissions of air pollutants such as volatile organic compounds (VOCs), solvents, and acid gases produced from chemical plants. We collected air samples from various processes, reactors and facilities using VOC detectors and workers' experience. We identified chemical structures and emission concentrations of air pollutants. We analyzed total emissions of air pollutants emitted from the chemical plants.

Also, we developed some emission reduction technologies based on chemical types and emission situations of the identified air pollutants. For reduction of air emissions of acid gases, we employed a method improving solubility of pollutants by reducing scrubber operation temperature, increasing surface area for effective contact of gas and liquid, and modifying or changing chemicals used in the acid scrubbers.

In order to reduce air emissions of both amines and acid gases, which have had different emission sources each other but treated by one scrubber, we first could separate gas components. And then different control techniques based on components of pollutants were applied to the emission sources. That is, we first applied condensation and then acid scrubbing method using H_2SO_4 solution for amine treatment. However, we only used an acid scrubbing method using H_2O and NaOH solution for acid gas treatment. In order to reduce air emissions of solvents such as dimethylformamide and toluene, we applied condensation and activated carbon adsorption. In order to reduce air emissions of mixture gases containing acid gases and solvents, which could not be separated in the processes, we employed a combination of various air pollution control devices. That is, the mixture gases were passed into the first condenser, the acid scrubber, the second condenser, and the activated carbon adsorption tower in sequence. In addition, for improvement of condensation efficiency of VOCs, we changed the type of the condensers attached in the reactors as a control device modification.

Finally, we could successfully reduce air emissions of pollutants produced from various chemical processes or facilities by use of proper control methods according to the types and specific emission situations of pollutants.

1. INTRODUCTION

There are many sources producing air pollutants, such as criteria pollutants, volatile organic compounds (VOCs), and hazardous air pollutants (HAPs) in the industrial areas (Lee and Cho, 1999a, Spicer *et al.*, 1996). These air pollutants emitted from the industrial complex often have been transported into urbanized areas. Thus the transported air pollutants degrade an air quality of the urbanized areas which were located near the industrial complex (Seiber, 1996). Especially, chemical plants have been one of important emission sources of air pollutants founded in the industrial complex and the urbanized areas. Actually, a lot of air pollutants, which mainly consist of acid gases, amines, solvents, and VOCs and HAPs, are produced from complex chemical plants (Lee *et al.*, 1997). Therefore, many people who live near chemical plants or industrial complaints have complained about air pollutants from various chemical processes. Because of this kind of complaints and the strict regulations concerning chemical plants or emission sources, many chemical plants have been forced to reduce emissions of the pollutants (Lee and Cho. 1999b). However, most of chemical plants have various production facilities or processes which generate complex emission situations. Therefore, a simple air pollution control (APC) method without careful consideration on emission situation is not enough to solve the problems concerning air emission reduction they have faced (Lee *et al.*, 1998).

In order to reduce emissions of pollutants from the chemical plants, we tried to apply various air pollution control techniques based on the materials or emission situations of pollutants (Buonicore, 1992). In this study we first measured emission concentrations of air pollutants including HAPs and VOCs produced from chemical processes and facilities. Then we evaluated emission situations and decided effective air pollution control (APC) methods. The applied APC methods included rearrangement of previously installed APC devices, addition of new APC facilities, component separation, and application of proper control tech-niques based on components, amounts emitted and emission situations, etc. Also, one of purpose of this study is to improve the urban air quality of the residential areas located near chemical plants or complex through emission reduction of air pollutants in the chemical plants (Seiber, 1996; Spicer, 1996).

2. MATERIALS AND METHODS

2. 1 Sampling and Analysis

Air samples were taken from various chemical processes and reactors and facilities, which might be emission sources, according to the recommendation of workers in the chemical plants. Air samples of VOCs and HAPs were collected at the places which had produced a lot of 1) acid gases such as HCl, H_2SO_4 and SOx, 2) amines such as methylmetha amine and methylethanol amine, 3) solvents such as dimethylformamide, toluene and xylene in the dye and agricultural chemical plants (Ruddy and Carroll, 1993). In order to find some processes and facilities which might be emitting air pollutants, we used N, S-detectors for an easy detection of compounds containing N and/or S and also used a Photo Ionization Detector (PID) for a detection of VOCs or some chlorine compounds. Detector tube methods were also applied for a prescreening of few compounds expected as high emission concentrations. Sampling and analysis concerning acids and amines were performed according to the guidelines by the KDE (Korea Department of Environment) regulations (KDE, 1996). For air samplings of VOCs, amines and solvents, a personal air sampling pumps (Gillian Low and High Flow Pump) with a flow rate of 1 l/min and Tedlar air bags (Supelco, Co. Ltd., 10 *l*) were used (Bradeley, 1995). For analysis of collected air samples, gas chromatography (GC) with a sample concentrator (Aero Trap DS-5000) and a mass sensitive detector (MSD, HP 5971A MSD) was employeed.

2. 2 Methods for Emission Reduction

Analyzed pollutants were properly categorized according to their physical and chemical characteristics and emission concentrations. The air pollution control (APC) devices, which were previously operated, were properly rearranged in the emission processes or facilities. Sometimes, separation of components as the first step was conducted, and then APC techniques and devices suitable for disposal of the components were newly combined or added according to the emission situations (Lee *et al.*, 1998, 1997). Concentrations of air pollutants taken at the inlet and the outlet of the APC devices or techniques were analyzed by gas chromatography and were compared to the previous emission concentrations of those pollutants. Then the removal efficiencies of the new APC systems were evaluat-

Table 1. Emissions of VOCs produced from the chemical plants.

Emission Source	Emission Concentration (mg/m³ · hr)	Total Emissions (kg/year)	Relative Emissions (%)
Dye Plant 1	19.62	0.0014	0.44
Dye Plant 2	382.50	0.0268	8.62
Agricul. Chem. (Raw Material)	1,181.40	0.0828	26.62
Agricul. Chem. (Intermediates)	473.16	0.0332	10.66
Epoxy Plant	623.22	0.0437	14.04
Fluorescent Whiten. (F.W.F.)	49.01	0.0034	1.10
Wastewater Disposal (W.D.P.)	1,710.12	0.1198	38.52
Total	4,439.00	0.3111	100.00

ed. We also employed pollution prevention concepts, such as change to more effective condenser type, for emission reduction of air pollutants to the chemical plants.

3. RESULTS AND DISCUSSION

3. 1 Source Identification and Emission Estimation of VOCs

Table 1 shows emissions of VOCs identified from various chemical plants and wastewater disposal plants. The total emissions of VOCs emitted from each plant were obtained by adding identified concentrations of VOCs emitted from all processes operating in the plant. Figs. 1, 2, 3, and 4 show the relative emission sources of the VOCs according to the chemical structure of the VOCs classified as aliphatic hydrocarbons (HCs), aromatic HCs, chlorinated HCs, and other miscellaneous HCs. From these figures we can evaluate the relative emissions and types of the VOCs produced at each emission place. While major emission sources of aliphatic HCs were the agricultural chemical plants, major emission sources of aromatic HCs were the wastewater disposal plants and the epoxy plant. Most of chlorinated HCs and other miscellaneous HCs emitted were produced from the wastewater disposal plants and the agricultural chemical plants. Table 1 and Figs. 1, 2, 3, and 4 also show that more than 75% of the total VOCs emitted from the chemical plants concerned were produced from the wastewater disposal plants and the agricultural chemical plants. Therefore, for emission reduction of the VOCs emitted from the chemical plants, proper APC technologies or devices should be apparently first applied in the wastewater disposal plants and the agricultural chemical plants. However, it is very difficult to say that this concept, first application of APC technologies or devices at the places which have a large amounts of emissions, can be always a reasonable choice. This is because emissions of VOCs produced from epoxy plant and dye plant are almost one fourth of the total VOCs emis-

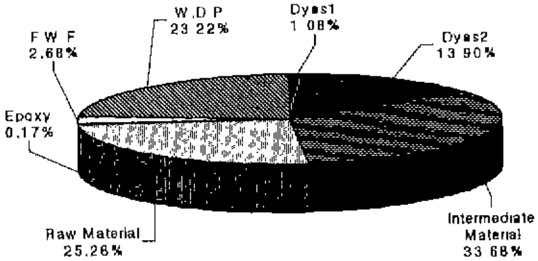


Fig. 1. Relative Emissions of Aliphatic Hydrocarbons.

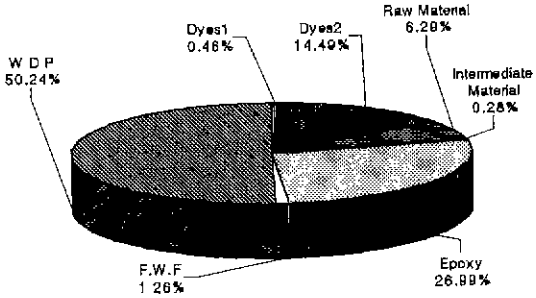


Fig. 2. Relative Emissions of Aromatic Hydrocarbons.

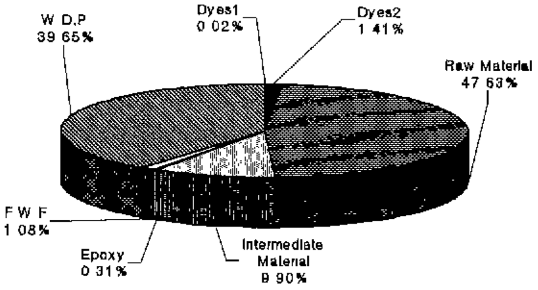


Fig. 3. Relative Emissions of Chlorinated Hydrocarbons.

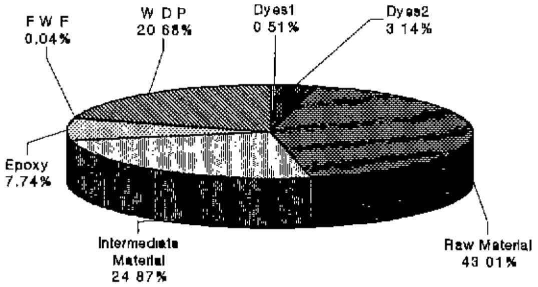


Fig. 4. Relative Emissions of other miscellaneous Hydrocarbons.

sions produced from the chemical plants. In addition, while the VOCs emitted from the wastewater disposal plants and the agricultural chemical plants consisted of a lot of chemical components, the VOCs emitted from epoxy plant and dye plant consisted of simple chemical components such as toluene and heptanes. As a management problems concerning effective plant operation, it should be decided investment priority for APC among various plants at given economy conditions. As a matter of fact, a simultaneous consideration including application feasibility of APC technologies or devices, emission concentrations and situations, and type of pollutants should be required.

3. 2 Acid Gases

Most of acid gases produced from various reaction processes of the chemical plants were identified as HCl, H_2SO_4, and SOx. However, sometimes. removal of acid gases by the previous wet scrubbing was not enough to satisfy the emission standards. In order to reduce emissions of acid gases, we first used acid gases at the lowest concentrations possible. That is, we maintained the least amounts of acid gases using in the processes or reactors to prevent emissions of the acid gases remained after reactions. Through this minimum quantity method we can reduce emissions of acid gases in the chemical processes or reactors.

Then we tried to improve a control efficiency of the APC system (wet scrubber), which was previously operated, for a better removal of acid gases. By lowering the scrubbing temperature in the wet scrubbers with a cooler, we could also improve solubility (or absorption) of HCl and H_2SO_4 in absorbing medium and thus reduce emissions of acid gases from the processes or the APC systems. We could also improve absorption efficiency of acid gases through improving a contact ratio of gases and liquids. That is, it was possible to improve surface areas for absorption by use of smaller size fillers and thus reduce dead surface areas for absorption in the wet scrubbers. Fig. 5 shows highly improved removal effects of acid gases by reducing temperature and increasing surface areas for absorption.

However, we sometimes meet a very complex emission situations which include process related acid gases and amines. In this case, we could not get sufficient removal efficiencies for both pollutants compared with the previous disposal method, which used only a single acid scrubbing method without a component separation of amines and acid gases. Therefore, for simultaneous disposal of the mixture including acid gases and amines, we first separated the components and then applied different disposal techniques based on components (see Fig. 6). That is, we applied condensation and adsorption methods for disposal of separated amines and applied acid scrubbing techniques using a different absorbing medium in the first and the second acid scrubbers for disposal of acid gases. Through separating components of pollutants in the proper process and

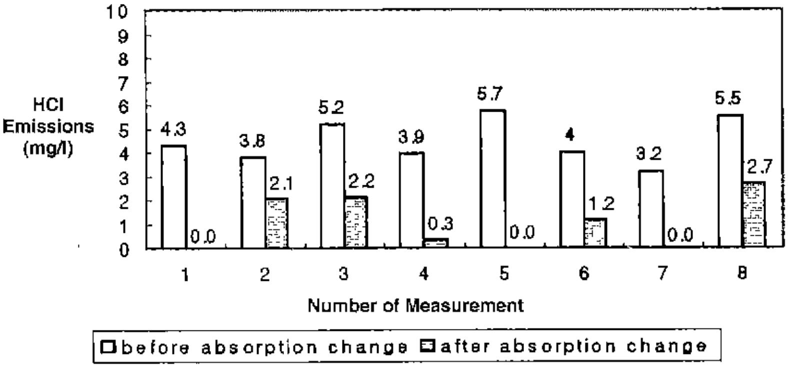


Fig. 5. Disposal of the HCl gas through a change of absorption processes.

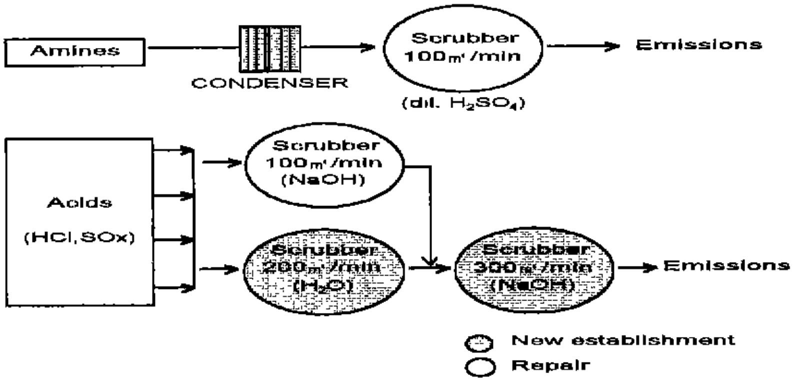


Fig. 6. New disposal of the gases by separation of components in the dye plant.

then applying proper disposal techniques suitable for each pollutant, we could get much more improved removal efficiencies of process acid gases and amines.

3. 3 Amine Gases and Vapors

Only an acid scrubbing was previously operated as disposal system for removal of amine gases and vapors from the dye plant 1. However, the removal efficiencies of amines in the scrubber were not good. This is due to the high concentrations of amines entering into the inlet of the scrubber. Therefore, we added a condenser before the scrubber in the previous APC system, and the condenser was added in order to remove effectively amines before high concentrations of amines were loaded into the scrubber system. Thus we could identify that most of amines produced from the emission facilities were removed in the added condensation step with high removal efficiencies (see Fig. 7). Through condensing high concentrations of amines we could solve problems concerning high emissions of amines from the plant.

3. 4 Solvent Vapors

The previous removal system of solvents produced from the dye plant 2 was only an adsorption tower using activated carbon as an adsorbent. However, removal of solvents was not enough to satisfy the emission standards and the operating costs concerning the control system of solvents emitted were also pretty expensive. Therefore, we added a condensation step

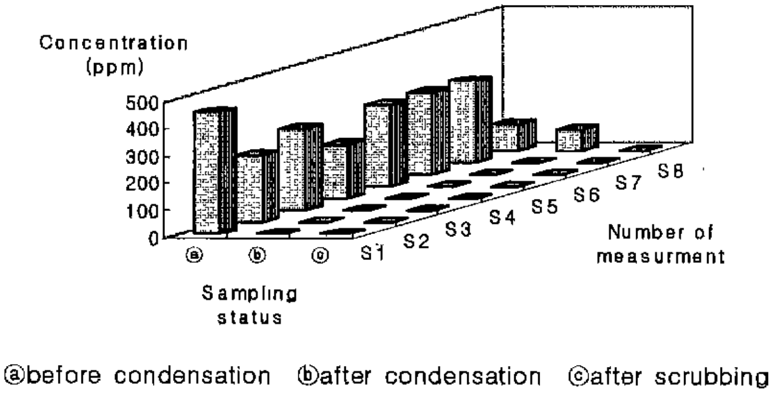


Fig. 7. Disposal of amine gases using condensation and wet scrubbing.

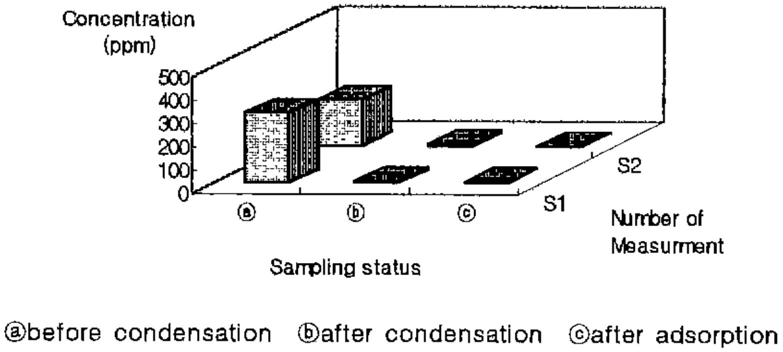
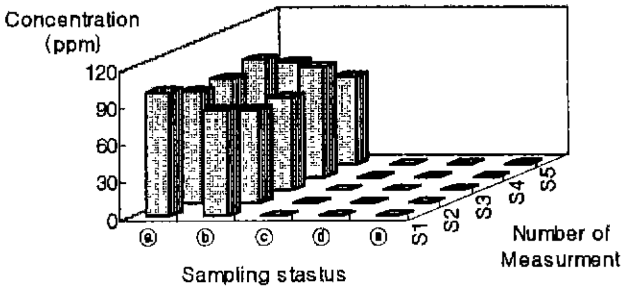


Fig. 8. Disposal of DMF using condensation and A/C adsorption.

before the adsorption step, and the condenser was added in order to remove effectively solvents before high concentrations of solvents were loaded into the adsorption tower. We could realize that most of dimethylformamide (DMF) and toluene produced from the dye plant 2 were removed by the condensation step (see Fig. 8). Thus we could also save operating and disposal costs by reducing load of pollutants into the adsorption tower.

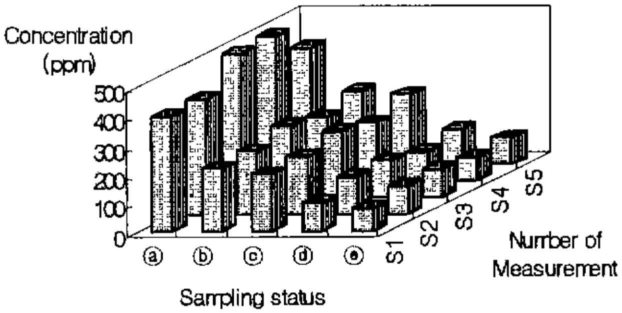
3. 5 Mixed Air Pollutants

Sometimes, it was unable to separate components of mixed pollutants. That is, we faced complex situation which should be simultaneously reduced emissions of both acid gases and solvent vapors which are very difficult to separate them. In order to find a new effective emission reduction system suitable for this situation, we built a new complex pollution control system as follows: both acid gases and solvent vapors simultaneously were passed through the first condenser, an acid scrubber, the second condense, and the adsorption tower in sequence. A large amounts of solvent vapors were condensed in the first condenser. Most of acid gases were removed by acid scrubbing. Fig. 9 shows that most of acid gases emitted, e.g. SOx, were removed at the acid scrubbing step of the total control sequence. In the second condenser, the remained solvent vapors were removed by recondensation. The final control step was to remove the still remained solvents by passing through the adsorption tower located at the



ⓐbefore 1st condensation ⓑafter 1st condensation ⓒafter scrubbing
ⓓafter 2nd condensation ⓔafter adsorption

Fig. 9. Disposal of SOx at the different sampling status without component separation.



ⓐbefore 1st condensation ⓑafter 1st condensation ⓒafter scrubbing
ⓓafter 2nd condensation ⓔafter adsorption

Fig. 10. Disposal of Xylene at the different sampling status without component separation.

last point of the control sequence. Fig. 10 also shows that a large amounts of solvents such as xylene and methanol were removed at the two condensation steps. However, the total condensation or control efficiencies of the VOCs was relatively lower than efficiencies in a single control system. This is because a lot of pollutants were included in the pollutant mixture. Also, since the removal of mixed pollutants could be affected by complex removal environment which might be less-effective conditions compared with removal environment of single component, the total control efficiencies of the mixed air pollutants probably decreased.

3. 6 Pollution Prevention and Condensation Improvement

Chemical plants have many reactors for desired chemical reactions A lot of reaction raw materials, intermediates, products, byproducts, or solvents could be emitted from the reactors or production facilities. High concentrations of pollutants emitted from various processes entered the APC system in the chemical plants and thus generated many difficulties in effective operation of the system. In order to reduce the total emissions of pollutants at the sources and the loading of pollutants into the APC devices, we introduced a concept of pollution prevention That is, a basic idea applied for pollution prevention was to add a condenser nearby the reactors to reduce pollutant loading into the APC devices (see Fig. 11). That idea was very effective. Thus loading amounts of pollutants were much more decreased and could prevent air emissions in the chemical plants.

It was also possible to improve condensation efficiencies by changing a type of condensers. Table 2 showed various characteristics of condensation efficiencies, operation costs, and maintenance of each type of condenser. From the table 2, we could identify that the Teflon lined plate type has much better characteristics than the G/L vertical type in all the characteristics compared. Table 3 also shows an example of another pollution prevention (air emission reduction) of methylene chloride and toluene by using better condenser type.

By introducing a pollution prevention concept and/or changing into the effective condenser type, we could also obtain economic benefits (by selling or reusing the solvents recovered). In addition, we could get the following non-economic benefits by using effective type of condenser: 1) reduction of process cycling time by decreasing distillation time, 2) reduction of loads into the APC devices for VOCs and HAPs, 3) an easy

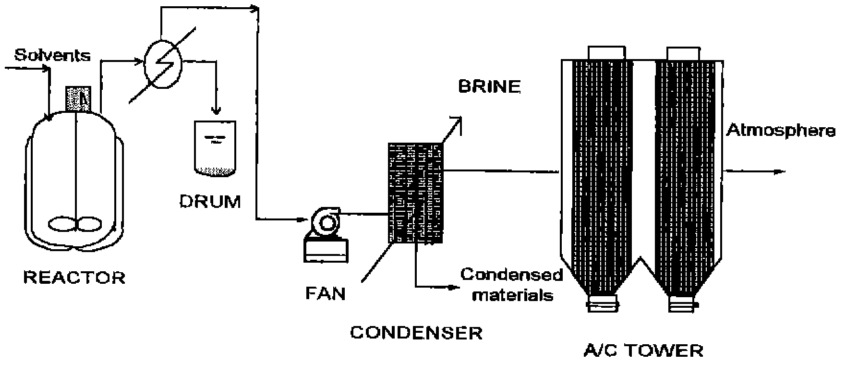


Fig. 11. Schematic diagram for disposal of solvents in the reactor system with condenser.

Table 2. Comparison of characteristics of the the condenser type.

Type	Plate	Shell & Tube	G/L Vertical
Material	Sus316+Teflon Lined	Sus 304	CS+G/L
Condensation Efficiency (based on MDC)	92%	80%	61%
Costs for establishment	14,000 US$	25,000 US$	19,000 US$
Uses	Acids, Bases, Neutrals	Bases, Neutrals	Acids, Neutrals
Maintenance	Very Easy	Difficult	Difficult

Table 3. Improvement of recovery of MDC and toluene through changing a condenser type.

Condenser	Chemicals	Solvents Used (*l*)	Recovery after Distillation (*l*)	Amounts of Loss (*l*)	Condensation Efficiency (%)
Previous	MDC*	1,200	730	470	61
(G/L Vertical)	Toluene	2,000	1,600	400	80
Current	MDC	1,200	1,100	100	92
(Teflon Lined)	Toluene	2,000	1,900	100	95

* MDC stands for methylene chloride (B.P =40.2°C, Specific gravity=1.30)
Toluene (B P =110 7°C, Specific gravity=0.87).

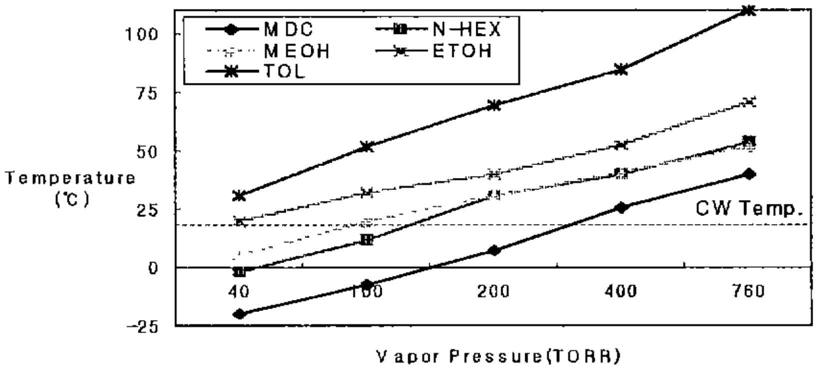


Fig. 12. Vapor pressure of solvents as a function of temperature.

application for further investment by identifying condensation efficiencies.

It was also necessary to consider the following experiences in setting up the condenser for better condensation of solvents: 1) In the simple distillation, the condensation efficiencies could be improved by increasing the capacity of the condenser. 2) In the vacuum distillation, however, it was required to use different coolants depending upon vapor pressure of solvents (boiling point of materials at the given pressure). That is, if the boiling points are higher than the temperature of a cooling water at the given pressure, the cooling water can be used as a coolant. However, if the boiling points are lower than the temperature of the cooling water at the given pressure, the low-temperature coolant (e.g., brine solution) should be used as a coolant (see Fig. 12).

4. CONCLUSIONS

On the study of emission reduction of air pollutants from the chemical plants, we could get the following conclusions:

First, we identified and categorized air pollutants produced from the chemical plants. Air pollutants identified in the chemical plants were mainly composed of acid gases, amine vapors and gases, solvent vapors, and mixtures including acid gases and solvent vapors. We could apply for proper air pollution control (APC) techniques or devices based on components and emission situations.

To reduce emissions of air pollutants, previously operated APC devices were rearranged and combined, and sometimes new APC techniques were added into the pollution control system. Also, by reducing the temperature and increasing surface areas for absorption and increasing contacts between gases and liquids, we could improve solubility of acid gases in the absorbing medium during operation of acid scrubbers. By introducing a concept of pollution prevention or changing into the effective condenser type, we could improve a condensation efficiency of solvents and save operating costs of the APC systems.

Finally, we could get better removal efficiencies of air pollutants from the chemical plants by optimizing the previously operated APC devices. In addition, we could also improve much more the air quality in the urbanized areas which were located nearby the chemical plants.

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