Environment Protection Engineering

Vol. 32 2006 No. 2

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VOCs CONTENT IN EXHAUST GAS FROM DIESEL ENGINES DEPENDING ON ENGINE RUN AND CATALYTIC TREATMENT SYSTEM USED

The effectiveness of reduction of volatile organic compounds in exhaust gas from a self-ignition engine was assessed. Theoretically, this efficiency should rise proportionally to engine load and, consequently, to gas temperature. This pattern, however, is disturbed by the formation of products of incomplete combustion in the catalytic afterburner, especially by those of aldehydes, even at high temperature. The efficiency of combustion of individual groups of compounds (aldehydes, ketones, alcohols, aliphatic and aromatic hydrocarbons) was analyzed. Two treatment systems were tested: a soot filter with Ce–Pt and the same filter with Pt–Ce as active agents. Of these, the Ce–Pt system was found to be more efficient. The study has revealed that the assessment of the volatile organic compounds' degradation must include the reduction of the most toxic pollutants.

1. INTRODUCTION

Air pollutants released with car exhaust gases contribute (directly or indirectly) to many ecological hazards. The rising concentrations of volatile organic compounds (VOCs), such as benzene, 1,3-butadiene and polycyclic aromatic hydrocarbons (PAHs) displaying carcinogenic and mutagenic properties, stimulate the development of cancer diseases [1]–[3].

The need to prevent the continuous rise in car emissions (or, furthermore, to considerably reduce the present volume of exhaust gas emitted by travelling vehicles) is a matter of great urgency because of potential health implications, on the one hand, and the necessity for full compliance with the rigorous toxicity standards, on the other hand [4].

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Table

Comparison of standards fixed for toxic compounds emissions [g/mile] in California

Toxic compound	Early 1950s	Recent times [ULEV]
NO_x	3.6	0.2
CO	87.0	1.7
HC, NM-HC	13.0	0.04
PM	no standards set	0.04

Owing to the technological progress in the design of automotive vehicles as well as to the advanced concepts of neutralizing the deleterious substances that are found in the exhaust gas, relevant requirements can be met. The most common approach is the use of catalysts. But there is also a rapid development of catalytic reactors, especially those used in self-ignition engines where the neutralization of solid particles is a problem of concern, as their combustion requires higher temperature than that of the exhaust gas.

Recent years have witnessed the development of many catalytic filter designs, where the combustion temperature of solid particles has been decreased by adding catalysts to the filters [5]–[10]. A promising solution to the problem of interest is the catalytic filter developed and used in Poland. It may be used for any vehicle with a diesel engine emitting large amounts of pollutants in the exhaust gas. The system consists of a filter made of heat resistant steel ("alumel" type) and of a catalyst spread on it [11], [12].

This paper aimed at assessing the content of the VOCs entering the atmosphere together with the exhaust gas from a self-ignition engine.

2. EXPERIMENTAL

Use was made of two treatment systems, with particular consideration being given to the engine running parameters. The efficiency of combustion of individual groups of compounds was analyzed.

The experiments were performed with real exhaust gases, under conditions of engine running in a test house installed at the laboratory of the Institute of Machines Design and Operation, Wrocław University of Technology. The engine under test, an 80 kW self-ignition engine with direct fuel injection, had a catalytic soot filter mounted at the outlet of the exhaust pipe.

Two treatment systems were tested:

1. → [Ce + Pt] → soot filter of KW 400 type, consisting of two parts. In one of these, at the inlet, cerium in the form of chloride was an active ingredient spread on the filter. In the other part, platinum was an active agent.

2. → [Pt + Ce] → soot filter as in item 1, but the inlet part was covered with plati-

num and the other part with cerium.

Based on the European toxicity test (ECE R49; Polish standard BN-84/1374-12), measurements were carried out using an 11-phase load cycle determined by the rotational speed of a crankshaft n (rpm), engine torque Mo (Nm), and exhaust gas temperature $T_{ex.g}$ (°C):

Phase 1: Mo = 40 Nm, 1600 rpm; $T_{ex.g}$ = 149 °C.
Phase 2: Mo = 100 Nm, 1600 rpm; $T_{ex.g}$ = 192 °C.
Phase 3: Mo = 200 Nm, 1600 rpm; $T_{ex.g}$ = 295 °C.
Phase 4: Mo = 300 Nm, 1600 rpm; $T_{ex.g}$ = 406 °C.
Phase 5: Mo = 400 Nm, 1600 rpm; $T_{ex.g}$ = 560 °C.
Phase 6: Mo = 0 Nm, 900 rpm; $T_{ex.g}$ = 93 °C.
Phase 7: Mo = 360 Nm, 2200 rpm; $T_{ex.g}$ = 569 °C.
Phase 8: Mo = 270 Nm, 2200 rpm; $T_{ex.g}$ = 456 °C.
Phase 9: Mo = 180 Nm, 2200 rpm; $T_{ex.g}$ = 354 °C.
Phase 10: Mo = 90 Nm, 2200 rpm; $T_{ex.g}$ = 261 °C.
Phase 11: Mo = 36 Nm, 2200 rpm; $T_{ex.g}$ = 220 °C.

VOCs content in the exhaust gas was analyzed with gas chromatograph, using a Hewlett 5890 Series II apparatus with a flame ionization detector and an HP-5 capillary column (30 m long; 0.56 m in diameter). Quantitative analysis was carried out on the basis of calibration and desorption coefficients for particular compounds.

Besides the compounds adsorbed on activated carbon, also reflux was analyzed (using the colorimetric method), but mainly for the presence of formaldehyde.

3. RESULTS AND DISCUSSION

Theoretically, the combustion process in a motor-car engine should yield carbon dioxide and water as the reaction products. Practically, the process runs through a stage where products of incomplete combustion are generated in the form of oxidized derivatives of the hydrocarbons occurring in the fuel. Thus, the combustion process proceeds as follows:

$$\text{hydrocarbons} \rightarrow \text{alcohols} \rightarrow \text{aldehydes} + \text{ketones} \rightarrow \text{acids} \rightarrow CO_2 + H_2O.$$

During running of the self-ignition engine, we analyzed (quantitatively and qualitatively) 33 compounds in the exhaust gas. As the pollutants occurred in large amounts and were therefore difficult to analyze, we classified them into the following groups, taking into account their chemical structure: aldehydes, alcohols, ketones, aromatic hydrocarbons (arenes), and paraffin hydrocarbons (paraffins). Such pollutants as acrolein, benzene and formaldehyde were analyzed separately because of their high toxicity.

A group of organic compounds found to be in abundance was that of aldehydes. Their mass fractions varied from 55 to 56% both at moderate and maximal engine loads. The overall mass fraction of the hydrocarbons did not change, while the mass fraction of paraffins decreased and that of arenes increased with the increase in the engine load (figure 1).

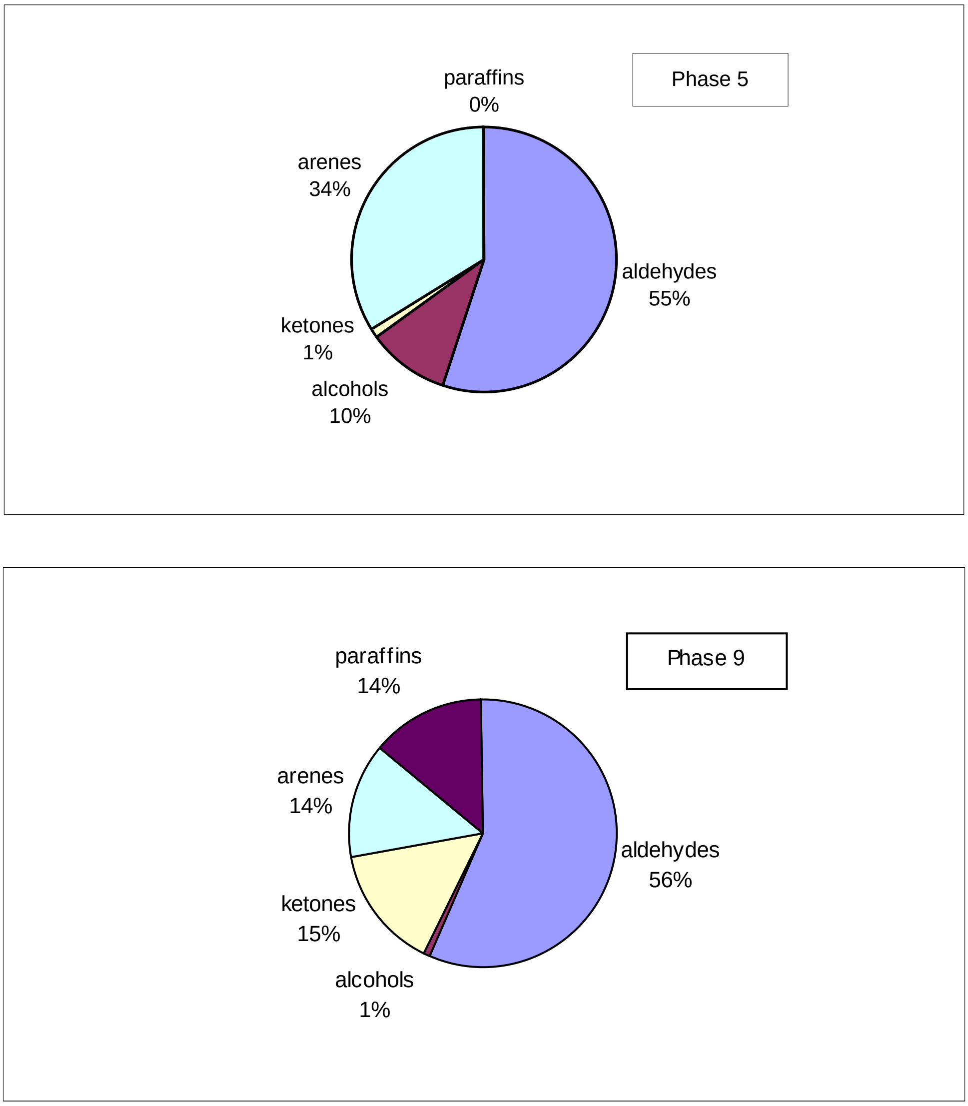

Fig. 1. Mass fractions of particular groups of compounds in selected measuring phases

The groups of the polluting species that occur in the exhaust gas differ in their chemical properties and are therefore degraded with various efficiency (figure 2). The highest efficiency – practically amounting to 100% (except for the zero-load, i.e., idle running) – was attained for the group of alcohols when the KW 400 catalytic filter contained cerium in the inlet part and platinum in the other part.

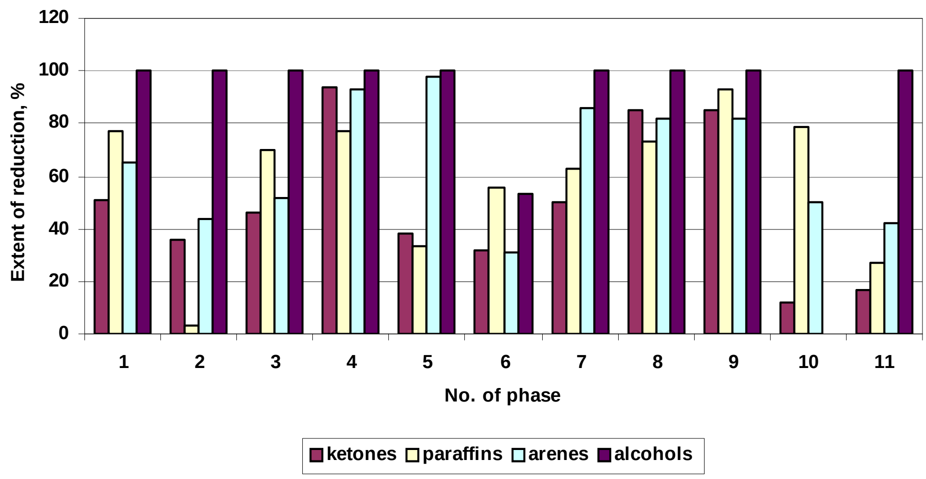

Fig. 2. Per cent reduction of some pollutants related to engine load
(catalytic filter KW 400 (Ce+Pt))

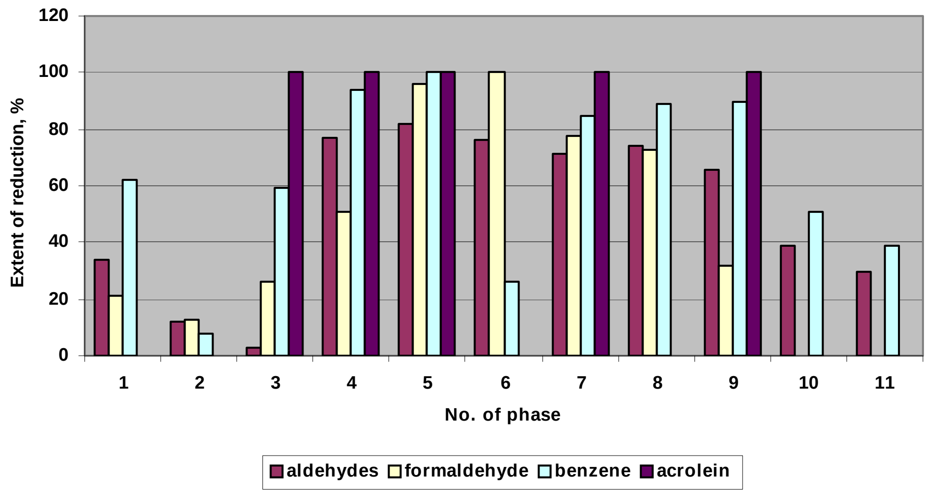

Fig. 3. Per cent reduction of selected pollutants and aldehydes related to engine load
(catalytic filter KW 400 (Ce+Pt))

The reduction of aromatic hydrocarbons totalled 90% when the temperature of the exhaust gas exceeded 400 °C. The reduction of paraffins and ketones followed a different pattern: it decreased as the engine load increased, which may be associated with the decreasing concentration of these species in the exhaust gas.

With the group of aldehydes (whose mass fraction in the exhaust gas was the highest), the maximal reduction at the highest engine load slightly exceeded 80% (figure 3). The reduction of pollutants belonging to this group is contributed primarily to the combustion of formaldehyde, which accounts for 50% of all the aldehydes in the exhaust gas. Under the conditions mentioned above, the reduction of formaldehyde totalled 96% at its concentration of 0.042 mg/dm^3. The high efficiencies of combustion of benzene and acrolein (which account for 12% and 2% of the mass fraction of the exhaust gas, respectively) show great promise, as both pollutants are highly toxic.

The maximal treatment efficiencies obtained with the KW 400 filter for the exhaust gas ranged from 75 to 89% at moderate and maximal engine running (figure 4). They should be attributed to the high mass fractions of arenes (34%) and alcohols (10%), whose reduction at maximal engine load amounted to 95% and 100%, respectively. The high reduction in the exhaust gas at idle running was influenced by the high mass fraction of aldehydes (77%). Their reduction at zero-load totalled 76%.

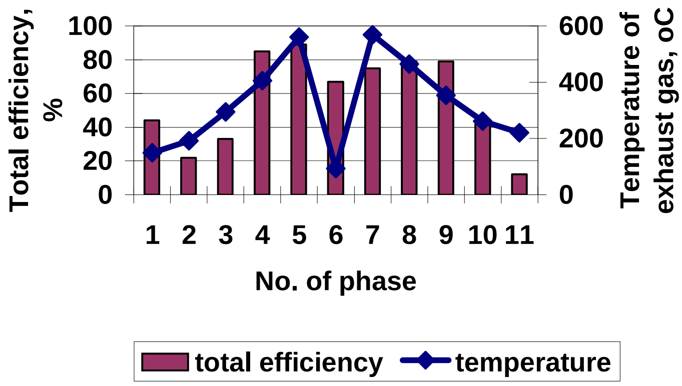

Fig. 4. Per cent reduction of total VOCs (catalytic filter KW 400 (Ce+Pt))

To assess the efficiency of both treatment systems, the per cent of exhaust gas neutralization at maximal load of the engine was analyzed. Both treatment systems provide a high reduction of alcohols and arenes as well as in the selected toxic pollutants: acrolein and benzene (figures 5 and 6).

In the Pt + Ce system, where the sequence of contact between the exhaust gas and the active ingredient had been changed, the reduction of aldehydes decreased notably, which was promoted by the formation of formaldehyde on the catalytic filter under such conditions, but at the same time had a beneficial effect on the reduction of ketones and paraffins. As for the other toxic compounds, acrolein and benzene, the sequence of the active agents did not affect the per cent of their reduction.

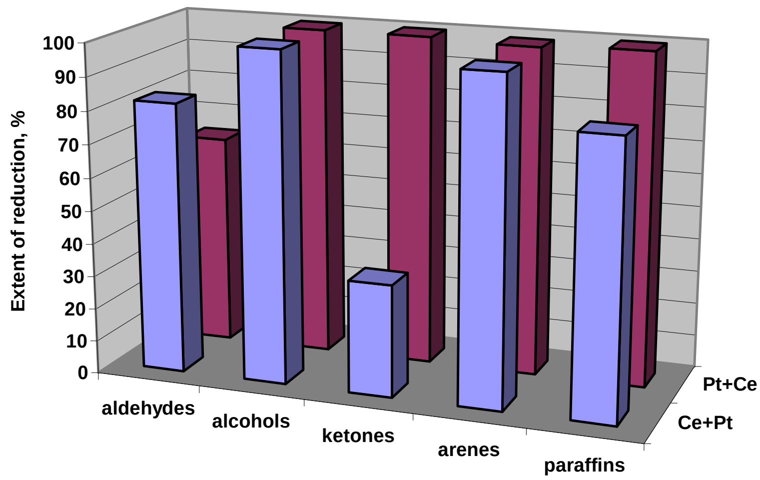

Fig. 5. Comparison of reduction efficiencies in particular groups of pollutants at maximal engine load

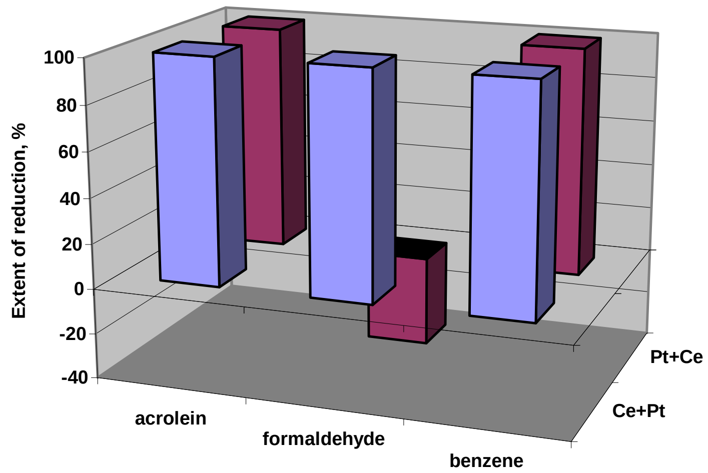

Fig. 6. Comparison of reduction efficiencies of toxic species at maximal engine load

Both the systems brought about a high VOCs reduction in the exhaust gas at high engine load, when the gas temperature was high (figure 7). At low loads, the Ce+Pt catalytic filter was found to be more efficient. Even at idle running of the engine, the per cent of reduction obtained with the KW 400 filter approached 70%. That attained with the Pt+Ce catalytic filter was comparable at maximal engine load, but noticeably lower at low loads (at idle running even by 40%).

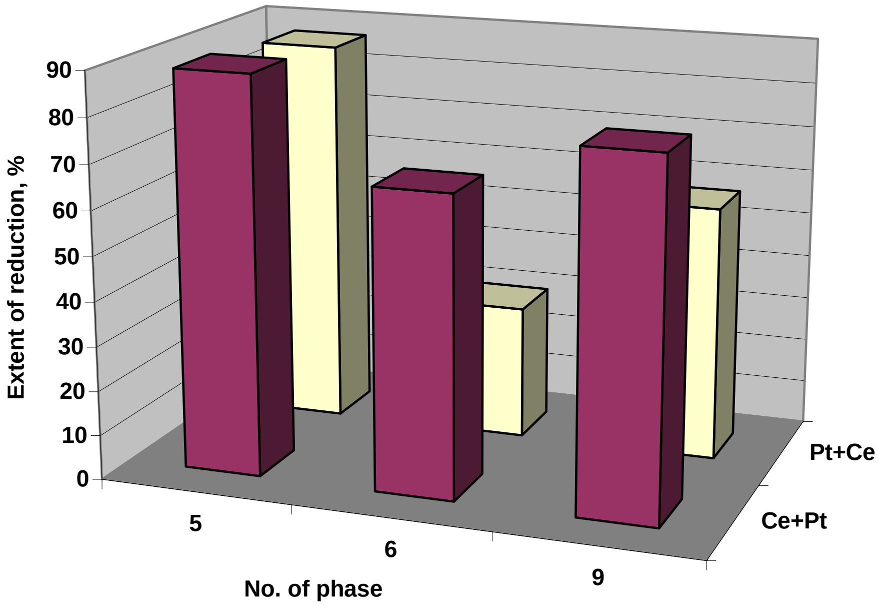

Fig. 7. Per cent reduction of total VOCs

4. CONCLUSIONS

1. The treatment systems tested remarkably reduced VOCs emissions from the self-ignition engine, especially at smooth running.

2. The per cent of VOCs reduction was the lowest at low engine load and at idle running.

3. Theoretically, the efficiency of exhaust gas treatment should raise proportionally to engine load and, consequently, to gas temperature. This pattern, however, is disturbed by the formation of incomplete combustion products in the afterburner, especially by those of aldehydes, even at high temperature.

4. As for the two treatment systems, the analysis was dominated by aldehydes, which practically accounted for the total efficiency of VOCs reduction owing to their very high

mass fraction in the exhaust gas and their tendency to form on the catalytic filter.

5. The systems for treating exhaust gas cannot be assessed based on the analysis of the overall VOCs combustion efficiency alone. It is necessary to take into account the percentage of the most toxic pollutants, the components of exhaust gas, being reduced.

6. The catalytic filter KW 400 (Ce+Pt) was found to be more efficient than the (Pt+Ce) system in treating the exhaust gas emitted by a self-ignition engine. This is so because owing to the presence of cerium at the inlet, the sooth is combusted first, while the other pollutants are burnt over platinum.

REFERENCES

[1] MENDYKA B., WALKOWIAK W., CZARNY A., *The effect of biodiesel exhaust composition on human lung cells*, Chemistry for Agriculture, 2005, Vol. 6, 599–606.

[2] MENDYKA B., ŚWIETLIK J., KOLANEK C., WALKOWIAK W., *Polycyclic Aromatic Hydrocarbons (PAH) in Diesel Engine Exhaust Gas*, Prace Naukowe Instytutu Chemii i Technologii Nafty i Węgla Politechniki Wrocławskiej nr 57, Konferencje nr 10, 2002, 413–419.

[3] MENDYKA B., KOLANEK C., WALKOWIAK W., *Extended composition of self-ignition engine combustion gas*, Environment Protection Engineering, 2001, Vol. 27, No. 3–4, 89–99.

[4] http: // www. auto-online.pl/serwis/wykaz/emisja

[5] DARKOWSKI A., GORZKOWSKA I., KOŹNICKA Z., *Badania nad utlenianiem sadzy za pomocą katalizatora dodawanego do paliwa*, Chemia i Inżynieria Ekologiczna, T. 6, nr 4, 1999.

[6] DARKOWSKI A., GORZKOWSKA I., *Studies of catalytic oxidation of soot from diesel engines*, Scien. Pap. of Inst. of Chem. and Techn. of Petrol. and Coal, 1999, 259–264.

[7] KLYUS O. et al., *Alternative feeding of diesel engines: Problems of maintenance of power units*, Scien. Journal of TKMA, special edition, 2002, 133–137.

[8] MENDYKA B., KOLANEK C., WALKOWIAK W., *Volatile organic compounds in diesel engine exhaust gas*, XXXII Mezinarodni Konference, katedra a pracovist spalovacich motoru, Ceske a Slovenske republiky, Vojenska Akademie v Brne, KOKA 2001, 167–172.

[9] KRUCZYŃSKI S., *Przegląd katalitycznego usuwania tlenków azotu ze spalin zawierających tlen*, Chemia i Inżynieria Ekologiczna, 2001, nr 12, 1221–1230.

[10] KRUCZYŃSKI S., *Trójfunkcyjne reaktory katalityczne – proces dezaktywacji*, Chemia i Inżynieria Ekologiczna, 2003, nr 6, 513–520.

[11] TYLUS W., *Katalityczne utlenianie sadzy ze spalin silników Diesla*, Wiadomości Chemiczne, 1999, Vol. 53, 887–903.

[12] ZABRZESKI J., TYLUS W., MUSIALIK-PIOTROWSKA A., CHĘCMANOWSKI J., *Badanie filtrów do usuwania sadzy ze spalin silników wysokoprężnych, emisje, zagrożenie, ochrona powietrza*, praca zbiorowa pod redakcją A. Musialik-Piotrowskiej i J.D. Rutkowskiego, 2004, nr 841, 301–310.

ZAWARTOŚĆ LOTNYCH ZWIĄZKÓW ORGANICZNYCH W SPALINACH W ZALEŻNOŚCI OBCIĄŻENIA SILNIKA ORAZ UKŁADÓW OCZYSZCZAJĄCYCH

Określono skuteczność redukcji lotnych związków organicznych (LZO) w gazach spalinowych z silnika o zapłonie samoczynnym. Teoretycznie skuteczność oczyszczania spalin powinna rosnąć proporcjonalnie do obciążenia silnika, a więc proporcjonalnie do temperatury gazów. Tak jednak nie jest, gdyż

w dopalaczu katalitycznym tworzą się, nawet w wysokich temperaturach, produkty niepełnego spalania, szczególnie aldehydy. Skuteczność spalania analizowano dla poszczególnych grup związków (aldehydów, ketonów, alkoholi, węglowodorów aromatycznych i alifatycznych). Przetestowano dwa systemy oczyszczania: filtr sadzy z Ce–Pt i ten sam filtr sadzy z Pt–Ce jako czynnikami aktywnymi. Z tych dwu systemów system Ce–Pt okazał się skuteczniejszy. Badania wykazały, że oceniając redukcję LZO, należy uwzględnić stopień usuwania najbardziej toksycznych zanieczyszczeń.