APPENDIX VIII

ADSORPTION CAPACITY OF IN-USE CARBON CANISTERS - INFLUENCE OF AGEING (CSIRO)

DIVISION OF COAL AND ENERGY TECHNOLOGY
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ADSORPTION CAPACITY OF IN-USE CARBON CANISTERS
INFLUENCE OF AGEING

by

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List of Contents

Adsorption Capacity of Carbon Canisters - Influence of Ageing

Summary

None of the canisters showed significant communition of their carbon granules.

The adsorptive capacity of carbon from in-use and new replacement canisters was measured by exposure to known amounts of butane, hexane and benzene. The extent of contamination by low volatile organic compounds was determined by solvent extraction.

It was estimated that fresh carbon could adsorb about 35 % by weight of hydrocarbons.

In-use carbons were found to have significant amounts of adsorbed material ranging from 5.4% to 25.7 wt % with an average value of 16.4%. It was demonstrated that the presence of adsorbed hydrocarbons reduced the capacity for further adsorption in an approximately proportional manner and that removal of such hydrocarbons that could be achieved by purging restored the adsorptive capacity also in a proportional manner.
Thus the adsorbed material found on the in-use carbons constitutes from 12% to 70% of the likely adsorptive capacity, averaging at 45%.

Analysis of the unpurgeable material recovered by solvent extraction was shown to consist mainly of C_9 to C_{11} hydrocarbons, 30 - 40 % of which was aromatic in nature.

The experiments also allowed measurement of the rates of desorption of butane, hexane and benzene. These became slower the less volatile the adsorbate. The data measured in this study strongly suggest that the heavier or less volatile components in petrol will not be fully desorbed in the purge time available to an urban motor vehicle. Consequently there will be a slow build up of the heavy ends on the canister.

Extensive purging with N_2 (10 $m^{3)}$ at 74^{o}C reduced the average amount 'permanent' adsorbate to 6.2% which represents about 16% of adsorptive capacity. In all probability, most if not all of the adsorptive capacity could be restored by purging at higher temperatures eg 150^{o}C. The feasibility of purging at higher temperatures will depend on the materials used in the construction of the canister.

1 Introduction

This report presents the results of testing carbon canisters removed from in-use motor vehicles whose emissions, both evaporative and exhaust, have been quantified as part of the FORS program. These tests were performed not only on carbon from the original canisters but also on that from the replacement new canisters for comparison purposes.

The objective was to determine if the adsorptive capacity of in-use canisters had deteriorated significantly compared with the replacement canisters, which had been exposed to one ADR37 test. To this end two types of experiments were performed, one to measure the adsorptive capacity, the other to quantify the build-up, if any, of low volatile organic compounds.

It is difficult to use petrol for such tests because it contains many hydrocarbons, both aromatic and aliphatic, (which range from C_4 to C_{12} in molecular size, with an average of C_6). Hence three hydrocarbons were used, butane being the most volatile component plus hexane and benzene to represent the average aliphatic and aromatic hydrocarbons.

2 Experimental Procedures

The following protocol was developed, based on results from preliminary tests on a carbon from a canister sourced outside the test program and on carbon from the first of the in-use test samples.

The canister was opened using a bandsaw or a metal grinder depending on the nature of the canister construction. The carbon granules were weighed and put into an airtight container. The extent of any significant communition was noted at this time. The sample was divided into two aliquots of known weight. One aliquot was extracted with hexane by soxhlet refluxing for 8 h and the solvent hexane evaporated off at room temperature under N_2. This technique quantifies the amount of adsorbed hydrocarbons of size C_8 + . The second portion (~ 200g) was placed in a steel container. This had a fine metal mesh at the bottom and could be closed with a second, spring loaded mesh (much as in the canisters) which was attached to a top plate sealed with an 'O' ring.. The container was suspended from a balance in a temperature controlled oven and attached by a swagelok fitting in the base to a gas supply system. The gas supply was passed along 4 m of 4mm dia copper tube to bring to the oven temperature, and exited from the container through a narrow hole in the top .

The gas supplied to the canister consists of one of the following :

a) ~ 6 l/min purge N_2
b) 1.2 l/min butane + 6 l/min N_2
c) 0.45 l/min N_2 saturated with hexane or benzene + 6 L/min N_2

The partial pressures of the dose hydrocarbons were: butane 0.19 bar, hexane 0.011 bar and benzene 0.0070 bar. The capacity of the carbon was measured for the following conditions:

i) butane in an 'as received' condition at 34^{o}C

ii) desorb at 74^{o}C with N_2 until rate of weight loss was slow (generally 18 h or more) iii) measure butane adsorption at 74^{o}C

iv) re-measure butane adsorption at 34^{o}C followed by hexane and benzene at the same temperature

The relationship between the amount of solvent extracted material and the weight lost during purging was assessed by repeating the solvent extraction on the samples used in the adsorption experiments ie after purging. Some other experiments were also performed to get an indication of the relationship between partial pressure and amount adsorbed.

3 Results and Discussion

No significant communition of the charcoal granules was observed.

A summary of the data is presented in Tables 1 and 2. Table 1 lists the vehicle registration numbers, the weight of the carbon as received, ie immediately after opening, the percentage weight of adsorbed hydrocarbons, the percentage weight of hydrocarbons recovered through solvent extraction with and without purging. The amount of adsorbed hydrocarbons was calculated as the sum of the weight lost during purging in the adsorption experiments plus the weight of materials subsequently extracted by solvent.

Table 1. Canister carbon weights and amount adsorbed

Vehicle	Canister	Wt Carbon (g)				
		As received	net	**% wt Adsorbate**	**% wt Extractable**	**% wt Extractable no purging**
2	old	316.7	252.01	25.67	8.57	17.45
6	old	288.5	230.23	25.31	8.61	19.28
3	old	351.3	298.98	17.50	6.00	12.43
1	old	325	295.66	9.92	7.92	13.37
9	old	450.5	391.50	15.07	5.65	10.59
8	old	352.5	310.16	13.65	8.35	12.07
7	old	239.37	202.11	18.44	3.44	10.00
5	old	342.1	338.30	5.43	1.12	5.26
Average		333.25	288.14	16.37	6.21	12.56
2	new	366.4	321.19	12.34	-	-
6	new	315	292.75	7.60	0.2	0.2
3	new	280.2	273.37	2.50	0.3	0.35
1	new	294.5	284.82	3.4	-	-
9	new	391.5	373.93	4.7	-	-
8	new	347.4	322.89	7.59	-	-
7	new	244.3	232.89	4.9	0.3	-
5	new	355.6	342.1	3.95	-	-
Average		324.36	301.4	7.47		

The validity of this was demonstrated by the fact that the solvent extractable material from carbon that had not been subjected to the adsorption/purge regime was, in all but one cases, greater than the weight extracted from carbon that had.

For the first vehicle in Table 1, it can be seen that 8.57 g of material remained on the carbon after the adsorption experiments, whilst 17.1 g were lost through purging giving a total of 25.7 g adsorbed material per 100g of the carbon when received. The purging volume was typically 10,000 l at 74^{o}C and 20,000 l at 34^{o}C, albeit with occasional doses of butane, hexane and benzene. This quantity lost through purging is considered to be equivalent to the lighter or more volatile portion of the adsorbed fuel.

The new or replacement carbons were expected to have very little solvent extractable material, which was borne out by results from three such carbons, and consequently no further extractions were carried out.

It was found, from some of the earlier experiments, that the amount of hydrocarbons that could be solvent extracted from 'as received carbon' was very similar to that remaining after prolonged purging with N_2 at 34^{o}C. Some limited data on the composition of the extract (see later) indicates that purging at 34^{o}C removes hydrocarbons up to about C_7 in size. Purging at 74^{o}C removes the C_8 and some C_9.

Table 2 lists the degree of adsorption per 100 g C (ie wt %) by the sample in an 'as received' condition of butane at 34°C, and then the amounts of butane, hexane and benzene after purging at 74°C for at least 15 h at 6l /min at the partial pressures listed in the experimental procedure. The final column is the amount of butane adsorbed at 74°C. In some instances for the new carbons, weight loss on purging was rapid enough to prevent sensible determination of butane adsorption for the 'as received' condition.

There is certainly some differences in the adsorptive capacities of the different new, replacement carbons, which, after purging, ranged from 15 - 22 % by wt for butane, 21 - 28 % for hexane and 21 - 30 % for benzene. This may reflect the normal variability in the automotive carbons. The capacities of the in-use carbons for the three test hydrocarbons, again after purging, were less and ranged from 9 - 17.5 %, 11 - 25% and 13 - 23% respectively. This decrease can be attributed to the presence of non-purgeable material.

The capacity of 100g activated carbon for butane at 34°C appears to be around 18 g for the conditions employed here, the values for hexane and benzene each being about 23 g. From extra measurements on the variation of adsorption with partial pressure,
the ultimate capacity for these three components is about 26 g, 30 g and 35 g respectively. If we assume that 35 g/100 g is as much petrol that a typical carbon can adsorb, then the carbons from in-use canisters had their capacity compromised by 30 - 60% by material that is difficult to remove by purging.

Table 2. Capacity of carbon canisters for butane, hexane and benzene

		Adsorption (g /100 g)				
		As received	After purging, 34°C			74°C
Vehicle	**Canister**	Butane	Butane	Hexane	Benzene	Butane
2	old	7.5	17.5	25	25	8
6	old	5	11	14	12.5	4.7
3	old	5	10.5	14	13	-
1	old	10.5	11	14.5	13	5
9	old	6	11	15	14	-
8	old	8.5	9	11	23	-
7	old	7	13.5	18.5	19	8
5*	old	4	6	-	11	-
Average		6.7	11.2	16	16.3	6.4
2	new	-	18	23	23	12
6	new	10	17	22	21	10
3	new	14.5	17	21.5	21	10.5
1	new	-	15	21	21.5	10
9	new	20	20	26.5	27	12
8	new	18	18	22	24	-
7	new	22	22	28	30	14
5*	new	-	15	-	22	-
Average		16.9	17.8	23.4	23.7	11.4

* performed under non-standard experimental conditions and values calculated from the variation of adsorption with partial pressure.

Typical rates of desorption of each of the hydrocarbons used are shown in Table 3 for two temperatures, 34°C and 74°C for the loadings resulting from the hydrocarbon exposure used in these experiments, approximately 40 - 60 % of ultimate capacity.

Table 3 Typical Desorption Times

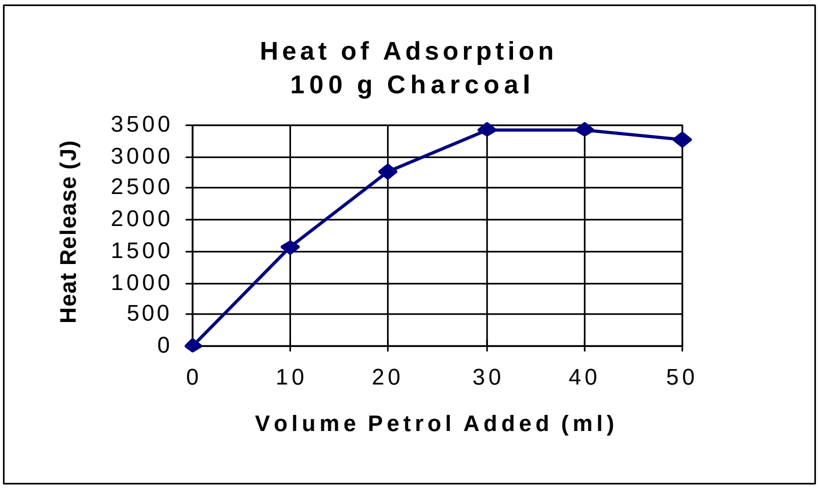
Desorption Time (min)						
Fraction desorbed	**Butane 34°C**	**Butane 74°C**	**Hexane 34°C**	**Hexane 74°C**	**Benzene 34°C**	**Benzene 74°C**
0.5	10-30	5-10	120-330	36	160-270	42
0.9	50-240	14-54	900-3000+	180	1200-3000+	150

The purging rate was ~ 6L/min for ~ 200 g of carbon, equivalent to ~ 10 L/min for a whole canister. The slower desorption rates were associated with carbon from the new or replacement canisters.

A possible explanation for this observation can be found in the heat of adsorption of petrol on clean carbon. We have measured this parameter in a simple, crude, way by adding 50 ml liquid petrol in 10 ml aliquots to 100 g carbon granules in a plastic container and observing the temperature rise. The data, which include a correction for heat loss, are shown in Figure 1, which indicates that this particular carbon had a capacity of ~ 30 - 40 mls per 100 g which released 3500 J. The 'in-use' carbons already had some hydrocarbon adsorbed on to it, which would have used up some of the available energy. Hence further adsorbed hydrocarbon should come off more readily.

Thus, for the in-use canisters, a minimum of 0.9 m^3 would be required to remove 90% of hexane at 34^{o}C and 1.2 m^3 would be needed for benzene, and at least three times as much again for new canisters. Even for butane, 1 h may be required at this flow rate for the in-use canisters. It is easier to imagine, from this data, that the less volatile components of petrol would never be fully removed at near ambient temperatures and would slowly accumulate in the canister, with consequent loss of absorptive capacity. At the higher temperature of 74^{o}C, the desorption rates are improved by about a factor of 5 for the three hydrocarbons, although there is only one measurement for hexane and benzene

Figure 1. Heat released by adsorption of liquid petrol on to carbon



Two of the extracts from the as received, in-use, canisters (Vehicle 6 and Vehicle 3) were examined by gas chromatography. The results showed, on the basis of residence times, that the extracts consisted mostly of C9 to C11 alkanes and aromatic hydrocarbons with small amounts of C8 and C12 compounds. Solvent extraction of a carbon that had been purged at 74°C showed that the C8 and C9 had been removed.

The two extracts were also analysed by NMR for the aromatic carbon content, which was found to be 38.7% and 40.7% respectively. After purging at 74°C, the former value fell to 33.4%. A 50:50 mixture of trimethylbenzene (mesitylenes) and nonane would give 33% aromatic C.

4 Conclusions.

No obvious or significant communition of the carbon granules was observed for any of the canisters

The in-use (ie the old) canisters had from 5.4% to 25.7% by weight of adsorbed material with an average value of 16.4%. The adsorptive capacity of fresh carbon was measured to be approximately 35% by wt. Thus the adsorbed material constitutes from 12% to 70% of the likely adsorptive capacity, averaging at 45%.

The results of the adsorption experiments showed that the presence of adsorbed hydrocarbons reduced the capacity for further adsorption in a proportional manner. Removal of such hydrocarbons that could be achieved by purging restored the adsorptive capacity also in a proportional manner.

The rates of desorption become slower the less volatile the adsorbate. Even for hexane and benzene, purging with N_2 for at least 15 hours at 10 l/min was required to remove 90% of the hydrocarbon. This leads one to expect that the heavier or less volatile components in petrol will not be fully desorbed in the purge time available to an urban motor vehicle. Consequently there will be a slow build up of the heavy ends on the canister. Confirmation of this viewpoint was found in the analysis of the unpurgeable material recovered by solvent extraction which was shown to consist mainly of C_9 to C_{11} hydrocarbons, 30 - 40 % of which was aromatic in nature.

Extensive purging with N_2 (10 m^3) at 74^{o}C reduced the average amount 'permanent' adsorbate to 6.2% which represents about 16% of adsorptive capacity. In all probability, most if not all of the adsorptive capacity could be restored by purging at higher temperatures eg 150^{o}C. At such a temperature, there may be damage to the canister, some of which are almost entirely made of plastic, and most containing some plastic. Care would also be needed to avoid oxidation of the carbon.