

Calculation Method of Adsorption and Desorption Performance of Butane Gas in Carbon Canister

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ABSTRACT

This paper presents how Computational Fluid Dynamics tool can be used for the numerical evaluation of n-butane adsorption and desorption performance in carbon canister.

Formula of material balance within activated carbon particles and formula of material/heat balance within activated carbon packed beds for n-butane as a single component were used in the simulation. These formulas were derived after experiments proved that water vapor in the air do not inhibit the adsorption of n-butane.

The experiments and the formulas are described and the significance of the simulation is investigated.

INTRODUCTION

Evaporative fuel gas from the fuel tank of the gasoline vehicle into the air is strictly controlled by regulations. Therefore, vehicles are equipped with an evaporative loss control device, in which one of its major parts is the carbon canister filled with activated carbon. Evaporation of evaporative fuel gas into the air can be prevented by adsorption/retention in activated carbon and by desorption/combustion. (Figure1).

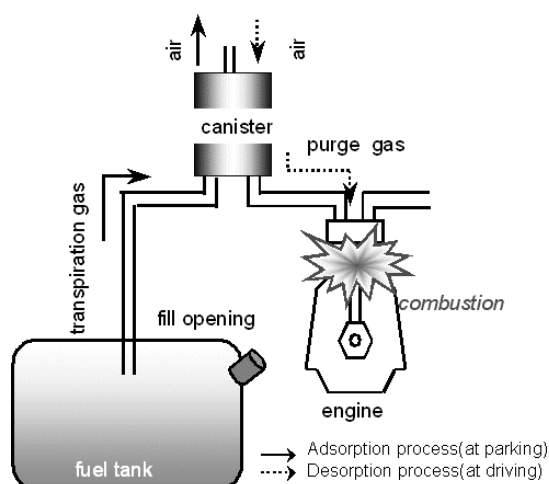


Figure 1. Schematic drawing of evaporative loss control device

Yamamoto et al [1], Lavoie et al [2], and Bai et al [3] have discussed in their papers the adsorption and desorption of evaporative fuel gas. These papers have reported the technology to simulate the adsorption and the desorption performance of carbon canister with 3D model using commercially available Computational Fluid Dynamics (hereinafter referred to as CFD) tool. However, so far, the development of 3D simulation technology based on the adequate experimental validation for the adsorption and desorption of hydrocarbon gas, a major component of evaporative fuel gas, has not been reported. As a result, canisters are designed by the trial-and-error method. Therefore, optimal designs based on the theoretical analysis of adsorption have not been achieved.

Although canister performance design by 3D fluid simulation with the CFD tool is effective for reducing the development period, 3D modeling system of aggregate of solid particles, such as activated carbon packed beds cannot be easily constructed. With STAR-CD, which is a commercially available CFD tool, modeling system of

fluids in discontinuous resistive elements as porous media can be easily constructed. Established balance formulas can be incorporated into the solver as subroutine program that can be created by the user. So, STAR-CD is used for this simulation.

ACTIVATED CARBON PERFORMANCE EXPERIMENT

In order to develop an effective simulation technology that will optimize product design, it is essential to know the adsorption phenomena under real conditions. Since the canister used in the actual vehicle inhales a large amount of air with water vapor at the same time of purge, there is a rising concern that the performance of high-performance activated carbon for gasoline vapor adsorption may deteriorate. Therefore, adsorption isotherm tests of n-butane, that are major components of evaporative fuel gas, and of water vapor were conducted in order to verify effects of water vapor on n-butane adsorption.

Figure 2 shows the results of adsorption isotherm test of n-butane and water vapor as separate single components.

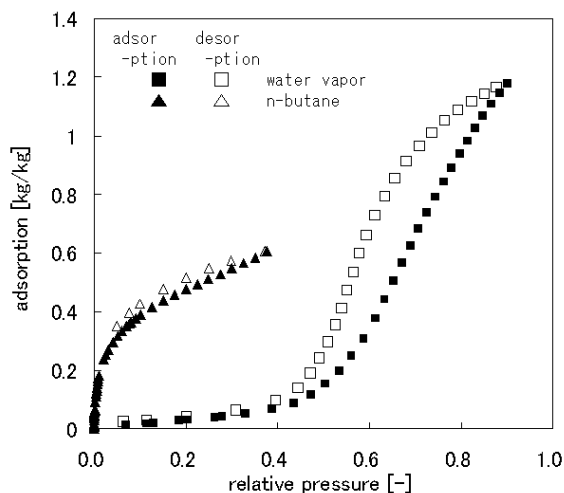


Figure 2. n-butane & water vapor adsorption & desorption isotherm curves (303K)

Looking at the entire range of relative pressure, the result of the adsorption isotherm curve shows that hysteresis is confirmed as the physical property of both n-butane and water vapor in most of the pressure range. This property is exhibited because the capillary condensation made the state of adsorption inside the pores of activated carbon particles close to that of liquid. Also, in the low-pressure range, n-butane bears a relatively adequate adsorption amount compared to that of water vapor. Water vapor exhibits adsorption characteristic specific to hydrophobic adsorbent, that is, adsorption amount is low. But, water vapor begins to adsorb rapidly around the relative pressure of 0.4. Thus,

there is a concern that water vapor might inhibit the adsorption performance of n-butane. To confirm if this concern is real or not, another adsorption isotherm test in binary adsorption of n-butane and water vapor was conducted.

Under normal circumstances, in the case that adsorption isotherm curve of each component and concentration of component are clarified in the vapor-phase adsorption of multicomponent, each formula assumes the mono layer adsorption since the amount of equilibrium adsorption of multicomponent can be obtained from the assumptive calculation, based on the Langmuir formula and Langmuir-Freundlich formula in reference [4]. However, as shown in Figure 2, since hysteresis is confirmed as the physical property of this activated carbon in both adsorption and desorption processes, it is considered that capillary condensation causes both n-butane and water vapor to be adsorbed close to the liquid state in this activated carbon. Therefore, this assumptive calculation is not applicable to this case.

Since the condition at the time of desorption was taken into consideration, the adsorptive equilibrium characteristics in binary adsorption of n-butane and water vapor, under the condition of nitrogen distribution as a carrier gas, were examined. The experimental devices are shown in Figure 3.

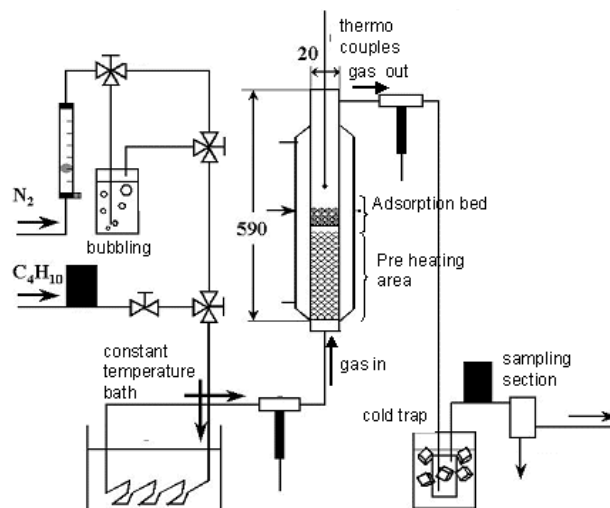


Figure 3. Schematic diagram of experimental devices

In this experiment, each flow volume of nitrogen, n-butane, and water vapor fluctuated so that the molar fraction in the sum of flow volume of each component could be constant when the n-butane concentration was measured by keeping the consistent condition of inside the packed bed for adsorption with 303 K.

When the fluctuation of molar fraction of n-butane is set as a parameter, the flow volume conditions of each component are shown on Table 1.

Table 1. Experimental condition

C ₄ H ₁₀ :H ₂ O	N ₂ [ml/min]	C ₄ H ₁₀ [ml/min]	H ₂ O [ml/min]
0.25 : 0.75	455.0	5	15
0.5 : 0.5	455.0	10	10
0.75 : 0.25	303.3	10	3.33

The amount of equilibrium adsorption obtained from these results and the equilibrium adsorption of n-butane and water vapor obtained from the single component are plotted against the molar fraction of n-butane are shown in Figure 4.

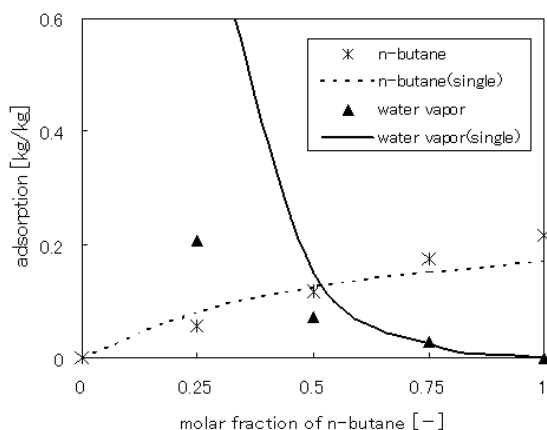


Figure 4. Amount of equilibrium adsorbed in single and binary adsorption

It became clear that for the amount of equilibrium adsorption of n-butane in the entire molar fraction of n-butane, the amount of equilibrium adsorption in the single component is nearly equal to the amount of equilibrium adsorption obtained from the experiment of binary adsorption within the range of experimental error. As for the amount of water vapor adsorption, the amount of equilibrium adsorption obtained from the test of adsorption isotherm in binary components is no greater than the amount of equilibrium adsorption in single component. These findings show that in the case where n-butane and water vapor coexist, n-butane adsorption to activated carbon is given priority leading to inhibition of water vapor adsorption.

In order to examine the factors that give priority in the adsorption of n-butane, the adsorption volume of adsorbate that occupies inside the pore and the adsorption area that occupies the pore wall are put together based on the obtained amount of equilibrium adsorption. The result is shown in Table 2.

Table 2. Possessions of pore volume or pore wall surface

	Volume of adsorbate			Cross-sectional area		
	[l/kg-adsorbent]			[m ² /kg-adsorbent]		
Molar fraction of butane	C ₄ H ₁₀	H ₂ O	sum	C ₄ H ₁₀	H ₂ O	sum
0.25	0.099	0.207	0.306	274000	904000	1178000
0.50	0.206	0.073	0.279	571000	318000	889000
0.75	0.308	0.027	0.335	854000	120000	974000
1.00	0.381	0	0.381	1056000	0	1056000

Table 2 shows the adsorption volume is calculated based on the liquid density of each component at the adsorption temperature; whereas the adsorption area is calculated based on the cross-sectional area of each component molecule. These results prove that under any conditions, the values are smaller than the pore volume of this activated carbon (1.03l/kg) and specific surface area (1490000.0m²/kg). Whereas the occupied volume of internal space of pore (sum of n-butane adsorption and water vapor adsorption) is approximately 30% to 40%, the occupied area of pore wall reaches 60% to 80% of the specific surface area. Based on this result, it is considered that inhibition of water vapor adsorption is caused by the preferential occupation of n-butane molecule in the pore wall of this activated carbon. This finding is reasonable considering the viewpoint of affinity between n-butane and activated carbon.

The results show that water vapor does not inhibit n-butane adsorption with activated carbon. The effects of water vapor on the n-butane adsorption and desorption calculation can be ignored. Thus, the next step of this study, simulation, can then be carried out.

PRECISE ADSORPTION AND DESORPTION SIMULATION

HYPOTHETICAL CONDITIONS AND BASIC FORMULAS

Based on the adsorption isotherm test that water vapor is insignificant, nitrogen gas was used as the carrier in the simulation of n-butane as a single component, so that the adsorption and desorption performance can be evaluated. As for the experimental device for activated carbon packed bed for adsorption, an analysis model of schematic diagram to carry out the simulation is shown in Figure 5.