Recovery of Gasoline Vapor by a Combined Process of Two-Stage Dehumidification and Condensation

Je-Lueng Shie^[1], Chen-Yu Lu^[2], Ching-Yuan Chang^[3]

Graduate Institute of Environmental Engineering, National Taiwan University Taipai, Taiwan 106, R.O.C.

Chun-Yu Chiu^[4]

Department of Environmental Engineering, Lan-Yang College of Technology I-Lan, Taiwan 261, R.O.C.

Duu-Jong Lee^[5]

Department of Chemical Engineering, National Taiwan University Taipei, Taiwan 106, R.O.C.

Shi-Ping Liu^[6]

Department of Public Health, Fu-Jen Catholic University Hsien-Chuan, Taipei, Taiwan 242, R.O.C.

Chang-Tong Chang^[7]

Department of Environmental Engineering, National I-Lan University I-Lan, Taiwan 260, R.O.C.

Abstract—The emission of gasoline vapor containing volatile organic compounds (VOCs) from gasoline service stations is becoming a significant environmental problem especially for the population densed area. A combined process of two-stage dehumidification and condensation (TSDC) is proposed as a method of recovery of VOCs from the emitted gasoline vapor. A two-stage dehumidification procedure, consisting of using a first-stage dehumidifier (at 4°C with removal efficiency of water of vapor, R_{wi} of about 67 wt%) and a second-stage adsorber (enhancing the R_{wi} to about 95 wt%), can be employed to remove most of water of vapor thus avoiding the possible icing problem for the subsequent condensation. Salable liquid gasoline can then be recovered by operating the condenser at the desired low temperature T_c depending on the emission and/or reduction regulation of VOCs. Aspen-plus, a software package for thermodynamic computation developed by Aspen Technology Inc., is used to simulate the condensation removal or recovery efficiencies of condenser (R_c , based on the inlet gasoline vapor entering the condenser) of VOCs at various T_c . The simulation results indicate that the values of R_c are about 73, 85, and 90 wt% at T_c of -40, -60, and -73°C, respectively. Thus, the operation of condenser at T_c of -60°C would meet the non-destructive reduction of VOCs at 85 wt% level. However, should the stringent regulation on the oil storage tank of chemical plant be applied to the gasoline service station, then the condenser operated at T_c of -60°C would have to recycle part of the outlet vapor from the condenser back into the undergrounded gasoline tank. This is to ensure that the emission of VOCs is less than 35 mg for refueling 1 L gasoline into the fuel tank of vehicle.

Key Words : Gasoline vapor, Dehumidification, Condensation

- [6] 劉希平
- [7] 張章堂

^[1] 謝哲隆

^[2] 呂辰宇

^[3] 張慶源, To whom all correspondence should be addressed

^[4] 邱浚佑

^[5] 李篤中

INTRODUCTION

Problem statement

The gasoline is a blend of varying quantities of paraffins, olefins, naphthenes and aromatics compounds. Its composition may vary from different refinery companies, geographical production sources and weather temperature conditions. Some components of HCs may not be easily identified. Due to the increasing demand of automobiles and motorcycles, the gasoline service stations are also increasing. Thus, the emission of gasoline vapor containing volatile organic compounds (VOCs) from gasoline service stations is becoming a significant environmental problem especially for the population densed area. The major sources of hydrocarbon emissions, if uncontrolled, are gasoline service stations and contribute about 66.2% stationary pollution source of hydrocarbons in Taipei, Taiwan (Jeng, 1987). The main evaporative emissions in gasoline service stations are characterized as (1) refueling loss; (2) loading loss from gasoline; (3) diesel fuel tanker trucks; and (4) breathing loss of the storage tank vents (Wark et al., 1998). In Taiwan, there are more than 2,253 gasoline service stations until 2002; the emissions of VOCs are more than 30,000 tons per year if uncontrolled. The major pollutants are benzene, ethylbenzene, toluene and xylene that are harmful to health and become the precursors of ozone. The Taiwan Environmental Protection Administration (TWEPA) supports more than 1,819 gasoline service stations to make up the control system facilities and reach about 81% until 2002 (TWEPA, 2002).

Current VOC control methods at gasoline service stations and gaseous wastes

Controls of emission of gasoline vapor from gasoline service stations are generally accomplished by using technologies referred to as Phases I and II. The facilities of Phase I control system capture the vapors that are emitted from gasoline storage tanks at local gasoline service stations when the underground storage tanks are refilled with gasoline by tanker trucks. The control system displaces the vapors by venting them back into the tanker trucks as its gasoline is displaced, often referred to as vapor balance method. The vapors are then transported back to the central treatment facility (commonly at refinery plant) when the tanker trucks are refilled with gasoline by using the similar control technique. Phase II control system facilities displace the vapors that are captured from the vehicle fuel tank during refueling. The vapors are back to the storage tank (referred to as vapor balance method) or pumped to the central treatment facilities (at the local gasoline service station) and storage tank (referred to as pumping support method).

For the vapor balance method, the automobile is filled with nozzle that consists of two concentric hoses and typically fitted with a soft gasket that effectively seals the vehicle's fuel tank opening when the nozzle is in place. As one hose fills the tank, the second hose, operating under a slight vacuum induced from the gasoline pumped from the supply tank, ducts the vapors back to the storage tank. The nozzles of the pumping support method have no soft gasket and the vapors are pumped back to the storage tank and the central treatment facilities. The volume of pumping back vapors using the pumping support method is in excess of the supply gasoline $(1.4 \sim 2.5)$ times), so there must have a central treatment facility to dispose the excessive vapors. Overall efficiency of VOCs captures ranges for pumping back vapors by pumping support method are from 88 to 92% (USEPA, 1996). The current central treatment facilities in Taiwan are direct incinerators (burners). The advantages of direct incinerator are: (1) lower emissions of VOCs concentration; (2) automation without workers; (3) mature and commercial technology. It burns the resources of gasoline vapors and has higher fire risk than other devices, especially when the gasoline service stations are located at the population densed area.

There are several techniques for recovering or disposing VOCs from gaseous wastes. In the industry, the commonly used techniques for recovering VOCs are adsorption (Yang, 1987; Benitez, 1993; Tsai et al., 1998, 1999), absorption (Cooper and Alley, 1994), condensation (Dunn and El-Halwagi, 1994; Nevers, 1995) and membranes separation (Moritaka, 1989; Ohlrogge, 1990; Deng, 1995). The four techniques can be used alone or combined with each other for further improvement of VOCs capture efficiency or for the goal of VOCs recovery. Crabtree et al. (1998) designed optimal hybrid systems that involved gas permeation membranes and vapor condensation systems. It was demonstrated that hybrid membrane/condensation systems possess advantages over either separation technique alone. For the streams with high humidity, components will react with carbon or are susceptible to polymerization or decomposition reactions at carbon desorption temperatures. On high humidity conditions, activated carbons are not feasible to the adsorption of VOCs and this may dictate the use of other adsorbents (Danielsson and Hudon, 1994). Also, the high humidity conditions would cause some problems on the membranes technology because water may permeate the membrane. For example, Deng (1995) studied the effect of the presence of water in the feed stream on the separation of hydrocarbon vapors from nitrogen and the separation of gasoline vapor by using an asymmetric aromatic poly (ether imide) membrane. It was found that the permeability of water is far greater than hydrocarbon vapors (Deng, 1995).

Je-Lueng Shie, Chen-Yu Lu, Ching-Yuan Chang, Chun-Yu Chiu, Duu-Jong Lee, Shi-Ping Liu, and Chang-Tong Chang: 607 Recovery of Gasoline Vapor by a Combined Process of Two-Stage Dehumidification and Condensation 607

On the other hand, the common VOCcondensation system consists of dehumidification, heat integration and VOCs condensation. El-Halwagi and Manousiouthakis (1990) addressed that the dehumidification controls the gaseous waste to a temperature that is slightly above the freezing temperature of water at which almost all the water vapor in the gaseous waste is condensed. However, the removal efficiencies of water at temperatures slightly above the freezing temperature of water are about 73.54 wt% at 1°C and 67 wt% at 4°C as estimated from the Aspen-Plus simulation. If the temperature is controlled at 4°C, the unremoved water is still as high as 33 wt%. The icing problems in the condensation system will also occur. In order to reduce the above disadvantages, a two-stage dehumidification with low cost dehumidifier and adsorption drier is thus employed in this study to minimize the water content of the gasoline vapor. Post-condensation is then followed to achieve the ultimate recovery of VOCs from the gasoline vapor.

Current VOC emission regulations and standards

The recently approved European Community stage 1 directive for gasoline emissions has established an emission limit of 35 g total organic compounds (TOCs) per cubic meter gasoline loaded (35 g TOC emitted/m³ gasoline loaded) for gasoline storage and distribution facilities. However, the emission limit of the United States Environmental Protection Agency (USEPA) Standard has been set as 10 mg TOC per liter of gasoline loaded (10 g TOC emitted/m³ gasoline loaded). The German TA-Luft standard, the most stringent known gasoline emission regulation, is 150 mg TOC (excluding methane) per cubic meter of loaded product (0.15 g TOC emitted/m' gasoline loaded). In Taiwan, the regulations on the gasoline storage and distribution facilities permit a non-destructive recovery efficiency of 85 wt% or less than 300 ppm (TWEPA, 1999). In the gasoline service stations, the standards of California regulations requested that the gasoline vapor recovery systems must be authenticated by California Environmental Protection Agency Air Resource Board (CARB, 1994) and the vapor gas pulled back efficiency must be higher than 95 wt% by 1990. As a result of the CAAAs (Clean Air Act Amendments) of 1990, all areas that were designated as moderate (or great) non-attainment areas were required to install the gasoline vapor recovery systems (Phase II controls) to reduce VOC emissions.

RESULTS AND DISSCUSSION

Composition of gasoline vapor

The vapor evolved from the fuel tank of vehicles

contains a mixture of hydrocarbons. Hydrocarbon concentration at the opening of the vehicle fuel tank is about 30 vol% in air. The reason of such a high concentration is because of the splash of refueling fuel from the nozzle (USEPA, 1996). The evolved hydrocarbon vapor being pumped back is transported along the pipelines. Part of it would be condensed during transport and is collected in a U type pipe. When the condensate liquid is overspill, it would flow to the storage tank of gasoline. From this reason, one may assume that the gasoline in the pipelines is static balance and the emission vapor gases are equilibrium with the gasoline. Thus, for the purposes of simulation, the concentrations of VOCs vapors balanced with gasoline of the feed stream are listed in Table 1. Table 1 indicates the analytical results of the static balance vapor gas of gasoline (95 unlead gasoline) at 27.3°C. The analytic equipment are GC-FID, GC-TCD and humidity meter. From Table 1, the total hydrocarbon concentration is 11.29 vol% and the major organic compounds are C₆ and C₄. The humidity is 2.34 vol%. There is no reports concerned with the feasibility of condensation technology combining with the drier and pressure swing adsorption for dehumidification on the gasoline service stations. The aim of this work is to examine the feasibility of condensation technology for the use in the gasoline service stations. A combined two-stage dehumidification and condensation (TSDC) process is proposed and studied.

Combined two-stage dehumidification and condensation system

In the gasoline service station, the pumping support methods of Phase II controls need a central treatment facility for further reduction or recovery of VOCs because the volume of pumping back vapors exceeds that of the refueling gasoline. This study proposes a combined process of two-stage dehumidification and condensation as a method for the central treatment facilities. The combined process first removes the humidity of gasoline vapors by the two-stage dehumidification and then recovers the VOC vapors by the subsequent condensation. Figure 1 illustrates the flow diagram of system of combined process of two-stage dehumidification and condensation.

The first-stage dehumidification unit consists of a compressor, a storage tank and a pre-dehumidification drier. In gasoline service station, the flow rate is not stable. The peak flow rate appears at heavy traffic period while the minimum flow rate is zero. For solving the unstable flow rate problem, one needs a compressor and a storage tank to stabilize the flow rate needed for the proper treatment. After the pressure of the storage tank reaching the set point,

| Item | Compound | Conc. (μg/L) C _{mv} at 27.3°C ^b | Vol. in 1 L at 27.3°C (L) | Concentration (vol%) |
|------|--|--|------------------------------|-------------------------|
| 1 | benzene, C_6H_6 | 45,074.05 | 0.0142375 | 1.4238 |
| 2 | toluene, C ₇ H ₈ | 21,249.77 | 0.0056907 | 0.5691 |
| 3 | ethylbenzene, C ₈ H ₁₀ | 1,127.32 | 0.0002620 | 0.0262 |
| 4 | xylene, C_8H_{10} | 6,247.22 | 0.0014521 | 0.1452 |
| 5 | methane, CH_4 | ND ^c | ND | ND |
| 6 | ethane, C_2H_6 | ND | ND | ND |
| 7 | propane, C_3H_8 | 34,991.19 | 0.0195933 | 1.9593 |
| 8 | butane, C_4H_{10} | 57,946.52 | 0.0246150 | 2.4615 |
| 9 | pentane, C_5H_{12} | 39,198.92 | 0.0134135 | 1.3414 |
| 10 | hexene, C_6H_{12} | 4,009.05 | 0.0011759 | 0.1176 |
| 11 | hexane, C_6H_{14} | 96,638.90 | 0.0276856 | 2.7686 |
| 12 | heptane, C_7H_{16} | 19,305.58 | 0.0047565 | 0.4757 |
| 13 | octane, C_8H_{18} | 128.51 | 0.0000278 | 0.0028 |
| 14 | nonane, C_9H_{20} | 9.70 | 0.0000019 | 0.0002 |
| 15 | sum of items 1 to 14 | 325,926.75 | 0.1129116 | 11.2912 |
| 16 | H_2O | 17,074.5 | 0.02337 | 2.337 |
| 17 | N_2 | 775,411.86 | 0.6823375 | 68.2338 |
| 18 | O_2 | 235,568.16 | 0.1813809 | 18.1381 |
| 19 | sum of items 15 to 19 | 1,353,981.27 | 1.00000 | 100 |

Table 1. Composition of vapor above 95 unleaded gasoline (with correction of mass balance)^a.

^a Composition of vapor above gasoline at 27.3°C.

^b Concentration of mass per volume (C_{mv}) based on 27.3°C.

^c Not detected (< $0.32 \mu g/L$).



Fig. 1. System of combined process of two-stage dehumidification and condensation (TSDC).

an auto-valve would open to turn on the process. The second-stage dehumidification unit employs a pressure swing adsorption (PSA) for the removal of water vapor. Two or more adsorption beds may be used to further reduce the humidity of stream from the first-stage drier continuously. Part of the stream that is further dehumidified from the adsorption tank (compressed pressure) is recycled (about 1/11) back

to the desorption tank (released pressure) and then to the first-stage drier. Adsorption and regeneration occur at the same time but at different columns of PSA system. The adsorption column is under the compressed pressure and the regeneration column is under the released pressure. The regeneration rate is far faster than the adsorption rate. Due to the regeneration rate is higher than that of adsorption rate, the

regeneration flow rate is only about 1/11 of the adsorption flow rate. The recycled gas is operated on no-heat desorption conditions because the released pressure would help to desorb the water on the adsorbents. The proper adsorbents for adsorption dehumidification are silica gel, active alumina and molecular sieve (Suzuki et al., 1985; Suzuki, 1990). Finally, the unrecycled stream that is dehumidified from the adsorption drier can be condensed at considerable low temperatures by a high efficiency condenser. The Dow Chemical Company has applied a patented SORBATHENE Solvent Vapor Recovery Unit technique for the recovery of VOCs (Pezolt et al., 1997). The apparatus of this patent uses a well-known pressure swing adsorption process (Suzuki, 1990) for VOC recovery that is similar to the second-stage dehumidification for the water removal of present study. However, the heat of adsorption or desorption of VOC within the SORBATHENE unit might cause a temperature rise within the beds. The adsorption or desorption pressures compressed or released operated in the flammable beds of VOC would have to consider the safety and reactivity problems, especially at the gasoline service stations. Without compression, the condenser must be operated at temperature well below 0°C in order to condense the light hydrocarbons. Due to the presence of high humidity in the stream from the desorption unit of SORBATHENE, operating at temperature below 0°C can result in the formation of ice within the condenser. In the combined process proposed in this study, the two-stage dehumidification employs a pre-dehumidifier operated at about 4°C to remove most of water vapor and an adsorption drier to further reduce the water content with recycled stream passing through the desorber and returning back to the pre-dehumidifier. The VOC-laden stream containing only insignificant or negligible amount of water vapor is then condensed to recover the VOCs. The proposed combined process may thus overcome the disadvantages of SORBATHENE in recovering the VOCs from the gasoline service stations.

Dehumidification and recovery of VOCs

The first-stage dehumidifier serves as a pre-drier to reduce the loading of the second-stage adsorption dehumidifier. It may be operated at some ordinary low temperatures. At 4°C, the pre-drier gives about 67 wt% removal of water of inlet gasoline vapor (R_{wi}). One option is available to handle the sporadic inlet flows associated with the operation of gasoline service station. A storage tank can be used to accumulate inlet flow surges for the subsequent treatment. If a storage tank is not used, the adsorbent beds of second-stage dehumidification must be sized to handle the instantaneous vapor flow rates that can be several times larger than hourly average flows. The second-stage dehumidification of adsorber using silica gel as adsorbent can further enhance the value of R_{wi} up to 95 wt% and remove most of water of vapor thus avoiding the possible icing problem for the subsequent condensation for VOCs recovery. Some amounts of VOCs will be adsorbed by the silica gel. For example, the monolayer adsorption capacity of n-hexane and benzene (the major components in gasoline vapors) are about 43.3 and 72.4 mg/g SiO₂ (estimated from four parameters of BDDT equation (Steffan and Akgerman, 1998)). Using the concentrations of Table 1, the uptake of n-hexane and benzene at the relative pressure (p/p^0) of 0.15 and 0.12 are about 24.25 and 40.54 mg/g SiO₂, respectively. These values are much lower than the water adsorption capacity of silica gel at the humidity of 64.5% (290 mg/g SiO₂ (Suzuki, 1990)). Temperature of the first-stage pre-dehumidification drier is controlled at 4°C with negligible recovery efficiency (R_{ci}) of gasoline vapors as illustrated in Fig. 2. The adsorbed amount of VOCs at 4°C is about 0.3 wt%. Because the adsorption system is a PSA system, the adsorption of VOCs on the silica gel will be desorbed directly back to the pre-dehumidification drier (4°C) by released pressure. Also noting that the recovery efficiency (R_{ci}) of VOCs at 4°C is 0.3 wt% (325,926.75 $\mu g/L \times 0.3$ wt% = 977.78 $\mu g/L$) while the removal efficiency of water at 4°C by two-stage dehumidification is 95 wt% (17,074.5 μ g/L \times 95 wt% = 16,220.78 $\mu g/L$), one sees that the pre-dehumidification drier and PSA system contribute mainly to the removal of water (16,220.78 / (16,220.78 + 977.78) = 94.31%). Hence, the concentrations of VOCs at point "a" (inlet of the first-stage pre-dehumidification, Fig. 1) are close to those at point "b" (inlet of the high efficiency condenser, Fig. 1).

The water adsorption may be slightly affected by the adsorption of VOCs on silica gel. It will decrease the breakthrough time of water adsorption on silica gel. Increasing the amounts of silica gel and the adsorption time can solve this problem. Most industrial solvents are flammable, with lower explosive limits (LELs) in the range from $1 \sim 2\%$ by volume. Because of the low adsorption of VOCs by using silica gel at low temperature, assurance of safety requirement does not present a problem. It is desirable to operate the system with concentrations as low as possible to 25% of LEL.

Salable liquid gasoline can then be recovered by operating the condenser at the desired low condensation temperature T_c depending on the emission and/or reduction regulation of VOCs. The most common equation used for simulating the condensation of vapor is the saturation vapor equation, $y_{iT} = p_i^0(T)/P_t$, where the y_{iT} and $p_i^0(T)$ are the mole fraction and vapor pressure of the *i*th vapor component at tem-



Fig. 2. Individual recovery efficiencies (R_{ci}) of gasoline vapors at various T_c .



Fig. 3. Concentrations of outlet vent stream vapors of condenser in combined TSDC system at various condensation temperatures T_c .

perature T and total pressure P_t , respectively. The ultimate target condensation temperature for the mixture of vapor gases depends on the target recovery efficiency and on the condensation temperatures calculated for each individual VOCs. Note that the saturation vapor equation does not concern of the interaction of components of VOCs. Its applicability depends on how close the gas mixture behaving as an ideal solution, which can be checked by the activity coefficients of all existing components. In doing this, a further work would be needed. Thus, in order to make sure to well simulate the condensation situations and also for simplicity, Aspen-plus, a software package for thermodynamic computation developed

by Aspen Technology Inc. (ATI, 1994), is used to simulate the condensation removal of VOCs at various T_c . In the simulation computation, the components and composition of VOCs are those specified in Table 1. The samples for analysis are taken under the gasoline balance conditions to represent the inlet flow. The outlet composition of the vent stream is then computed using the Aspen-plus thermodynamic equations.

Model and equations used in Aspen-plus software

The model that we used in the Aspen-plus soft-

ware is Flash 2. There are three stream sections, one is the inlet flow and the others are outlet flows. Among the two outlet flows, one is vapor stream and the other is liquid stream. The pressure is set at 1 atm in order to simulate the atmosphere pressure.

The equations that we chose for the calculation are NRTL-HOC (nonrandom two-liquid – Hayden-O'Connell). The NRTL equations were derived from the Scott's two-liquid theory of binary mixture for an expression of the excess Gibbs energy and Wilson equation. Wilson (1964) suggested a relation between local mole fractions X_{11} of molecule 1 and X_{21} of molecule 2 that are in the immediate neighborhood of molecule 1:

$$\frac{X_{21}}{X_{11}} = \frac{X_2}{X_1} \frac{\exp(-g_{21}/RT)}{\exp(-g_{11}/RT)},$$
(1)

where g_{21} and g_{11} are energies of interaction between a 1-2 and 1-1 pair of molecules ($g_{12} = g_{21}$), respectively. In Eq. (1), X_1 and X_2 are object mole fractions of components 1 and 2 in the mixture, respectively.

Renon and Prausnitz (1968) assumed that the relation between the local mole fractions X_{21} and X_{11} , and X_{12} and X_{22} are given by a modification of Eq. (1):

$$\frac{X_{21}}{X_{11}} = \frac{X_2}{X_1} \frac{\exp(-\alpha_{12} g_{21} / RT)}{\exp(-\alpha_{12} g_{11} / RT)},$$
(2)

$$\frac{X_{12}}{X_{22}} = \frac{X_1}{X_2} \frac{\exp(-\alpha_{12} g_{21} / RT)}{\exp(-\alpha_{12} g_{22} / RT)},$$
(3)

where α_{12} is a constant characteristic of the nonrandomness of the mixture. The local mole fractions are related by

$$X_{21} + X_{11} = 1, (4)$$

$$X_{12} + X_{22} = 1. (5)$$

From Eqs. (2) and (4), and (3) and (5), the local mole fractions of X_{21} and X_{12} are obtained:

$$X_{21} = \frac{X_2 \exp[-\alpha_{12}(g_{21} - g_{11})/RT]}{X_1 + X_2 \exp[-\alpha_{12}(g_{21} - g_{11})/RT]},$$
 (6)

$$X_{12} = \frac{X_1 \exp[-\alpha_{12}(g_{12} - g_{22})/RT]}{X_2 + X_1 \exp[-\alpha_{12}(g_{12} - g_{22})/RT]}.$$
 (7)

The molar excess Gibbs energy (g^E) for a binary solution is the sum of two changes in residual Gibbs energy:

$$g^{E} = X_{1} X_{21} (g_{21} - g_{11}) + X_{2} X_{12} (g_{12} - g_{22}).$$
 (8)

Equation (8), coupled with Eqs. (6) and (7), formed the NRTL (nonrandom, two-liquid) equations. From NRTL equations, one can figure out the object mole fraction of a binary mixture.

Renon and Prausnitz (1968) also compared the calculated results with experimental data for binary vapor-liquid data. In all calculations, the saturation pressures of the pure components were those reported in the literatures (Renon, 1966). The root-mean-square deviations of calculated values from experimental vapor phase mole fractions and the root-mean-square relative deviation of calculated values from experimental pressures were computed for a large number of isothermal vapor-liquid data and some isobaric data. The results indicated that the NRTL equations among four different equations (Wilson, Vam Laar, Heil, and NRTL) gave the best fit for all types of mixtures by proper selection of the constant α_{12} . Thus, NRTL equations are used to simulate the gasoline vapor condensation at various temperatures in this study. The choice is satisfactory by noting the reasonable simulation results thus obtained. To check if the NRTL model is the best choice would need further work involving experimental verification.

Simulation results by Aspen-plus software

The concentrations of the outlet flow at various condensation temperatures T_c by Aspen-plus software simulation are presented in Fig. 3. Temperature variations of concentrations of individual components of VOCs in Fig. 3 show a sigmoidal shape depending on their boiling points. For example, the reflection temperature of butane's sigmoidal shape in Fig. 3 is about -50°C. As the boiling points of VOCs increase, the temperatures of the sigmoidal reflection points also increase. The individual recovery efficiencies (R_{ci}) of VOC components by condensation can be obtained by using Table 1 and Fig. 3. The results are presented in Fig. 2. A higher molecular weight of VOC component yields a higher recovery efficiency. The condensation temperatures of benzene (B), toluene (T), ethylbenzene (E) and xylene (X) at 90 wt% recovery efficiency are about -30, -15, -5, and -5° C, respectively. The total recovery efficiency (R_c) of vapor gas of gasoline by condensation is illustrated in Fig. 4. The results indicate that the values of percent removal of total VOCs of inlet gasoline vapor by condensation (R_c) are about 73, 85, and 90 wt% at T_c of -40, -60, and -73°C, respectively. The total recovery efficiency depends on every individual recovery efficiencies of light VOCs, especially $C_3 \sim C_4$. The low temperatures of -60 and -73°C need a high efficiency condenser. Reducing the light VOCs in the gasoline would greatly reduce the concentration temperature

of VOCs in the vent stream. The mass fractions of condensate liquid components condensed from the gasoline vapors on the condenser as computed by using the Aspen-plus simulations are presented in Fig. 5. The most two majors are hexane and benzene, for $T_c > -65^{\circ}$ C.

Regulation limits on recovery efficiency and emission of VOCs

From Table 1, the concentration of total VOCs of vapors balanced with gasoline is about 326 mg/L. Thus, the operation of condenser at T_c of -60° C



Fig. 4. Total recovery efficiency (R_c) of outlet vent stream gasoline vapors at various T_c .



Fig. 5. Mass fractions of condensate liquid components condensed from gasoline vapors as computed by using Aspen-plus simulations.

would meet the non-destructive reduction (R_c) of VOCs at 85 wt% level with the emission concentration of about 49 mg/L. Should the stringent regulation on the oil storage tank of chemical plant (35 g TOC emitted/m³ gasoline loaded) be applied to the gasoline service station, then the condenser operated at T_c of -60° C ($R_c = 85$ wt%) would have to recycle part of outlet vapor from the condenser back into the underground gasoline tank. For example, if the refueling fuel to the tank of vehicle is 1 L and 1.4 L vapor gas is pulled back to the central treatment facility, then one liter outlet vapor from the condenser may be pumped back into the underground gasoline tank and the other 0.4 L vapor gas emitted. This would fit the pumping support method for the recovery of gasoline vapors. The emission of VOCs (about 19.6 mg = 326 $mg/L \times 0.15 \times 0.4 L$) is less than 35 mg for refueling 1 L gasoline into the fuel tank of vehicle. The recycled vapor would balance the pressure loss due to the uptake of gasoline from the underground gasoline tank.

In the above computation, the vapor balanced with gasoline with composition as listed in Table 1 is taken as the inlet flow into the combined process of two-stage dehumidification and condensation. Its concentration of total VOCs is about 11.3 vol%. On the other hand, if one considers the total recovery efficiency (R_s) of system of Phase II control (pumping support method), which includes the pipe lines of transport of gasoline vapor from the opening of fuel tank of vehicle to the system of combined process of Fig. 1, the corresponding inlet concentration of the overall system is about 30 vol%. During the transport along pipelines, parts of VOCs are condensed and back into the underground storage tank. This reduces the concentration of total VOCs from 30 vol% to the balanced concentration of 11.3 vol%. With the vapor of VOCs of 11.3 vol% as the feed to the subsequent two-stage dehumidification and condensation system (Fig. 1), the condenser operated at T_c of -40° C would give the system total recovery efficiency (R_s) of 90 wt%. The cost of condenser with moderate efficiency operated at -40°C is much lower than that of condenser with high efficiency operated at -60°C or -73 °C. When the condensation temperature is down to -73° C, the system total recovery efficiency (R_s) is up to 96 wt%.

Power consumption

In gasoline service station, the volume of off-gas flow to be treated depends on the refueling numbers of vehicles. The power consumption depends on the scale (numbers of gasoline nozzle guns) of gasoline service stations. If the average flow rate (Q_{avg}) is 1.4 times of the average sale volume of gasoline at Taipei, then Q_{avg} is about 0.4537 L/s. Further, if the peak flow rate of refueling vehicles is 4 times of average flow rate, one has the design flow rate of gasoline waste (Q_d) of about 1.8148 L/s. Certainly, the design flow rate is low that most commercial devices or condensers are suitable.

The power consumption for this process can be divided in four units. For the first unit, *i.e.*, compressor, the power consumption is about 0.75 hp \times $0.746 \text{ kW/hp} \times 24 \text{ h/day} \times 350 \text{ days/yr} = 4,700$ kW·h/yr. As, for the second unit of pre-dehumidification drier, the power consumption is about 0.2 hp \times $0.746 \text{ kW/hp} \times 24 \text{ h/day} \times 350 \text{ days/yr} = 1253$ kW·h/yr. For the third unit of the high efficiency condenser and refrigerator, the power consumption is about 0.2 hp \times 0.746 kW/hp \times 24 h/day \times 350 days/yr = $1253 \text{ kW}\cdot\text{h/yr}$. In this process, the major pressure drop (ΔP) is in the forth unit, the pressure swing adsorption (PSA) system. The value of ΔP is about 27.543 N/m². Therefor, under the design flow rate Q_d = 1.8148 L/s, the power consumption of PSD unit is about $1.8148 \times 10^{-3} \text{ m}^3/\text{s} \times 27.543 \text{ N/m}^2 \times 10^{-3}$ W/kW \times 24 h/day \times 350 days/yr = 419.85 kW·h/yr. This value is far below those of the other units. The total power consumption of the overall process is about 7625.85 (= 4700 + 1253 + 1253 + 419.85)kW·h/yr. The detail of the above computations may be referred to the work of Lu (2000).

Cost effective analyses for TSDC and direct incineration

For the economic cost effective analysis, one can compare the costs of TSDC and direct incineration. Economic cost effective analysis can be divided into five parts: (1) total capital investment (TCI); (2) total annual cost (TAC); (3) fuel recovery effective analysis; (4) recovery time estimation; (5) total cost effective calculation (Benitez, 1993). Table 2 listed the cost effective analysis and comparisons of the TSDC process and direct incineration. The detail calculation can be referred to Lu (2000). When the estimation is based on the VOCs concentration at inlet of fuel tank of 300,000 ppmv and on $R_s = 90$ wt%, the total benefit with 20% tax rate (including depreciation, i = 6%) of the TSDC process of 583,337 NT\$ after 10 years is higher than that of the direct incineration of 329,209 NT\$ after 10 years. Furthermore, when the estimation is based on the VOCs concentration at inlet of TSDC or direct incineration of 113,000 ppmv, the annual treatment cost of VOCs of the TSDC process (with R_c of 73.43 wt%) of 22,203 NT\$/ton VOCs-yr is lower than that of the direct incineration (with 100% destruction efficiency) of 23,275 NT\$/ton VOCs-yr. From the cost analysis, it appears that the TSDC process is more financially feasible compared to the direct incineration.

| | TSDC | Direct Incineration | |
|--|--|--|--|
| Unit | Compressor, storage tank, pre-dehumidification drier, PSA adsorbers, high efficiency condenser, and refrigerator | Vacuum pump and direct incinerator | |
| Total capital investment ^b | 801,880 NT\$ | 600,000 NT\$ | |
| Total annual operating cost, including 10-year based depreciation | 152,610 NT\$/yr | 110,930 NT \$/yr | |
| Amount of recovered gasoline 1. Based on 300,000 ppmv ^c 2. Based on 113,000 ppmv ^d | 1. 11.4 ton/yr with <i>R_s</i> of 90 wt% 2. 3.5 ton/yr with <i>R_c</i> of 73.43 wt% | 7.9 ton/yr with <i>R_p</i> of 62.37 wt% 0 | |
| Benefit of recovered gasoline 1. Based on 300,000 ppmv ^c 2. Based on 113,000 ppmv ^d | 1. 243,950 NT\$/yr 2. 74,900 NT\$/yr | 1. 169,050 NT\$/yr 2. 0 | |
| Recovery time (attractive rate of return, i = 6%), including depreciation 1. Based on 300,000 ppmv ^c 2. Based on 113,000 ppmv ^d | 1. 6.47 yr 2. — | 1. 7.08 yr 2. — | |
| Total benefit with 20% tax rate, includ- ing depreciation, $i = 6\%$ 1. Based on 300,000 ppmv ^c | 1. 583,337 NT\$ after ten yr | 1. 329,209 NT\$ after ten yr | |
| Annual treatment cost of VOCs 2. Based on 113,000 ppmv ^d | 2. 22,203 NT\$/ton VOCs·yr ^e | 2. 23,275 NT\$/ton VOCs·yr ^f | |

Table 2. The cost effective analysis and comparison of the TSDC process and direct incineration^a.

^a Based on the price index of 1999.

^b Total capital investment = equipment cost + preliminary fixed capital cost (installation). Based on average 60 gasoline guns in a gasoline station and on sale volume of gasoline of 28 kL/station day at 350 days/yr.

^c The inlet concentration of the overall system (or concentration at inlet of fuel tank). $R_s = 90$ wt%, $R_p = 62.37$ wt%.

^d The balanced concentration of total inlet VOCs (or concentration at inlet of TSDC process). $R_c = 73.43$ wt%.

^e Annual treatment cost of VOCs = (total annual operating cost – annual benefit of recovered gasoline)/amount of recovered gasoline = (152,610 - 74,900)/3.5 = 22,203 NT\$/ton VOCs·yr. ^f VOCs to be treated = $3.5/R_c = 3.5/0.7343 = 4.766$ ton/yr. 110,930/4.766 = 23,275 NT\$/ton VOCs·yr.

CONCLUSION

- (1) The proposed combined process of two-stage dehumidification and condensation meets the requirement for compliance of Phase II control on the emission of volatile organic compounds (VOCs) from gasoline service stations.
- (2) The advantages of the proposed combined process include: recovery of gasoline, safe operations (no accumulations of VOCs and heat, and without fire), easy operation without icing problem (pre-dehumidification at 4°C, and postcondensation with insignificant water content), and low flammable possibility for the VOCs reduction at the gasoline service stations.
- (3) The techniques and equipments of the proposed combined process are mature, compact and commercially available. Hence, the process is feasible and competitive on the reduction of VOCs emission from the gasoline service sta-

tions.

(4) From the cost analysis, it appears that the TSDC process is more financially feasible compared to the direct incineration.

ACKNOWLEDGEMENT

We express our sincere thanks to the Environmental Protection Bureau of Taipei County for the financial support.

NOMENCLATURE

| C_{mv} | concentration of mass per volume, µg/L |
|----------|--|
| g^{E} | molar excess Gibbs energy, kJ/mol |
| g_{ij} | energies of interaction between an <i>i-j</i> pair |
| | of molecules $(g_{ij} = g_{ji})$, kJ/mol |

Je-Lueng Shie, Chen-Yu Lu, Ching-Yuan Chang, Chun-Yu Chiu, Duu-Jong Lee, Shi-Ping Liu, and Chang-Tong Chang: 615 Recovery of Gasoline Vapor by a Combined Process of Two-Stage Dehumidification and Condensation 615

| p, p^0 | partial | and | saturation | pressures | of | vapor, |
|----------|---------|-----|------------|-----------|----|--------|
| | N/m^2 | | | | | |

 p_i^0 p^0 of component I, N/m²

 P_t total pressure of system, N/m²

 Q_{avg} average flow rate of gasoline vapor to be treated, L/s

- Q_d designed flow rate of gasoline vapor to be treated, L/s
- *R* universal gas constant, kJ/kmol·K
- R_c removal or recovery efficiency of total VOCs based on inlet gasoline vapor in TSDC process of Fig. 1, wt%
- R_{ci} removal or recovery efficiency of component *i* in VOCs based on inlet gasoline vapor in TSDC process of Fig. 1, wt%
- R_p removal or recovery efficiency of VOCs of pipelines of transport of gasoline vapor from the opening of fuel tank of vehicle to the point before TSDC process, wt%
- R_s total recovery efficiency of system of phase II gasoline vapor control including the pipelines of transport of gasoline vapor from the opening of fuel tank of vehicle to the outlet of system of TSDC process of Fig. 1, wt%
- R_{wi} removal efficiency of water of inlet gasoline vapor, wt%
- *T* temperature, °C

 T_c operating temperature of condenser, °C

- X_1, X_2 object mole fractions of components 1 and 2 in the mixture
- X_{11}, X_{21} mole fractions of molecules 1 and 2 those are in the immediate neighborhood of molecule 1
- X_{12}, X_{22} mole fractions of molecules 1 and 2 those are in the immediate neighborhood of molecule 2
- y_{iT} mole fraction of component *i* at *T*

Greek symbols

| $lpha_{ij}$ | nonrandomness constant for binary ij i | n- |
|-------------|--|----|
| | teractions | |
| ΔP | pressure drop, N/m ² | |

Acronyms

| benzene, ethylbenzene, toluene, xylene | | |
|--|--|--|
| Clean Air Act Amendments | | |
| California Environmental Protection Agency Air Resource Board | | |
| hydrocarbons | | |
| Hayden-O'Connell | | |
| lower explosive limits | | |
| mass exchange networks | | |
| nonrandom two - liquid | | |
| pressure swing adsorption | | |
| | | |

- TOCs total organic compounds
- TSDC two-stage dehumidification and condensation
- VOCs volatile organic compounds

REFERENCES

- ATI (Aspen Technology Inc.), "ASPEN PLUS User's Guide," Cambridge, MA, U.S.A. (1994).
- Benitez, J., Process Engineering and Design for Air Pollution Control, Prentice-Hall, Inc., Englewood Cliffs, New Jersey, U.S.A. (1993).
- CARB (California Environmental Protection Agency Air Resource Board), *Gasoline Facilities Vapor Recovery Phases* 1 & 2 (1994).
- Cooper, C. D. and F. C. Alley, *Air Pollution Control-a Design Approach*, 2nd Ed., Waveland Press, Inc., Prospect Heights, IL, U.S.A. (1994).
- Crabtree, E. W., M. M. El-Halwagi, and R. F. Dunn, "Synthesis of Hybrid Gas Permeation Membrane/Condensation Systems for Pollution Prevention," J. Air Waste Manage. Assoc., 48(7), 616 (1998).
- Danielsson, M. A. and V. Hudon, "VOC Emission Control Using a Fluidized-Bed Adsorption System," *Metal Finishing*, **92**(6), 89 (1994).
- Deng, S., "Study of Volatile Hydrocarbon Emission Control by an Aromatic Poly(ether imide) Membrane," *Ind. Eng. Chem. Res.*, **34**(12), 4494 (1995).
- Dunn, R. F. and M. M. El-Halwagi, "Optimal-Design of Multicomponent VOC Condensation Systems," J. Hazard Mater., 38(1), 187 (1994).
- El-Halwagi, M. M. and V. Manousiouthakis, "Simultaneous Synthesis of Mass-Exchange and Regeneration Network," *AIChE J.*, 8, 1209 (1990).
- Jeng, F. T., "The Study on the Stationary Air Pollution Sources Investigation and Their Effects on the Air Quality of Taipei City," Taiwan, Report of Environmental Protection Bureau of Taipei City, Taiwan (1987).
- Lu, C. Y., "Recovery of Gasoline Vapor from Gas Station by Condensation," M.S. Thesis, Graduate Institute of Environmental Engineering, National Taiwan University, Taipei, Taiwan (2000).
- Moritaka, K., "Hydrocarbon Vapor Recovery with Membrane Technology," *NKK Tech. Review*, **56**, 67 (1989).
- Nevers, N. D., Air Pollution Control Engineering, McGraw-Hill, Inc., New York, U.S.A. (1995).
- Ohlrogge, K., "Separation of Hydrocarbon Vapors with Membranes," Sep. Sci. Technol. Knoxville, 25, 13, TN, U.S.A. (1990).
- Pezolt, D. J., S. J. Collick, H. A. Johnson, and L. A. Robbins, "Pressure Swing Adsorption for VOC Recovery at Gasoline Loading Terminals," *Environ. Prog.*, 16(1), 16 (1997).
- Renon, H., Doctoral Dissertation, Univ. California, Berkeley, U.S.A. (1966).

- Renon, H. and J. M. Prausnitz, "Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures," *AIChE J.*, 14(1), 135 (1968).
- Steffan, D. G. and A. Akqerman, "Single-Component and Binary-Mixture Adsorption of Volatile Organic Contaminants on Silica Gel," *Environ. Eng. Sci.*, 15(3), 191 (1998).
- Suzuki, M., M. Hori, and K. Kawazoe, Fundamental of Adsorption, 619 Eng. Foundation, New York, U.S.A. (1985).
- Suzuki, M., Adsorption Engineering, Elsevier Science Publishers B. V., Amsterdam, The Netherlands (1990).
- Tsai, W. T., C. Y. Chang, and C. Y. Ho, "Adsorption Equilibrium of 1,1-Dichloro-1-Fluoroethane (HCFC-141b) on a Hydrophobic Zeolite," *Adsorption Sci. Technol.*, 16(2), 67 (1998).
- Tsai, W. T., C. Y. Chang, C. Y. Ho, and L. Y. Chen, "Simplified Description of Adsorption Breakthrough Curves of 1,1-Dichloro-1-Fluoroethane (HCFC - 141b) on Activated Carbon with Temperature Effect," *J. Colloid and Interface Science*, **214**, 455 (1999).

- TWEPA (Taiwan Environmental Protection Administration), Air Pollution Control Regulations and Emission Standards on the Volatile Organic Compounds, p. 119 (1999).
- TWEPA (Taiwan Environmental Protection Administration), http://www.epa.gov.tw (2002).
- USEPA (United States Environmental Protection Agency), Compilation of Air Pollution Emission Factors, Chap. 4.4 Transportation and Marketing of Petroleum Liquids (Sept. 1985). Available on the CHIEF Bulletin Board of the U.S. EPA QAQPS TINWeb (http://www.epa.gov/ttn) (1996).
- Wark, K., C. F. Warner, and W. T. Davis, *Air Pollution-Its Origin and Control*, 3rd Ed., Addison-Wesley, Menlo Park, California, U.S.A. (1998).
- Wilson, G. M., "Vapor-Liquid Equilibrium, XI, A New Expression for the Excess Free Energy of Mixing," J. Am. Chem. Soc., 86, 127 (1964).
- Yang, R. T., Gas Separation by Adsorption Processes, Butterworths, Stoneham, Massachusetts, U.S.A. (1987).

(Manuscript received Jun. 19, 2003, and accepted Oct. 14, 2003)

利用脉階段除濕度令凝程的呼收油氣之研究

謝哲隆 吕辰宁 張慶源

國立台灣大學環境工程學研究所

邱浚佑

蘭陽技術學院環境工程學系

李篤印

國立台灣大學化學工程學系

劉希平

輔仁大學公共衛生學系

張彰掌

國立宜蘭大學環境工程學系

搖 ヲ

加油站油氣所含揮發性有機化合物 (VOCs) 之逸散已成為人口密集地區的一種重要污染問題。本研究提出一兩階段除 濕和冷凝 (TSDC) 結合之程序作為回收逸散油氣中 VOCs 之方法。除濕程序分為兩階段,第一階段以除濕機控制在 4°C 以移除 67 wt% 進流油氣中之水氣;第二階段更進一步以吸附裝置增進此値到 95 wt%,此可避免下一階段冷凝出現結冰阻 塞問題。依據 VOCs 排放或削減法規規範,藉控制冷凝器於適當之低溫,可回收液體汽油。為模擬於各不同溫度下冷凝回 收油氣中之 VOCs,本研究使用 Aspen 科技公司所發展之熱動力學套裝軟體 Aspen-plus 作為模擬工具。模擬結果指出,冷 凝溫度分別為 -40、-60 和 -73°C 時,TSDC 程序進流油氣中 VOCs 冷凝回收效率 (*R*。依據進入 TSDC 程序之油氣濃度 與流量) 分別為 73、85 和 90 wt%。於溫度為 -60°C 時,即可符合 VOCs 非破壞性削減率 85 wt% 之要求。若以化學工廠 儲油槽的嚴格規範應用到加油站,則冷凝器操作於 -60°C 時須迴流部分冷凝器出流蒸氣回地下油槽。此乃為確保再加 1 L 汽油入油箱時,VOCs 逸散小於 35 mg。另外,迴流油氣亦可平衡抽出汽油之地下油槽壓力。