

Control of VOCs emissions by condenser pre-treatment in a semiconductor fab

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Abstract

The performance of a modified design of local condensers to pre-treat a variety of volatile organic compounds (VOCs) emitted from the stripping process of a semiconductor fab was tested in this study. The reaction temperature of the condensers was controlled at around 10 °C, it is relatively higher than the traditional condenser reaction temperature. Both VOCs and water vapors were condensed and formed liquid films. This resulted in an enhancement of the VOCs removals, especially for VOCs of high boiling points or solubility. This can help to prevent the follow up zeolite concentrator from damage. The performance of the integrated system of condenser/zeolite concentrator could, therefore, remain highly efficient for a longer operation time. Its annualized cost would also be lower than installing the zeolite concentrator only. © 2005 Elsevier B.V. All rights reserved.

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1. Introduction

The exhaust gas from semiconductor manufacturers has characteristics of high-flow rate with a variety of VOCs emitted at low concentrations [1]. Besides, the boiling points of VOCs may vary over a wide range from less than 50 °C to over 200 °C. They are usually treated by regenerative adsorption/desorption devices such as the rotary zeolite concentrators to increase the VOCs concentrations. Then, the concentrated VOCs are further treated by incineration devices. The initial operation efficiencies of zeolite concentrators in terms of total hydrocarbon (THC) emitted from semiconductor fab are well above 90% in laboratory tests [2–6] and field operations [7,8].

But when high boiling-point VOCs are treated during desorption process, they tend to gradually occupy the adsorption sites and deteriorate the performance of an adsorber [4]. The installation of condensers before a VOCs adsorber to

condense the high boiling-point VOCs may be an effective method to prevent the decreasing of VOCs removal efficiency. However, limited information is available in the literature for the integrated process of condensers plus a zeolite concentrator.

In general, condensation involves a refrigerator to lower the temperature of the exhaust gas until it is below the dew point. And the removal is performed by the condensation of gaseous VOCs on the chilled parts of the condenser. The modules of a VOCs condenser system usually include the dehumidification module and the refrigerator module [9]. Dehumidification is performed to reduce the moisture and prevent the detrimental icing effects that would otherwise occur when the VOCs exhaust is cooled to a temperature below 0 °C in the VOCs condensation section. Besides, a dehumidification pretreatment is also beneficial for the purpose of VOCs recovery.

Zeiss and Ibbetson [10] showed that the successful application of condensation technology depended on two factors—low temperature capability and a high vapor phase concentration of VOCs. And it is known that the condensa-

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tion of VOCs is a proper technique to decrease the emission level for single compound, high concentration and low gas flow rate VOCs at below 0 °C. But whether a condenser is suitable to treat VOCs exhaust that has the characteristics of multiple compounds, low concentrations and high gas flow rate at the temperature of above 0 °C has rarely been studied.

The practical performance of a condenser in reducing low VOCs concentrations has not been sufficiently understood. In order to keep the condensers with economical performance, this study proposes a modification on the traditional condenser design. Both condensation and liquid absorption were effective in the condensers to enhance the removals of VOCs.

2. Experiments

The design of condensers for such purposes is slightly different from the traditional ones operated under ultra-low temperatures. The ice water inside the tubes and fins type coil was operated at 10 °C, thus the moisture can condense and form a liquid absorption film that enhances the condensation of some hydrophilic VOCs. With the design of dual effect (condensation plus film absorption) of the condensers employed herein, it is expected that not only the VOCs removal efficiency can be increased but also the power consumption cost can be reduced as compared to the traditional condensers.

Table 1 presents the operating parameters of the condenser set in this study. The indoor temperature of the location of condensers was maintained at around 22–23 °C dry bulb (db). The VOCs emitted from the stripping process were at temperatures of 35–60 °C before inlet to the condensers. The outlet temperature of the VOCs stream was around 10–14 °C and the water content in the condensed solvents was about 40–50% by weight.

Table 1
Operating parameters of the condenser

Operating parameters	Value
Tube and fins type heat coil	330 mm (<i>L</i>) × 608 mm (<i>W</i>) × 457.2 mm (<i>H</i>)
Total area of cooled surface for condensation (m ²)	20
Total area of wetted surface for condensation (m ²)	40
Maximum treated flow-rate by the condenser (SCMH)	3000
Maximum VOCs inlet concentration (designed value) (ppmv)	100
Superficial velocity of inlet VOCs flow (m/s)	1.0–3.0
Retention time of VOCs flow in the condenser (s)	0.11–0.33
Temperature of the fab (dry bulb) (°C)	22–23
Humidity of the fab (%RH)	40–45
Inlet temperature of VOCs laden air flow (°C)	35–60
Temperature of ice water chilling coil (°C)	10
Temperature of outlet VOCs flow (°C)	10–14
Water content of condensed VOCs (wt.%)	40–50
Cooling capacity (kJ/h)	51000–53500
Water condensed weight (designed value) (kg/h)	1.5

Fig. 1 presents the schematic of the stripping process of a semiconductor fab in Taiwan as well as its VOCs removal process including two parallel condensers and a zeolite concentrator/incinerator unit. The stripping process was composed of one strip step and three rinse steps. The wafer boat was immersed in the first strip tank at a temperature below 110 °C and then transferred to the rinse tanks. The VOCs exhaust emitted from the strip and the first two rinse tanks was introduced into the condensers and then sent to the zeolite concentrator/incinerator for final treatment. The condensed organic solvent was drawn into the daily tank. Because stripper and rinse solutions used in stripping process of the semiconductor industry were composed of several organic solvents so the constituents of exhausted VOCs were complicated. And the purity of organic solvents required by every manufacturing process was so high that the condensed VOCs could not be recycled for stripping and rinsing purposes again.

The concentrations of VOCs were measured at the inlet and the outlet of the condensers and the removal efficiencies of the two condensers were calculated. The VOCs concentrations were analyzed according to the USEPA TO-14A method [11]. The VOCs were sampled by stainless-steel tube sampling. The sampling tube drew a VOCs sample from the stream by the drop in pressure ($\Delta p = 10^{-2}$ mmHg). The sample was then analyzed by GC/MS in the laboratory. The equipments for analyzing VOCs included a VOCs autosampler (Xontech, 911/912 systems), a Cryogenic Concentrator (Nutech, 3350A), a Gas Chromatograph (HP 5890 Series II) and a Mass Selective Detector (HP 5971 Series II) coupled with a GC column (Rtx-502.2, 60 m, 0.25 mm i.d., 1.4 μm f.m.). Furthermore, a continuous emission instrument (GC/FID detector) was installed at the pipe-end for on-line measurements of the THC removal efficiency.

3. Results and discussion

3.1. Analysis of VOCs emitted from the stripping process

Fig. 2 presents the dominant species detected by GC/MS during the stripping process of a semiconductor fab. The largest quantity of VOCs emitted during the stripping process was dimethyl sulfoxide (DMSO, 63%). Other major VOCs being detected included the dimethyl sulfide (DMS, 15%), isopropylalcohol (IPA, 11%), dimethyl disulfide (DMDS, 6%), 1-methyl-2-pyrrolidinone (NMP, 2%) and trace amounts of toluene, *N,N*-dimethyl acetamide, and acetone, etc. The total concentrations of VOCs emitted during the stripping process depended on the product yields and were varied from 16,000 to 42,000 ppbv.

The VOCs emitted from the stripping process are mainly due to heating and agitating steps in the first and second tanks as well as the rinsing step in the third tank. The compounds of DMS, DMDS, DMSO, NMP, and *N,N*-dimethyl acetamide were emitted when the stripper is heated and agitated, while

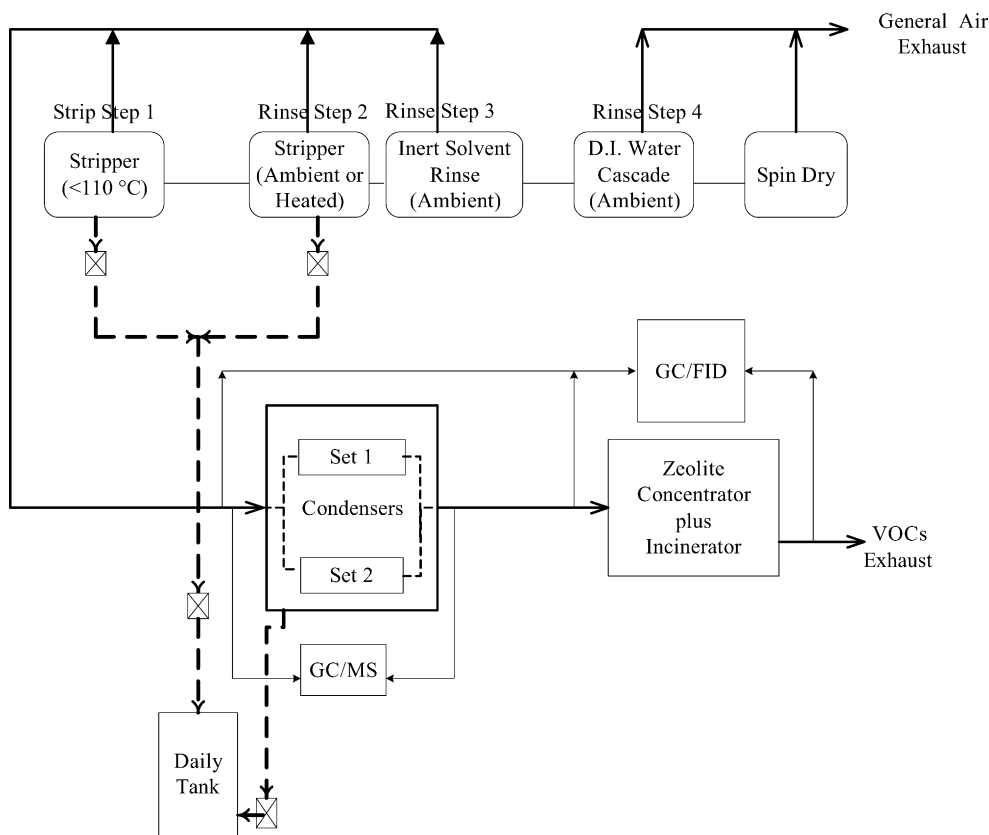


Fig. 1. Schematic of the stripping process (upper plot) and the VOCs control devices (bottom plot) that composed of an integrated system of two condensers and a zeolite concentrator/incinerator unit in a semiconductor fab (the solid lines are the VOCs exhaust streams and the dashed lines are the condensed liquid streams of the VOCs).

IPA, acetone and toluene were emitted during the rinsing and agitating steps of the organic solvents as shown in Fig. 1.

3.2. The removal efficiency of VOCs by condensers

For a traditional condenser, the VOCs are removed if their partial pressures are larger than the saturation vapor pressures at the condenser temperature. Fig. 3 shows the ratio of partial

pressures of VOCs detected in the emitted gas stream at $10\text{ }^\circ\text{C}$ to their saturation vapor pressures. One can see that only the pressure ratio of DMSO was larger than 1, the others should be too low to be removed by condensation mechanism. But in this study all VOCs were more or less removed in the condensers as observed in Fig. 4(a) and (b).

Fig. 4(a) presents the relationship between boiling points of various VOCs and their average removal efficiencies by

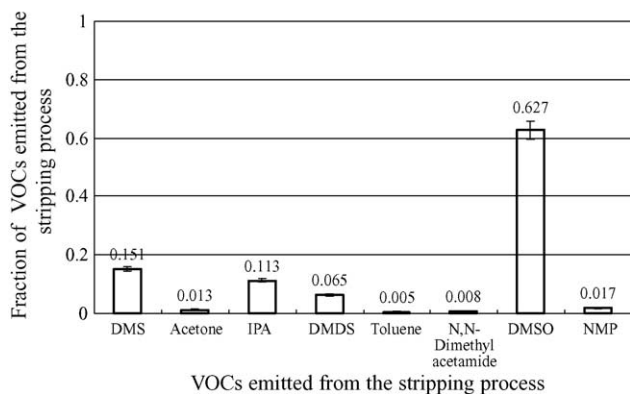


Fig. 2. Principal compounds of VOCs emitted during the stripping process of a semiconductor fab.

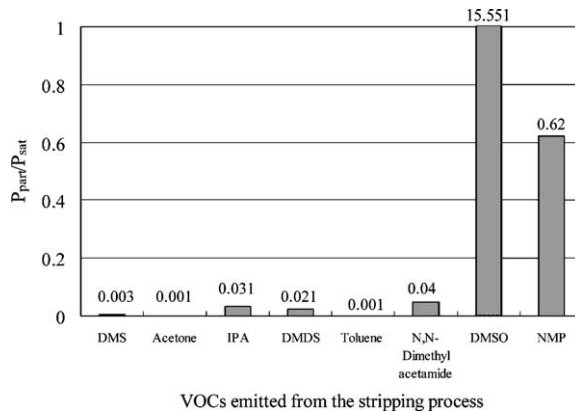


Fig. 3. Average ratio of partial pressures of VOCs emitted from the stripping process to their saturation vapor pressures at the condenser operating temperature of $10\text{ }^\circ\text{C}$.

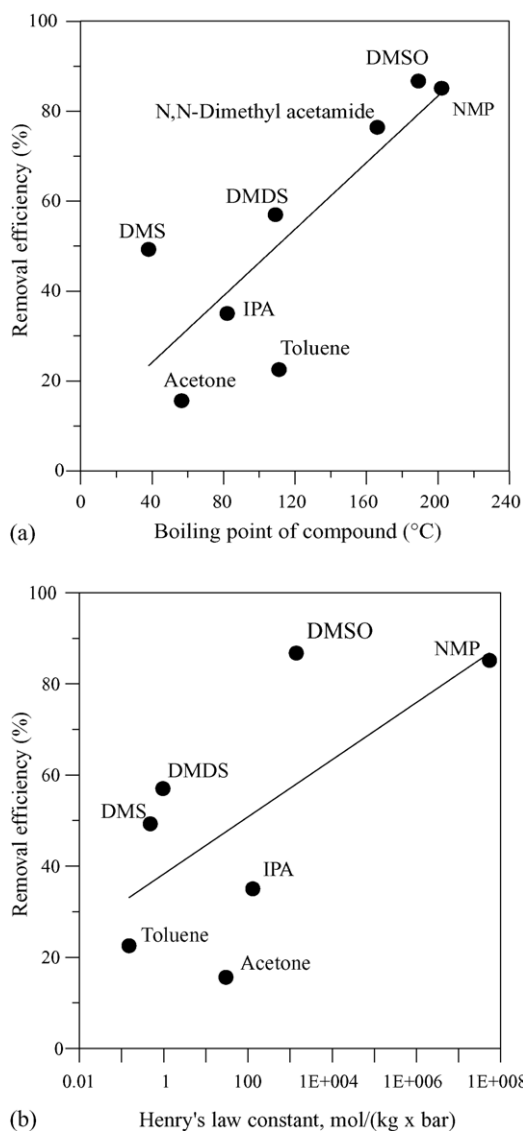


Fig. 4. Removal efficiencies of VOCs as functions of (a) boiling points and (b) Henry's law constants.

the condensers. Owing to the manufacturing process was changed during the test period, the inlet concentrations of VOCs to the condensers varied, but one still observed that the removal efficiencies of VOCs were roughly proportional to their values of boiling points except toluene and DMS.

The toluene has relatively low removal efficiency as compared to other VOCs of similar boiling points. Because the moisture was simultaneously removed with VOCs in the condenser, the condenser removal efficiency should be a function of the Henry's constants also. As indicated in Fig. 4(b), the low removal of toluene may be attributed to its low Henry's constant (H) in water, 0.15 mol/(kg bar) at 25 °C [12]. The roughly increase of VOCs removals as their Henry's constants were increased as shown Fig. 4(b) revealed that the water film also played an important role in the condenser system.

On the other hand, the removal efficiency of DMS abated by the condenser is better than several other VOCs, even though its boiling point is the lowest and its solubility in water is also relatively low with $H=0.48$ mole/(kg bar) in water at 25 °C. This may be because that DMS can dissolve in the DMSO, the organic with the most condensation potential [13].

The removal efficiencies of high boiling-point compounds such as NMP and DMSO abated by the condensers were above 80%, and these compounds were responsible for over 60% of VOCs emitted from the stripping process. So, the condensers were good choices for the pre-treatment of high boiling-point VOCs and they prevented the follow up zeolite adsorber from gradual deterioration caused by low desorption rate of the high boiling-point VOCs.

If the condenser system is to be applied to other fields, it must be noted that the effective functioning of the proposed device depends critically on the VOCs being hydrophilic or they can be dissolved in other condensable species. Therefore, it is most suitable to plants which emit VOCs with relatively high solubility in water or organic solvents.

Fig. 5 presents the effect of superficial velocity on the THC removal efficiency. The superficial velocity was increased when the loading of stripping process was increased. One can see that the removal efficiency of THC abated by condenser was close to 60% when the stripping process was full loaded with a superficial velocity of 3.0 m/s in the condensation. Furthermore, THC removal could be as high as 80% at the superficial velocity of 1.5 m/s. It was observed that the emitted THC concentrations were not linearly proportional to the process loading, and the THC removal did not depend

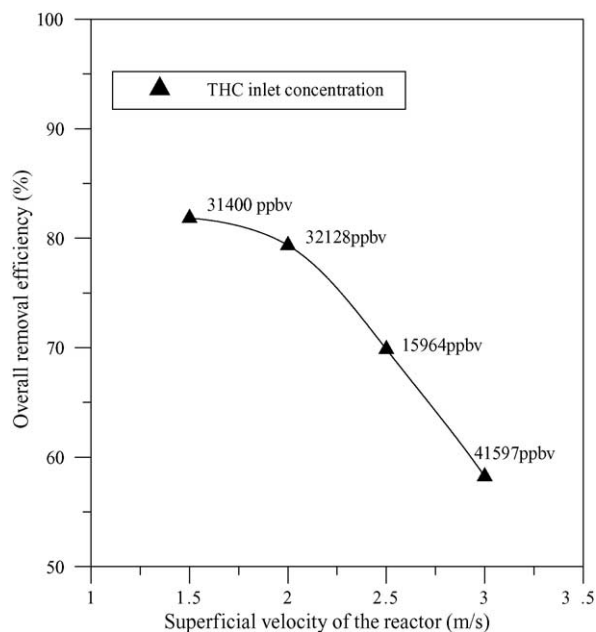


Fig. 5. The effect of superficial velocity on the THC removal efficiency. The numbers shown above each symbol are their corresponding THC inlet concentrations.

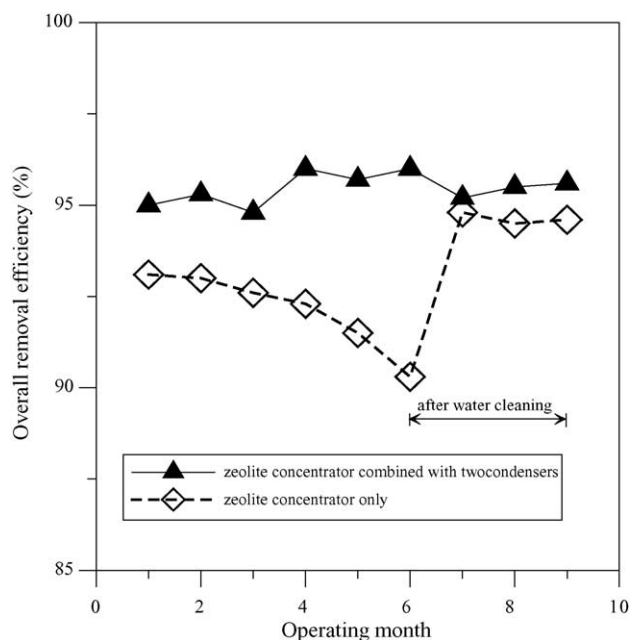


Fig. 6. Comparison of the THC removal efficiencies obtained by the zeolite concentrator and the integrated system of condenser/zeolite concentrator.

on their inlet concentrations either. For example, the lowest THC inlet concentration, 15,964 ppbv, appeared at a superficial velocity of 2.5 m/s with a THC removal of 70%. And the lowest THC removal appeared at the highest THC inlet concentration of 41,597 ppbv.

3.3. Comparison between the integrated system and the zeolite concentrator

To prove the effectiveness of the condenser pre-treatment devices, there were two zeolite concentrators of identical geometry being installed in the semiconductor fab. Each zeolite concentrator removed, the VOCs exhausted from separate stripping process of the same design. The only major difference is that one zeolite concentrator was operated with two parallel condensers as pretreatment devices, while the other one was operated without any condenser.

Fig. 6 presents the THC removal efficiencies obtained by the independent zeolite concentrator as well as by the inte-

grated system of condenser/zeolite concentrator. For the independent zeolite concentrator, all VOCs including the high boiling-point temperature ones were removed by the zeolite concentrator. Because the high boiling-point VOCs were difficult to be desorbed, they were accumulated onto the active sites of the zeolite concentrator after repeated adsorption/desorption process. Hence a viscous film was gradually formed and resulted in a decrease in the removal efficiency of the zeolite concentrator. After six months of operation, the removal efficiency of the VOCs by the zeolite concentrator system was decreased to the critical value, 90%, allowed by Taiwan’s air pollution regulation. Thus, the zeolite rotor must be shut down and water washed to clean out the occupants. This washing procedure increased the removal efficiency of the zeolite concentrator to almost 95%. The washing frequency of the zeolite concentrator depended on the yield of fab, and was usually once per half-year to per quarter year. Although regular washing of the zeolite concentrator could resolve the problem of high boiling-point VOCs, companies with high yield, especially those without back-up abatement advices, could not tolerate the frequent recess of the process. Besides, the frequent washing of the zeolite concentrator would reduce its lifetime.

On the other hand, after the installation of two parallel condensers the integrated condenser/zeolite concentrator system kept a high VOCs removal efficiency for a long period of time as shown in Fig. 6. The removal efficiency remained at around 95% even after nine months of operation. Thus, after the high boiling-point VOCs were pretreated in the condenser, the deterioration problem of the zeolite concentrator could be effectively resolved.

Table 2 compares the installation, operation and maintenance (O&M) costs of a zeolite concentrator with the integrated system (zeolite concentrator plus two condensers). Under the assumption of an average water usage of 20 tons and washing cycle of per quarter year, the O&M cost of the zeolite concentrator was US\$ 27,430/year. The O&M cost mentioned above excluded incinerator cost but included the cost of washing the rotor. The renewing cost of the rotor was US\$ 171,450.

The rotor was assumed to be renewed every five years with a minimum rate of return of 10%, the annualized present cost of the zeolite concentrator was US\$ 45,263/year. Therefore, the total annualized net cost of a zeolite concentrator was

Table 2
Annualized installation and operating costs of zeolite concentrator and the integrated system of condenser/zeolite concentrator

Installation	Zeolite concentrator	Integrated system of condensers/zeolite concentrator	
		Condensers	Zeolite concentrator
Capital cost (US\$)	171450	57150	171450
Useful life (year)	5		7
Minimum rate of return (%)		10	
Annualized present cost of the installation (US\$/year)	45263		46863
O&M cost (US\$/year) (excluding the incineration consumption)	27430		22858
Total annualized net present cost (US\$/year)	72693		69721

US\$ 72,693/year. The installation cost of two condensers for the field test shown in this study was around US\$ 57,150. The useful life of the condensers was assumed to be seven years and they had zero salvage value. The useful life of zeolite rotor was assumed to be seven years also. The two years extension in the useful life of zeolite rotor in the integrated system was due to the installation of the condensers that help to protect the zeolite concentrator from deterioration caused by high boiling-point VOCs.

The annualized present cost for the integrated system was about US\$ 46,863/year with minimum rate of return of 10%. The O&M costs of the integrated system included the treatment cost of the waste organic solvent (US\$ 10,290/year), the average cost of power consumption (US\$ 5710/year), and the washing cost of the zeolite rotor per year. Therefore, the total O&M cost of the integrated system would be around US\$ 22,858/year. As a result, the estimated total annualized net present cost of the integrated condenser/zeolite concentrator system, US\$ 69,721/year, was lower than applying the zeolite concentrator alone, US\$ 72,693/year.

4. Conclusions

This study employed a modified design of local condensers operated at temperatures relatively higher than the traditional condensers to pre-treat a variety of VOCs emitted from the stripping process in a semiconductor fab. Both VOCs and water vapors were condensed to form liquid films and thus effectively remove a majority of VOCs as characterized by high boiling points and hydrophilic properties. The removal efficiency of low to medium boiling-point VOCs such as IPA, acetone, and toluene were only between 10 and 50%, but these compounds could be further introduced into the zeolite concentrator and lead to over 90% of THC removals.

Because the high boiling-point VOCs were pre-treated with over 80% efficiencies, the performance of the integrated system of condenser/zeolite concentrator could remain high efficiency for a longer period of operation, and its annualized cost was lower than installing the zeolite concentrator alone.

In addition to the semiconductor manufacturing fab, the optoelectronic industry such as a TFT-LCD manufacturing fab has a more severe problem on the deterioration of VOCs adsorption devices due to the presence of a significant quantity of high boiling-point VOCs. The replacement frequency of a zeolite concentrator in a TFT-LCD plant could be less than two years without applying the condenser. Thus the opto-

electronic industry may also be beneficial from the integrated system of condenser/zeolite concentrator. The integrated system of condenser/zeolite concentrator is also applicable to remove VOCs emitted from painting booths of automobile, aircraft, and printing industries, etc.

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