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다양한 여재를 이용한 자동차 증발가스 저감용 Hydrocarbon-트랩에 대한 연구

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The Study on Hydrocarbon Trap Based on Various Media to Reduce Evaporative Emission from Automotive Vehicles

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초록: 본 논문에서는 자동차의 증발 가스를 효과적으로 감소시킬 수 있는 탄화수소(HC)-트랩을 제조하였다. HC-트랩은 분말화된 네 종류의 활성탄을 함유하는 각각의 수용액에 부직포를 침지시키는 방법으로 제조하였다. 제조된 HC-트랩은 주사 전자 현미경(SEM), porosimeter(기공크기 측정) 및 tensometor(기계적 특성)로 특성을 조사하였다. 또한 증발가스의 흡착성능을 측정하기 위하여 butane working capacity(BWC) 및 차량 증발 배출 시험을 실시하였다. 중간 공극이 높은 경우의 HC-트랩은 높은 BWC 및 낮은 차량 증발 배출량을 보여주었다. 또한 HEEL 안정화 실험에서 상대적으로 크기(5~11 nm)가 작은 중간공극들은 증발가스에 의해 쉽게 포화될 수 있음을 알 수 있었다. 결론적으로 제조된 HC-트랩은 차량 증발가스의 우수한 배출성능과 증발 배출량의 높은 감소를 보여 주었으며, 차량 전체 배출가스 중 18.4 mg의 감소를 나타냈다.

Abstract: This paper reports on the preparation of hydrocarbon (HC) trap, which can exhibit the capability to effectively reduce evaporative emission from automotive vehicles. The preparation of HC-trap was accomplished by a dipping method which involved the immersion of a nonwoven material in an aqueous solution containing powdered activated carbon. Four kinds of activated carbon are used for HC-trap preparation. HC-traps were then characterized by scanning electron microscopy (SEM), porosimeter (measurement of pore size) and tensometer (mechanical properties). We conducted butane working capacity (BWC) and vehicle evaporative emission test to check adsorption performance of evaporative emission. Given the high mesopore volume, the HC-traps exhibited high BWC and low vehicle evaporative emissions. It was also revealed that relatively smaller pore size (5~11 nm) of mesopore could be easily saturated by evaporative emissions with HEEL stabilization. Finally, prepared HC-trap showed excellent performance of vehicle evaporative emission test and high reduction of evaporative emissions which showed 18.4 mg of reduction of total vehicle emissions.

Keywords: hydrocarbon-trap, evaporative emission, automotive.

Introduction

Environmental pollution has become a critical problem in recent years. Air is essential for the survival of organisms. Atmospheric contamination can be lethal to organisms.[1] Atmospheric contamination stems from the combustion process, organic solvent and whole industries but the emission from mobile sources has around 24% of the whole of the emissions.[2] Global vehicle sales are growing continuously at approximately 5% every year.[3] The emerging market is pulling sales volume increase. But the China market which is the biggest market among emerging markets showing the decreased rate of sales increases, and global vehicle sales have been recently shown to increase by just 1.9%.[4]

In particular, automotive vehicles are one of the well-known pollution sources. As such, many countries have constituted and imposed new laws and regulations to minimize environmental pollution. Automotive vehicles generate various

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gaseous emissions containing hydrocarbons. The major composition of hydrocarbons are butane (C4) ~ dodecane (C12) which are hazardous to human health.[5] So, highly restricted regulations are proposed every day to reduce evaporative emission.[5] Low emission vehicles III (LEV 3) is the most restricted regulation for evaporative emission reduction.[6,7] Maximum evaporative emission of LEV 3 is 0.3 g/test. The evaporative emission is often produced from fuel systems and some technology including Canister is applied to reduce hydrocarbon-based gases in fuel tanks.[8,9] However, reduce of evaporative emission with current technology is not enough to meet ever-intensifying regulation.[10]

In this study, a HC-trap system is newly introduced to reduce the evaporative emission coming out through the air intake system of vehicles. A new concept of HC-trap can reduce evaporative emission effectively because air intake system does not have any technology to reduce evaporative emission. Four kinds of activated carbon were selected, and their effects on the performances of new HC-trap based on their mechanical properties and pore properties were investigated. Tests were performed on the butane working capacity (BWC) to check its performance and then vehicle evaporative emission test.

Experimental

Materials. Activated carbons were obtained from diverse countries such as Japan, USA, and China to examine the adsorption of evaporative emission. All activated carbons were obtained from wood and were activated by gas and chemical activation process. Polyethyleneterephthalate (PET) nonwoven, thermoplastic polyurethane (TPU) were obtained from Japan Vilene Company, and Freudenberg Filtration Technologies.

Preparation of HC-trap Media. 20~100 μm powdery activated carbons were deposited on nonwoven polyethyleneterephthalate (PET) substrate material and were selected to prepare HC-trap media. And thermoplastic polyurethane (TPU) was used to bind the activated carbon on the base nonwoven material. Water was used as a solvent to thoroughly mix granular activated carbons and TPU powders homogeneously.

Pore Properties of Activated Carbon. The pore properties of activated carbons were analyzed by BET (Quadroasorb SI, Quantachrome Company, USA), which can measure the surface area of materials using the equation below (1).

$$\frac{\frac{P}{P_0}}{V\left(1-\frac{P}{P_0}\right)}=\frac{1}{V_m C}+\frac{C-1}{V_m}\times\frac{P}{P_0} \tag{1}$$

P/P_0: relative pressure
V: molar volume of the adsorbate gas (at P/P_0)
V_m: volume of adsorbate gas constituting a monolayer of surface
C: BET constant

Porosimeter (AutoPore IV 9520, Micromeritics Company, USA) was also employed to examine open and closed pores using mercury. This analysis is known to be favorable for bigger pore sizes compared to the BET approach, where the pore size was calculated using the following eq. (2).[11]

$$D=\frac{-4\,\tau\cos\theta}{P} \tag{2}$$

P: Pressure
D: Pore diameter
τ: Surface tension of mercury
$\cos\theta$: Contact angle between pore surface and mercury

Preparation of HC-trap. The HC-trap was prepared with powdery activated carbon with powdery TPU on P nonwoven material to attach on the part of vehicles. In this study, we used 100% PET dry laid nonwoven as base nonwoven and similar size of activated carbon and TPU powder. And we suggested the concept structure of media type as shown in Figure 1.

The composition of the raw material solution is shown in Table 1.

The media type HC-trap was prepared with the raw material solution with the preparation process (Figure 2).

First, the base nonwoven is supplied with un-winder then the nonwoven passes through the dipping bath filled with the acti-

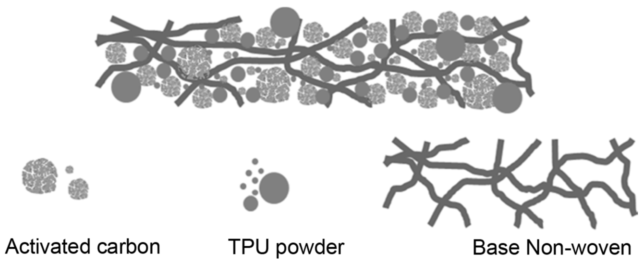

Figure 1. Concept scheme of a HC-trap.

Table 1. Activated Carbon Solution Composition of HC-trap Media

	AC	TPU	Di-Water
KFT-100 (AC-100)	20.9%	3.5%	75.6%
KFT-200 (AC-200)	20.9%	3.5%	75.6%
KFT-300 (AC-300)	20.9%	3.5%	75.6%
KFT-400 (AC-400)	20.9%	3.5%	75.6%

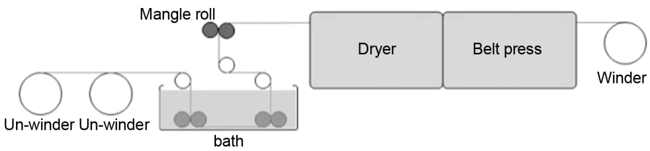

Figure 2. HC-trap preparation process scheme.

vated carbon solution. The mangle roll is located in the next step to squeeze the activated carbon solution. The dryer is the next step to dry water and make TPU powder partially molten at 180 ºC for 10 min. And the next step is belt press to press all together to increase density for mechanical strength with 200 ºC and 6 bar for 30 sec. The final step is winder for the HC-trap.

SEM Image and Pore Properties of HC-trap. Prepared HC-trap was analyzed with SEM and Porosimeter. SEM images were analyzed by SU8220, Hitachi company, Japan, to verify combination among activated carbon, TPU, and base nonwoven. The pore properties of HC-trap were analyzed by porosimeter as activated carbon analysis. But the HC-trap has TPU and base nonwoven material, so pore volume of HC-trap will be decreased compared to the same amount of activated carbon itself.[12,13]

Performance Test of HC-trap. To check the performance of HC-trap, HC-trap was installed on the wall of air-cleaner box and tests were conducted. Performance tests on HC-trap were conducted using butane gas. First, butane working capacity (BWC) test was conducted. Then, HEEL stabilization was processed to saturate pores in activated carbon. Saturated pores no longer absorb appropriate gases and cause performance to decrease.[14,15] And then BWC test was conducted to check absorption ability with saturated pores. We called the first BWC test the pre-BWC test, and after HEEL BWC test is a post-BWC test. The BWC and HEEL procedures are summarized in Table 2.[16]

Table 2. Test Procedure of BWC (Butane Working Capacity) and HEEL Stabilization

		Test procedure
BWC	Cycle	13 cycle of loading and purging
	Pre conditioning	110±5 ºC, 3 h
	Loading	50:50 butane:nitrogen 10.0±0.5 g/hr (89.3 mL/min) Saturation : 54 mg of break through
	Purging	2200 ft^3 with 19.3 ft^3/min (546.5 L/min for 114 min)
HEEL	Cycle	500 Cycle of loading and purging
	Pre conditioning	110±5 ºC, 3 h
	Loading	50:50 (40:60) fuel vapor and nitrogen, 24±2 ºC 10.0±0.5 g/hr until saturated
	Purging	Air flow rate of 96.5 ft^3/min and volume of 2204 ft^3 (2.73 m^3/min for 22.8 min)

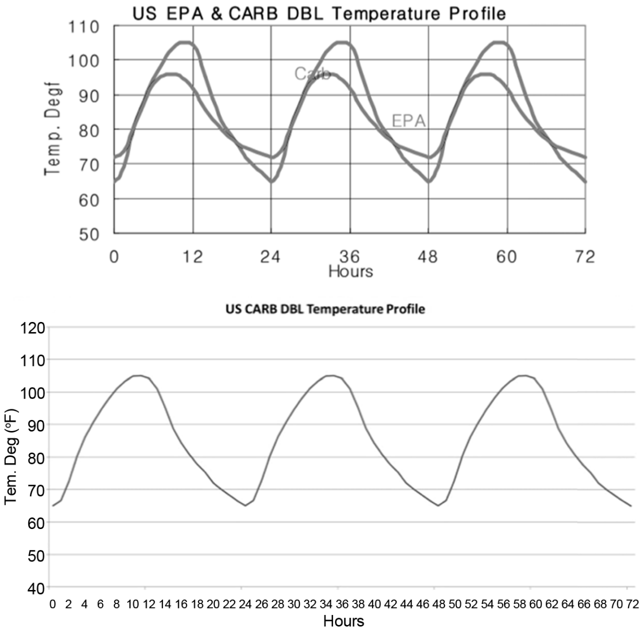

Figure 3. CARB DBL temperature profile.

Evaporative Emission Test with Vehicle. Vehicles were installed in shed to check evaporative emission. Evaporative emission test was conducted with both of diurnal breathing loss (DBL) test and hot soak loss (HSL) test. DBL test measures the amount of hydrocarbons (or methanol) generated after the test vehicle has undergone specified temperature changes in a sealed housing for 72 h. It is a regulation to simulate evaporative emission for day stop situation. For DBL test vehicles should be installed in the sealed housing for evaporative determination (SHED). In order to check the evaporative emission vehicles were also placed with the California Air Resource Board (CARB) temperature profile (Figure 3) for 3 days.[6] Evaporative emissions were analyzed by flame ionization detector (FID).

HSL test is a regulation to check evaporative emission directly after driving mode. Fuel temperature is elevated with driving and this hot fuel is re-supplied into the fuel tank. Then heated fuel in the fuel tank is easily evaporable. The HSL test condition is a vehicle placed in 46 °C for 1 h and evaporative emission is analyzed by FID.

Results and Discussion

Pore Properties of Activated Carbon. Porosimeter and BET analysis were performed to analyze the pore structure of activated carbon. Figure 4 showed the comparison of pore volume for the series of activated carbon.

The AC-100 sample showed the lowest mesopore volume of 0.31 mL/g. Mesopore volume of AC-200 and AC-300 are 0.56 and 0.57 mL/g, and AC-400 have the highest pore volume with 0.71 mL/g. BET analysis showed similar pore volume results with porosimeter. BET analysis is of advantage to smaller pore size analysis. However, AC-200 and AC-300 showed different results between porosimeter and BET. Porosimeter of AC-200 and AC-300 were almost the same, but BET of AC-200 and AC-300 showed 0.64 and 0.72 cc/g of mesopore volume. In Figure 5, we found that pore size with 12~50 nm of AC-200 and AC-300 showed similar distribution, but pore volume of AC-300 showed much higher pore volume in the below 11 nm pore size than AC-200.

This result shows BET analysis has high resolution for

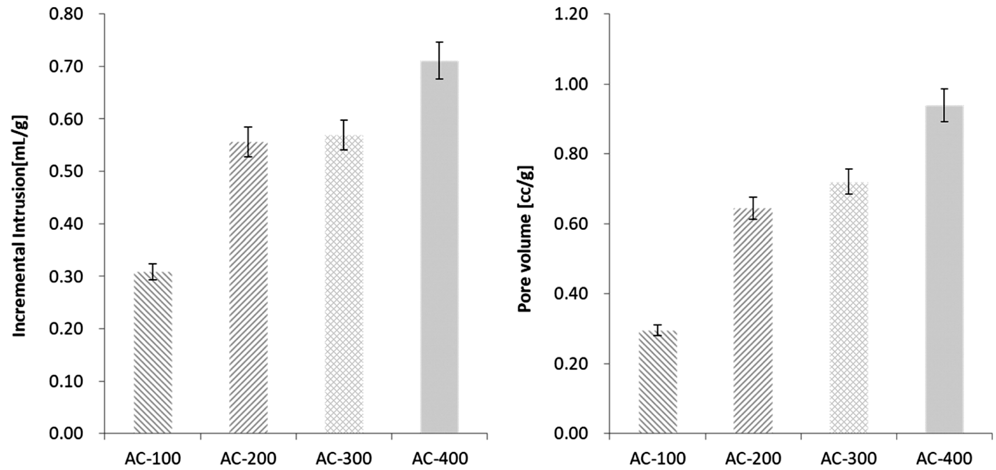

Figure 4. Pore volumes in mesopore size, porosimeter (left) and BET (right).

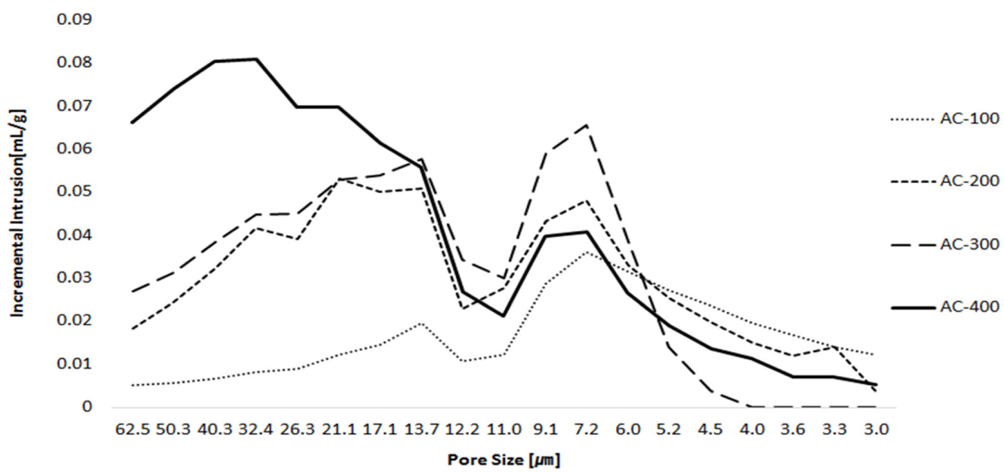

Figure 5. Pore distribution of mesopores of activated carbon.

smaller pore size in the mesopore size range. It can be easily expected that AC-100 has relatively much smaller pores and AC-400 has relatively much larger pores with 12~50 nm.

SEM Image Analysis of HC-trap. Prepared HC-trap structure was analyzed by SEM image. Figure 6 showed SEM images of HC-trap (KFT-100, KFT-200, KFT-300 and KFT-400).

Fibril structure of the image is the fiber of base nonwoven, and the powdery structure is activated carbon and TPU powder. Some pores among the HC-trap structure were observed in the SEM image (white arrows). Air with evaporative emission was passing through these pores into the HC-trap, and evaporative emissions could be adsorbed in mesopores of activated carbon.[9] We found that the TPU powder was homogenously distributed in the structure and binding activated carbon well. The activated carbon powder in the structure was not spilled out to outside when we checked the appearance of HC-trap.

Pore Properties of HC-trap. Pore properties of prepared HC-trap were analyzed by porosimeter to check decrease in pore volume from activated carbon itself. Figure 7 showed pore volume of HC-traps. This result showed how many pore volumes were decreased by the network of base material and TPU. It was found that the around 50~60% pore volume decreased after HC-trap preparation from activated carbon. The complex reason causes the decrease of mesopore volume because TPU and base nonwoven are non-porous materials. We conducted pore volume analysis with De-AC. De-AC can be defined that the activated carbon which is separated from HC-trap. We used these results to check the blocking effect of TPU for activated carbon. De-AC results showed around 70~80% of activated carbon pore volume, which meant 20~30% of activated carbon mesopores were blocked by TPU. Then we performed pore distribution analysis of HC-trap to check the change of pore properties. Figure 8 shows the result and there are no significant changes in pore distribution with HC-trap preparation.

Performance Test of HC-trap. BWC and HEEL stabilization test were conducted to check evaporative emission adsorption performance of HC-trap. BWC tests were conducted using pre-BWC and post-BWC. Pre-BWC results showed a similar trend compared to pore volume analysis according to activated carbon type. These results show that the pore properties and BWC have a close relation to each other. In contrast, post-BWC results showed that KFT-200 and KFT-300 have contrary results between pore volume and BWC. These results show there are some changes with HEEL stabilization (Figure 9).

Post-BWC results show a decrease of BWC performance (Figure 10).

KFT-100 showed 0.15 g of BWC decrease, KFT-200 was

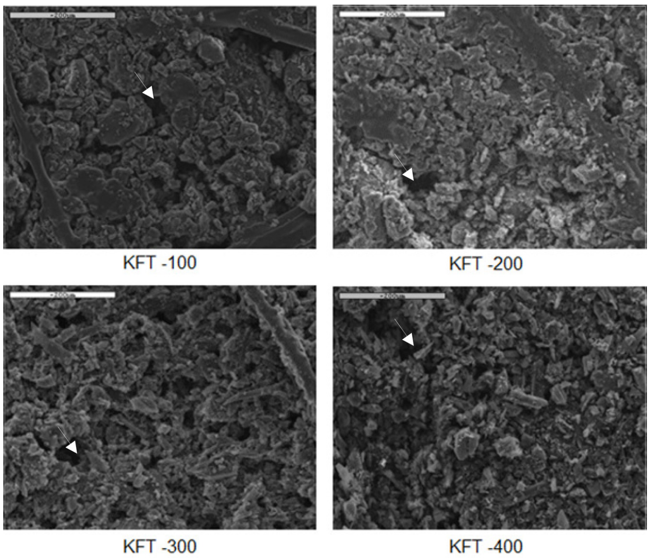

Figure 6. SEM image of a HC-trap.

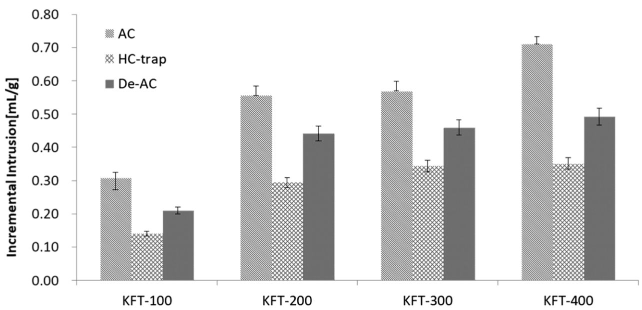

Figure 7. Pore volume in mesopores with AC, HC-trap, and De-AC.

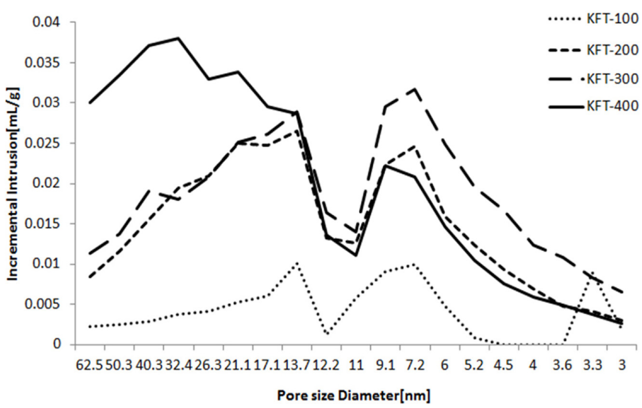

Figure 8. Pore distribution of mesopores of a HC-trap.

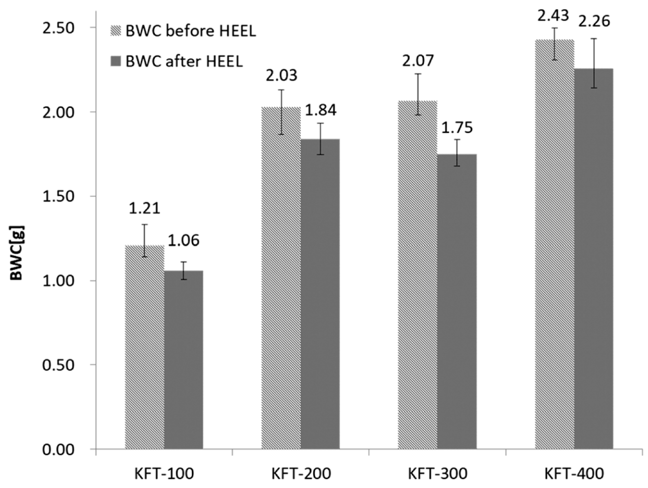

Figure 9. Pre-BWC and post-BWC of a HC-trap.

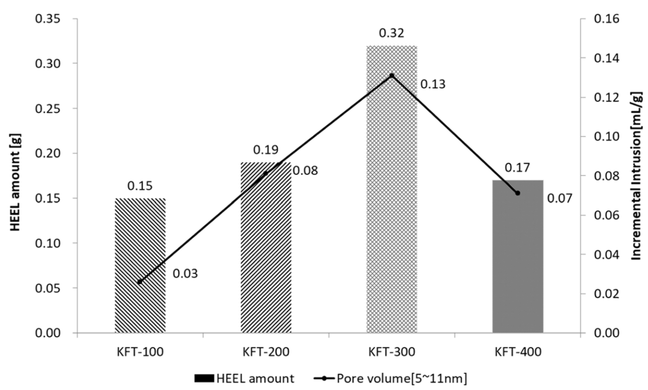

Figure 10. BWC decrease *vs* smaller size pore volume [5~11 nm].

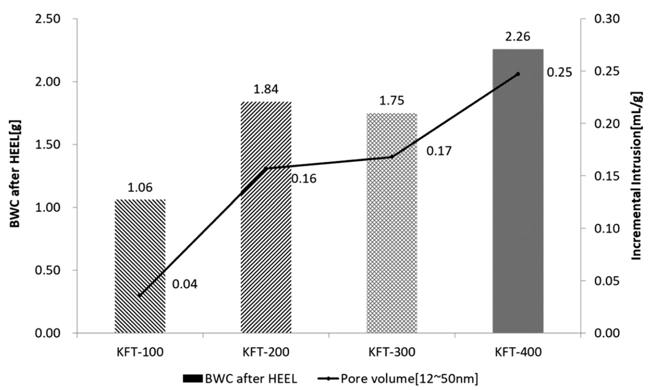

Figure 11. Post-BWC *vs* bigger size pore volume [12~50 nm].

0.19 g, KFT-400 was 0.17 g; however, KFT-300 showed 0.32 g. 0.32 g of KFT-300 is a relatively large value compared to the others. For this reason, we divided the test results into 5~11 nm and 12~50 nm pore volume to figure out the effect of pore size on the amount of BWC decrease. We found that the pore volume of 5~11 nm was very similar to the BWC decrease amount. And, the pore volume of 12~50 nm pore size showed a similar trend with post-BWC. However, only in KFT-200 and KFT-300 were small contrary results shown. We think these results emerge due to the larger macropores, which are over 50 nm. We believe that KFT-200 has more pore volume than KFT-300 in over 50 nm (Figure 11).

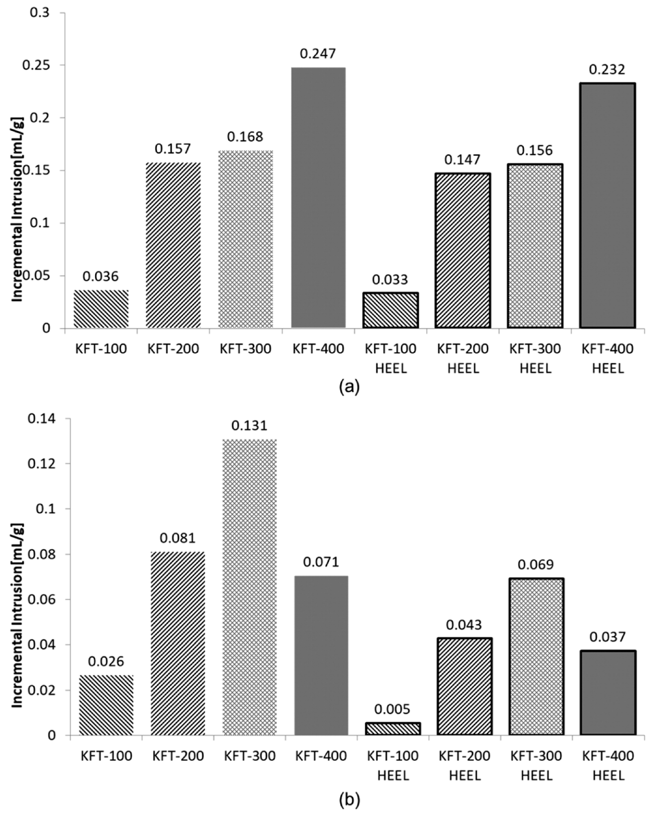

Figure 12. Pore volume before and after HEEL stabilization: (a) 12~50 nm; (b) 5~11 nm.

Based on the test results, 5~11 nm pores can be easily saturated by evaporative emissions. So we conducted analysis on pore properties for after HEEL stabilization. Figure 12 showed pore volume before and after HEEL stabilization.

After HEEL stabilization pore volume showed 92~94% of before HEEL stabilization in Figure 12(a), in contrast, Figure 12(b) showed only 19~53% of pore volume after HEEL stabilization. This result showed that pores under 11 nm were saturated mostly by evaporative emissions. It could be concluded that pore volume decrease by aging with evaporative emission led the decrease in BWC performance.

Vehicle Evaporative Emission Test. Finally, vehicle evaporative emission tests were conducted with prepared HC-trap. Figure 13 showed the test results of the vehicle test. Blank sample with no HC-trap applied showed 252 mg in evapo-

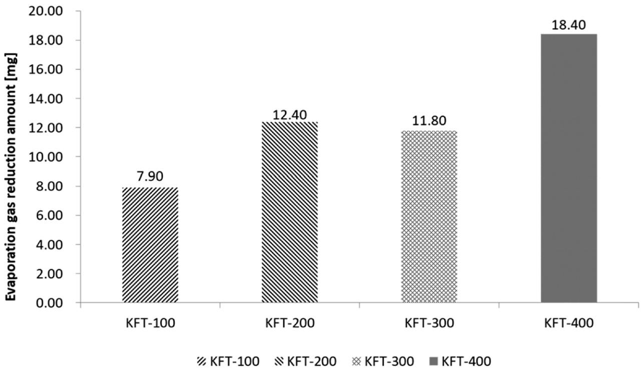

Figure 13. Vehicle evaporative emission test.

rative emission reduction.

KFT-100 showed 7.9 mg, KFT-200 was 12.4 mg, KFT-300 was 11.8 mg and KFT-400 was 18.4 mg reduction. This value is not a big effect compared to the total value, 252 mg. However, the most evaporative emission is coming from the fuel tank and fuel supplying chain, and we assume that the evaporative emission through the air intake system is around 10% of the total. So, when we calculate the reduction ratio based on 10% of evaporative emission in total, KFT-100 has 31.3%, KFT-200 has 49.2%, KFT-300 has 46.8% and KFT-400 has 73% of evaporative emission reduction in air intake systems. These results showed very similar values and trends with pore properties and BWC results. We believe that this study can be applied to evaporative gases adsorption studies for further research.

Conclusions

In this study, we developed HC-trap with powdery activated carbon, TPU, and base nonwoven. The pore property analysis of each activated carbon was conducted using porosimeter and BET to investigate the adsorption performance for evaporative emissions. The pore properties of HC-trap were also performed using porosimeter. The pore volume of HC-trap showed 50~60% pore volume of activated carbon. It was found that the reduction of pore volume occurred by TPU and base material in HC-trap structure. And we analyzed the pore properties of decomposed activated carbon to discover a blocking effect of TPU on the activated carbon surface. The pore volume of de-activated carbon showed 70~80% pore volume of the activated carbon. This result means that 20~30% of pores in activated carbon are blocked by the binding structure with TPU. The BWC performance tests before and after HEEL were conducted to check adsorption performance of HC-trap. We found that BWC performance was increased with increase of pore volume. And we confirmed that pore volume of post-BWC was decreased in all kind of activated carbon. This result means that some of the pores can be saturated by evaporative emissions. We conducted pore property analysis of HC-trap after HEEL stabilization to check the saturation of pores. Our results showed that the pores in a range of 5~11 nm were decreased by around 50%. In this result, we found that smaller pores, especially in a range of 5~11 nm could be easily saturated by evaporative emissions. So, we thought KFT-400 which had relatively bigger size pores in 12~50 nm, showed the best BWC performance in both of adsorption and desorption. Lastly, we conducted evaporative emission vehicle test to check the performance of HC-trap. This vehicle test showed similar results with BWC and pore properties. KFT-400 showed 18.4 mg (73%) of evaporative emission reduction in the vehicle air intake system. This result is a relatively similar value compared to that of the commercial product. But we have a more simple production process which is economically advantageous. We believe this new HC-trap can contribute to environmental friendly technology for life.

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