

Development of Adsorption Buffer and Pressure Swing Adsorption (PSA) Unit for Gasoline Vapor Recovery

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Abstract—The effect of a double layered adsorber on the recovery of gasoline from gas emitted from a gasoline storage tank was investigated. The adsorber consists of two different adsorbents: silica gel and activated carbon. A pilot system consisting of an adsorptive buffer for the collection of contaminated air sporadically emitted and a PSA system was installed and operated. Gas from a gasoline tank was fed to the adsorption buffer for a period of time, and subsequently the enriched hydrocarbon stream obtained during the regeneration of the adsorptive buffer was treated by the PSA system. Regeneration of the adsorbent was done by flowing clean air under vacuum. Approximately 21-48 liters of gasoline per hour was recovered with the pilot-scale PSA unit filled with 435 kg of adsorbent in total. The gas emitted from the system contains light hydrocarbon less than 100 ppmv.

Key words: Adsorptive Buffer, Gasoline Vapor, Pilot Unit, PSA

INTRODUCTION

Volatile organic compounds (VOCs) in the atmosphere comprise a number of chemicals with various properties. Some of these compounds directly influence human health. VOCs are also important precursors of photochemically formed secondary pollutants, such as ozone, which poses a serious air pollution problem. Since individual VOCs react at different rates with different mechanisms, they make different contributions to the photochemical ozone formation.

Various technologies have been introduced for the treatment of VOCs [Jung and Hong, 2003; Yoo et al., 2003]. Adsorbent-based separation processes for the separation of multicomponent gaseous mixtures are becoming increasingly popular [Na et al., 2001; Choi et al., 2003; Chang et al., 2004; Jeon et al., 2004]. Adsorption technology nowadays is being implemented successfully for its commercial applications to the removal of VOCs [Ghoshal and Manjare, 2002].

The evaporation loss of gasoline occurs from distribution facilities and storage tanks at the ambient temperature. Approximately 0.1 to 0.3% of liquid gasoline is evaporated to the atmosphere every time where it is loaded from a storage tank to a tank truck. For controlling evaporative emission and the gasoline recovery, different vapor recovery unit (VRU) methods based on adsorption, membrane, and chilled pressurized absorption have been applied. The contaminated air is emitted sporadically to the atmosphere associated with intermittent loading operation on gasoline distribution sites. When this instantaneous vent flow is to be treated directly, the installation cost for a VRU becomes very high and the efficiency of daily utilization becomes low. In order to reduce the size and cost of the VRU equipment, a vapor holding tank containing an internal floating vapor bladder is used to accumulate vent flow

surges for subsequent treatments [Pezolt et al., 1997; Wongwises et al., 1996].

In this paper, PSA process consisting of an adsorptive buffer and a two-bed PSA unit was investigated in order to treat the contaminated air with gasoline compounds. Instead of a vapor holding tank, an adsorptive buffer was used to accumulate the sporadic vent flow, and subsequently the enriched hydrocarbon stream obtained during the regeneration of the adsorptive buffer was treated by a double layered PSA system. We analyzed the effect of the regeneration condition of the adsorptive buffer on the gasoline recovery through the PSA unit and the hydrocarbon concentration in clean air released from the PSA unit to atmosphere.

EXPERIMENTAL

1. Equilibrium Isotherms

The typical concentration of gasoline vapor was 19.2% C₄'s, 8.0% C₅'s, 2.6% C₆'s and 0.2% C₇'s with the balance air. Equilibrium isotherms for pure nC₄, iC₅ and nC₆ were established by using the microbalance (RUBOTHERM) on silica gel (RD, Fuji Syllisia) and activated carbon (BPL F-3, Cargon Carbon Corp.) at 20, 40, and 60 °C. The adsorbates used were n-butane, i-pentane, and n-hexane.

2. Cyclic Operation

A schematic diagram of the proposed vapor recovery unit is provided in Fig. 1a for the treatment of contaminated air. It consists of an adsorptive buffer (O.D 80 cm×170 cm H), two adsorbers (O.D 25 cm×1.2 m H), a condenser, and an oil-sealed vacuum pump (7.5 kWh). Each adsorption bed was packed with silica gel and activated carbon in equal volume. The former in the upper part of the adsorption bed can remove C₆'s and a part of C₅'s and the latter adsorb C₄'s and a part of C₅'s. The feed gas to the system was obtained by bubbling air to the gasoline reservoir (O.D 80 cm×1.8 m H). The flow rate of air to the gasoline reservoir was maintained at 1,300-1,350 Nl/min.

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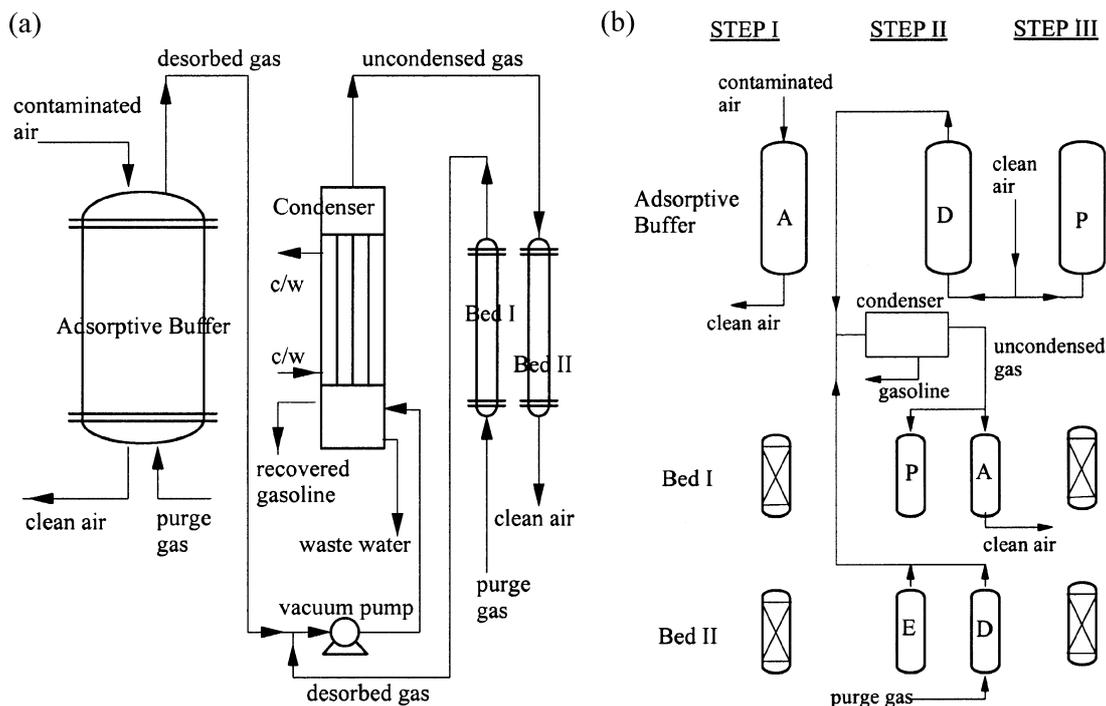


Fig. 1. Schematic diagram of gasoline recovery unit (a) and operation sequence of the proposed vapor recovery unit (b): A - Adsorption, P - Pressurization, D-Desorption with purge, E-vacuum evacuation.

The proposed VRU was operated with three steps in sequence as shown in Fig. 1b. In Step I, hydrocarbons in the feed gas are adsorbed on the adsorptive buffer and the clean air is released to the atmosphere. Step I is continued until the hydrocarbons in the effluent reach to the concentration level of 0.05-0.5 vol%. The hydrocarbon concentration was analyzed by using a gasoline vapor detector (COSMOTECH XP-311A) which was calibrated with iC_4 . In step II, the adsorptive buffer is regenerated by lowering the pressure under a vacuum with flowing the purge gas. The purge gas flow rate was varied from 50 to 200 Nl/min. The enriched hydrocarbon gas discharged from the oil-sealed vacuum pump was fed to the bottom of the condenser where gasoline is recovered. The gas stream leaving the top of the condenser was treated continuously with a two-bed PSA system which was operated in the four-step sequences of pressurization (P), adsorption (A), vacuum regeneration (E), and desorption with purge (D). The adsorption pressure was maintained around 780 mmHg and desorption pressure from 65 to 100 mmHg. The flow rate of purge gas introduced to the adsorber during the desorption process was varied from 30 to 40 Nl/min. The enriched hydrocarbon stream from the adsorber undergoing vacuum regeneration (E) and desorption with purge (D) was introduced to the bottom of the condenser along with desorbed gas from the adsorptive buffer. In step III, the adsorptive buffer was pressurized with purge gas to atmospheric pressure.

RESULTS AND DISCUSSION

1. Equilibrium Isotherms

Isotherms for pure nC_4 on activated carbon and pure iC_5 and pure nC_6 on silica gel are shown in Fig. 2a and 2b, respectively. The isotherm of nC_4 on activated carbon is of the favorable type, while the

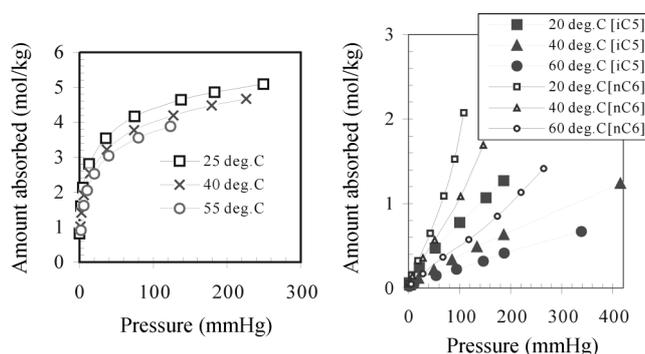


Fig. 2. Equilibrium isotherms for (a) n-butane on activated carbon, and (b) i-pentane and n-hexane on silica gel.

isotherms of iC_5 and nC_6 are of linear type. It may be seen that silica gel is profitable for the removal of relatively heavy components in gasoline vapor mixture and easily regenerated by lowering the pressure.

2. Cyclic Operating Results

In the same operating sequence as shown in Fig. 1a, repetitive adsorption and desorption was carried out. Gasoline vapor was fed to the adsorptive buffer at the rate of 1,450-1,500 Nl/min. The flow rate decreased with time during the collection of the contaminated air by the adsorptive buffer due to the decrease in the amount of most evaporable hydrocarbon components in the gasoline reservoir.

With an adsorptive buffer packed with 435 kg of adsorbent, the contaminated air could be collected for about 57 minutes. Then, the clean air with iC_4 concentration of less than 0.001 vol% could be released to the atmosphere, and for a period of 52-57 minutes the hydrocarbon content increased sharply from 0.001 to 0.15 vol%.

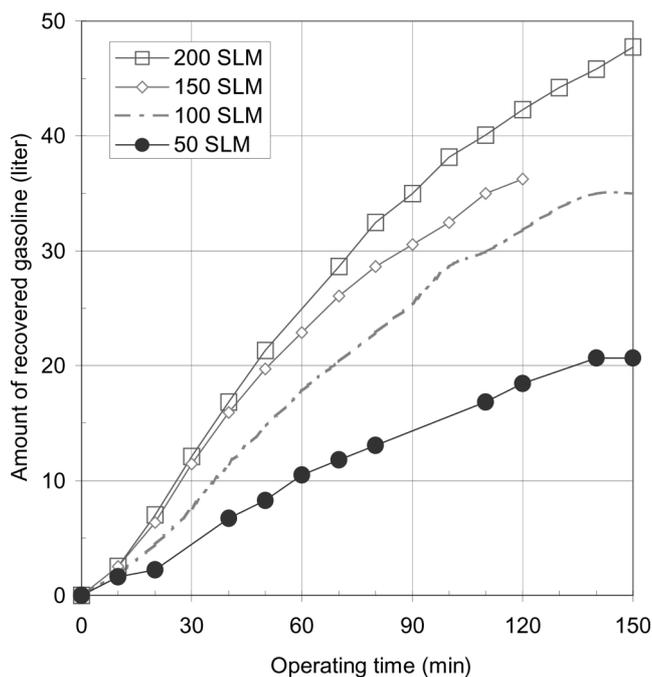


Fig. 3. Effect of purge gas flow to the adsorptive buffer on the amount of recovered gasoline.

Average concentration of hydrocarbons in the gas from the adsorptive buffer during the collection of the contaminated air was estimated less than 0.01 vol%.

During the regeneration of adsorptive buffer, the effect of flow rate of purge gas on the performance of the proposed VRU was investigated. The regeneration of the adsorptive buffer was carried out for 120-150 minutes (Fig. 3) at the different flow rates (50, 100, 1,500 and 200 Nl/min) of the purge gas. However, the flow rate of purge gas to the two-bed PSA adsorber, in step I and step II in Fig. 1b, was kept at 30-40 Nl/min. Fig. 3 shows the amount of recovered gasoline depends upon the purge gas flow rate fed to the adsorptive buffer. It was clear that the purge gas flow rate played an important role in the desorption of gasoline compounds.

The larger flow rate of purge gas for a given adsorptive buffer and desorption duty leads to the more efficient desorption of gasoline compounds from silica gel and activated carbon. During the regeneration of the adsorptive buffer, 21 to 48 liters of liquid gasoline which is equivalent to 0.016 to 0.036 liter-gasoline/kg-adsorbent/hr was recovered depending on the purge gas flow rates, which corresponds to the electricity consumption of 0.31-0.65 kWh/liter-gasoline.

In this process, the enriched hydrocarbon stream leaving the oil-sealed vacuum pump during the regeneration of the adsorptive buffer was connected to the bottom of the condenser where the temperature was maintained at about 25 °C. At the bottom of the condenser, a part of enriched hydrocarbons reabsorbs in cold gasoline and the uncondensed stream from the top passes through the adsorber of the two-bed PSA system. To meet the environmental regulations on gasoline emission, the operating conditions should be optimized in terms of vacuum pressure, flow rate of purge gas, and cycle time. The two-bed PSA was operated with the cycle time of 840 seconds (14 min), i.e., 15 seconds for evacuation (E), 15 seconds

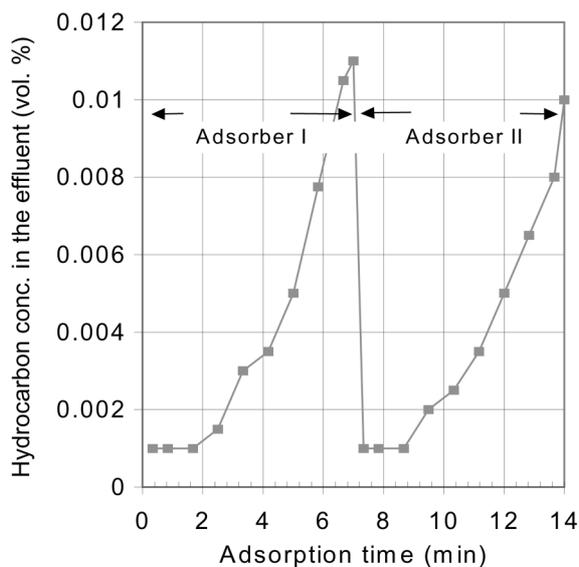


Fig. 4. Hydrocarbon concentration in a vent stream from two-bed PSA.

for pressurization (P), 405 seconds for adsorption (A), and 405 seconds for desorption with purge (D) (Fig. 1b). As other process conditions, the end pressure of the adsorption bed was kept at about 100 mmHg. Fig. 4 shows the variation of hydrocarbon concentration of the gas from the two-bed PSA adsorbers during the cyclic runs.

CONCLUSIONS

For the recovery of gasoline from the contaminated air sporadically emitted from loading facilities, the feasibility of a vapor recovery unit consisting of a fixed-bed adsorptive buffer and two-bed PSA system was investigated. Instead of a vapor holding tank, an adsorptive buffer can be used for the treatment of an intermittent vapor emission. Through the operation of the vapor recovery unit, 21 to 48 liters of liquid gasoline, or 0.016 to 0.036 liter-gasoline/kg-adsorbent/hr, was recovered depending on the purge gas flow rates to the adsorptive buffer, which corresponds to the electricity consumption 0.31-0.65 kWh/liter-gasoline.

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