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DESTRUCTION OF VOLATILE ORGANIC MIXTURES BY CATALYTIC COMBUSTION

Solvent vapours are amongst the most common air pollutants released from industrial sources. The experiments reported were run to investigate destruction of some typical solvent components (toluene, n-heptane, ethanol, butanol, n-butyl and ethyl acetates, acetone, methyl ethyl ketone) by catalytic combustion both separately and in six three-component mixtures of varying qualitative composition. Two platinum catalysts were involved with 0.05 and 0.15 wt % Pt content. Both catalysts were deposited onto identical supports (γ-Al$_2$O$_3$) in the form of drawpieces. The destruction of the investigated compounds was related to platinum content of the catalyst. Consideration was also given to the composition effect of the mixture on the destruction efficiency of individual component.

1. INTRODUCTION

The contribution of volatile organic compounds to the overall air pollution load coming from industrial sources, specifically from varnish manufacture and enamelling processes, continues to increase. Most of the gaseous pollutants owe their origin to solvent coating applications and drying. These specific volatile organics are solvent vapours which consist of aromatic and aliphatic hydrocarbons, as well as of some oxygen derivatives (alcohols, acetates, ketones). The concentrations at which they are emitted rarely reach high values (if at all) and, on the other hand, these pollutants occur in mixtures rather then singly. And that is why thermal combustion or sorption fail to work economically. Now, catalytic combustion to reduce emission of volatile organic compounds has found world-wide acceptance.

The Institute of Environment Protection Engineering, Technical University of Wrocław, has been doing research on the preparation of catalysts to destroy the air pollutants of interest. The noble metal catalyst (platinum on γ-Al$_2$O$_3$ support) prepared there displays high thermal, mechanical, and chemical strength. The platinum ingredient varies from 0.15 to 0.05 wt %, depending on the pollutant to be destroyed. For a quick evaluation of catalytic activity, as

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well as for comparative purposes, there were carried out the tests of the oxidation of vapours which contained compounds differing in their chemical structure (toluene, n-heptane, and ethanol). As the catalytic combustion has become a widespread practice to degrade solvent vapours carried by the flue gas stream, we decided to investigate the operating conditions using different mixtures of these types.

2. SCOPE AND METHODS

The content of hydrocarbons and their oxygen derivatives differ from one type of solvent to another. A typical industrial solvent emission contains toluene, n-heptane, ethanol, butanol, ethyl acetate, n-butyl acetate, acetone, and methyl ethyl ketone.

The two platinum (0.15% and 0.05%) catalysts tested (referred to as ZChO-80 and ZChO-85 0.05, respectively) were placed onto identical, barium stabilized γ-Al_2O_3 supports (drawpieces, 3–6 mm long and 4 mm in diameter). The catalyst was deposited in 10 cm^3 portions in an electrically heated glass reactor. The concentration of the investigated organics and air mixture ranged between 1 and 1.5 mg/dm^3. Reaction temperature was varied from 450 to 750 K at two space velocities – 10,000 and 20,000 h^{-1}.

At the initial stage of the study, the compounds were oxidized separately. But solvent vapours are generally multicomponent mixtures of various hydrocarbons and their derivatives, so the successive stages involving six three-component mixtures can be itemized as follows: 1) toluene, n-heptane, ethanol, 2) toluene, n-heptane, butanol, 3) toluene, n-heptane, n-butyl acetate, 4) toluene, butanol, methyl ethyl ketone, 5) toluene, acetone, n-butyl acetate, and 6) n-heptane, acetone, n-butyl acetate. The combustion of single compounds and compound mixtures was carried out under identical conditions. Destruction efficiency was measured for each component of the mixture.

Concentrations were measured by gas chromatography. Analytical conditions have been established so as to enable a good separation of the mixture elements (including potential products of non-complete combustion).

3. RESULTS

Figure 1 shows the test results obtained for single compounds over ZChO-80 and ZChO-85 0.05 at space velocity of 10,000 h^{-1}. Thus, ZChO-80 at 495 K yields a destruction efficiency of 90% for toluene and butanol vapours (fig. 1a). At reaction temperatures below 495 K, the combustion of butanol is associated with the formation of butyraldehyde (at 470 K approaching 8% of the butanol reacted). The amount of aldehyde decreases with the increasing temperature, and never exceeds 1% at temperatures above 530 K.

Ethanol and methyl ethyl ketone vapours are less susceptible to combustion, and they cannot be destructed with 90% efficiency below 555 K and 560 K, respectively. It is interesting to note that the combustion of ethanol is associated with acetaldehyde formation, specifically at lower reaction temperatures. Ethyl acetate is most resistant to destruction by catalytic combustion. While the temperature, at which a 90% destruction efficiency of ethyl acetate
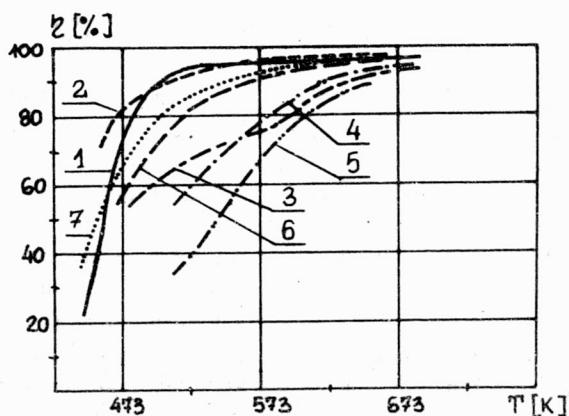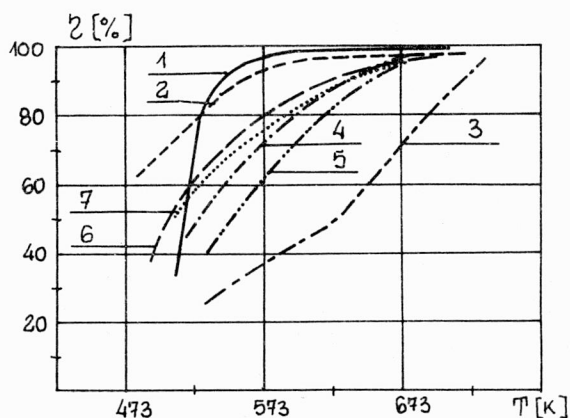
Fig. 1. Destruction efficiency of the investigated compounds when combusted separately in atmospheric
air over ZChO-85 0.05 (a) and ZChO-80 (b) at space velocity of 10,000 h^{-1}
1 – toluene, *2* – butanol, *3* – n-heptane, *4* – n-butyl acetate, *5* – ethyl acetate,
6 – methyl ethyl ketone, *7* – ethanol

is achieved, equals that of n-heptane and is higher by 10 degrees than of n-butyl acetate, the
destruction efficiencies obtained at lower reaction temperature differ significantly.

Of the investigated compounds, toluene and butanol also show the highest susceptibility
to combustion over ZChO-85 0.05. But the temperature, at which 90% destruction efficiency
of these compounds is achieved, approaches 543 K and is by 50 degrees higher than that re-
quired for ZChO-80. Equally or less prone to destruction over ZChO-85 0.05 are methyl ethyl
ketone, ethanol, and n-butyl acetate vapours. The temperature of their 90% destruction effi-
ciency varies from 615 to 625 K. Of the compounds tested, n-heptane is the most resistant to
destruction in the presence of ZChO-85 0.05. The temperatures of 50 to 90% destruction effi-
ciency of n-heptane are by about 80 degrees higher than those of ethyl acetate.

Thus, according to the destruction efficiency, the compounds can be listed as follows (in ascendent order):

Over ZChO-80: toluene = butanol > ethanol = methyl ethyl ketone > n-butyl acetate = n-heptane > ethyl acetate.

Over ZChO-85 0.05: toluene = butanol > methyl ethyl ketone > n-butyl acetate > ethanol > ethyl acetate ≫ n-heptane.

When space velocity was doubled (20,000 h^{-1}), destruction efficiency dropped considerably. Thus, the temperatures of achieving the destruction required must have been increased by approximately 40 degrees and by 50 to 70 degrees for ZChO-80 and ZChO-85 0.05 respectively.

4. EFFECT OF MIXTURE COMPOSITION ON THE DESTRUCTION OF SINGLE COMPOUNDS

The data in figs. 2–6 show the destruction efficiencies of the investigated organics combusted both separately and in mixtures over ZChO-80 or ZChO-85 0.05 at space velocity of 10,000 h^{-1}.

Significant differences in destruction efficiency are found for n-heptane when tested alone and in mixtures, specifically over ZChO-85 0.05 (fig. 2). A similar relationship was reported by TICHENOR [1], who tested multicomponent mixtures containing, e.g., benzene, n-hexane, iso-propanol, ethyl acetate or methyl ethyl ketone. He found that the presence of specific compounds in the mixture and the qualitative composition of the mixture had a significant effect on the destruction of n-hexane (an aliphatic hydrocarbon). As shown by the plots in fig. 2, the destruction efficiency is the highest when n-heptane has been combusted separately in atmospheric air. Over ZChO-85 0.05, at the reaction temperatures between 580 and 670 K, the destruction efficiency of n-heptane is slightly better (by about 8%) when the compound was tested in a mixture with acetone and n-butyl acetate. For example, n-heptane achieved the poorest destruction efficiency when incinerated in the presence of toluene and ethanol. Over ZChO-85 0.05, the differences in reaction efficiency between single compound and multicomponent mixture in some instances amounts to 20%. In the presence of ZChO-80, similar relationships are observed. The destruction efficiency of n-heptane is poorer in the presence of acetone and n-butyl acetate then in the presence of toluene and ethanol or toluene and n-butyl acetate which exert an inhibiting effect.

Figure 3 shows that the type of mixture has a distinct effect on the destruction of n-butyl acetate. In the presence of ZChO-85 0.05, n-butyl acetate is most effectively destroyed when incinerated with toluene and n-heptane. When n-butyl acetate is incinerated separately at elevated temperatures, the differences in the efficiency of oxidation are very small and increase by 15 to 18% at reaction temperatures below 570 K. The presence of toluene and acetone only slightly improves its destruction. In the presence of acetone and n-heptane, n-butyl acetate is destroyed less efficiently than when combusted separately. Over ZChO-80, the reaction efficiency is higher when the compound is incinerated in a mixture, specifically in the presence of toluene and acetone This finding holds for entire range of the investigated temperatures.
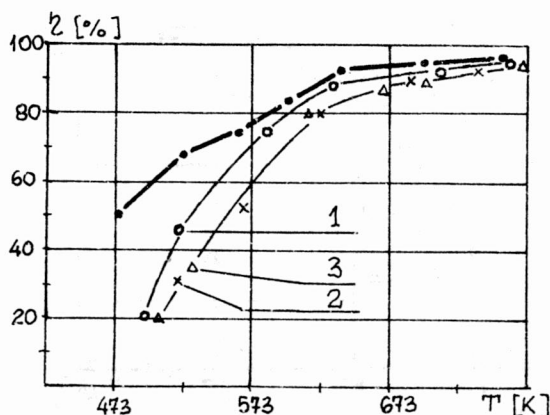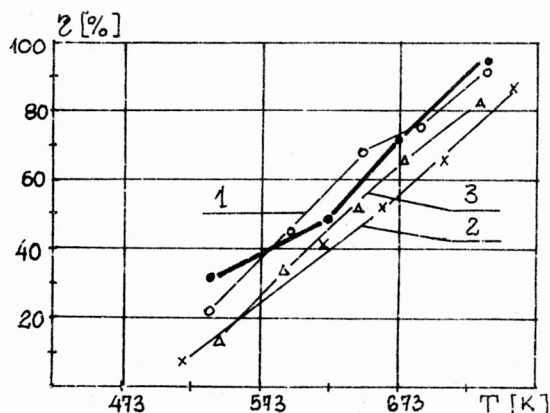
Fig. 2. Destruction efficiency of n-heptane when combusted separately
and in mixtures over ZChO-85 0.05 (a) and ZChO-80 (b)
1 – with acetone and n-butyl acetate, *2* – with toluene and ethanol,
3 – with toluene and n-butyl acetate

Interesting data have been obtained on the destruction of toluene (fig. 4). In the presence of ZChO-80, toluene is most effectively destroyed when incinerated alone. The destruction effect of mixtures is insignificant, though temperatures below 523 K favourize a slight influence. The reverse holds for the effect of compound mixture in the presence of ZChO-85 0.05. Thus, at temperatures below 548 K, the destruction of toluene when burned separately is rapidly reduced. The presence of other compounds in the mixture increases the activity during toluene combustion at temperatures lower than 530 K. For example, a mixture of toluene, n-heptane, and n-butyl acetate, achieved 50% destruction at 475 K (this temperature is by 40 degrees lower than that when toluene was incinerated separately).

The mechanism governing the oxidation of alcohols is more sophisticated [2], [3]. There may occur intermediate stages, yielding products of incomplete combustion (aldehydes or fatty acids). Butanol, which is widely used as a component of various solvents, may yield
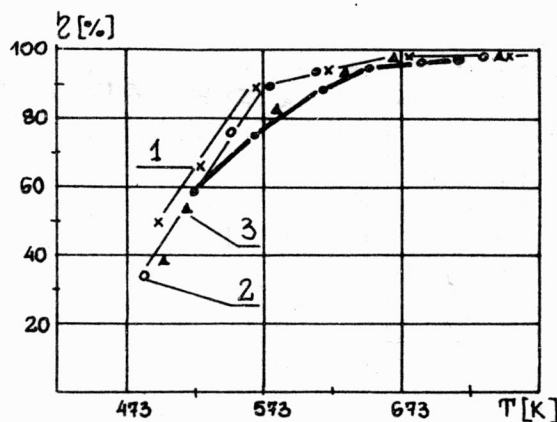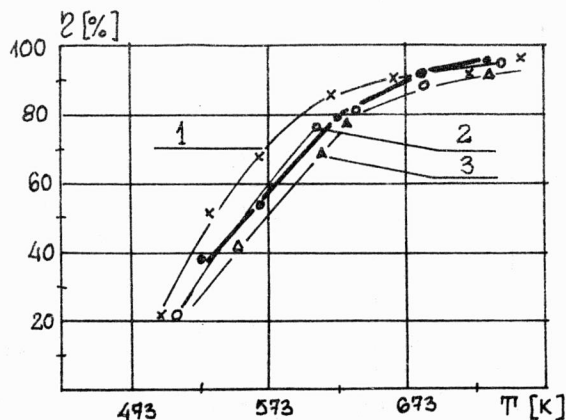
Fig. 3. Destruction efficiency of n-butyl acetate when combusted separately
and in mixtures over ZChO-85 0.05 (a) and ZChO-80 (b)
1 – with toluene and n-heptane, *2* – with toluene and acetone, *3* – with n-heptane and acetone

butyraldehyde as a product of incomplete combustion (ethanol yielding acetaldehyde or,
under certain conditions, formaldehyde). When butanol alone was incinerated over ZChO-85
0.05 (fig. 5a), the quantity of butyraldehyde produced at the lowest investigated temperature
(480 K) amounted to 25% of destroyed butanol. Combustion in the presence of other com-
pounds brings about an increase in the catalytic activity, an improvement in the destruction
of butanol, and a reduction in the quantity of aldehyde produced. In the presence of ZChO-80,
the amount of butyraldehyde was only half that produced in the presence of ZChO-85 0.05.
There is no noticeable difference in the destruction efficiency of butanol or butyraldehyde
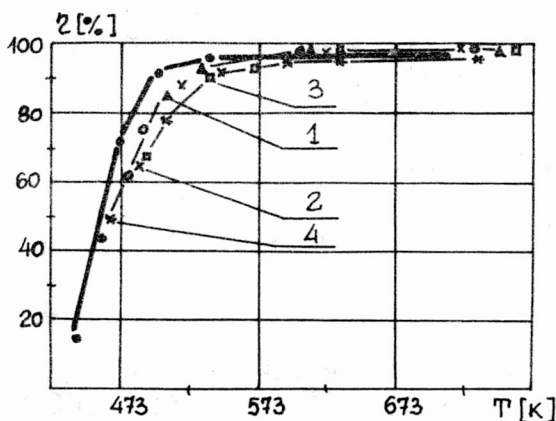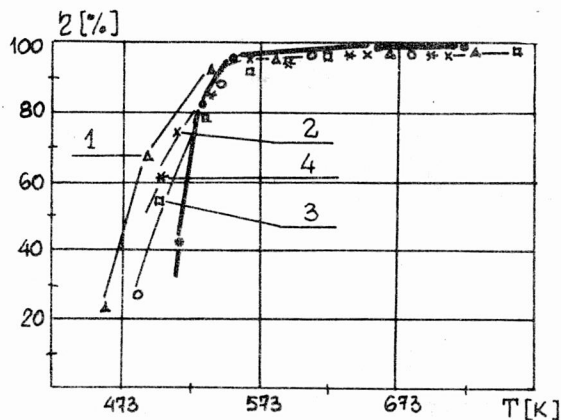production when tested separately compared to that when tested in mixtures (fig. 5b).

Fig. 4. Destruction efficiency of toluene when combusted separately
and in mixtures over ZChO-85 0.05 (a) and ZChO-80 (b)
1 – with n-heptane and n-butyl acetate, *2* – with ethanol and n-heptane, *3* – with butanol and n-heptane,
4 – with butanol and methyl ethyl ketone

The combustion of ethanol, which runs with acetaldehyde as an intermediate product, was investigated only in mixture with toluene and n-heptane. The composition effect on the destruction efficiency was poor, but varied, according to the catalyst involved (fig. 6). In the presence of ZChO-85 0.05, ethanol is destroyed less efficiently in the mixture than alone, yielding higher aldehyde concentrations in the reaction products. Over ZChO-80, the destruction efficiency is slightly higher when ethanol is combusted in the mixture. The amount of aldehyde is half the quantity produced when incinerated separately.
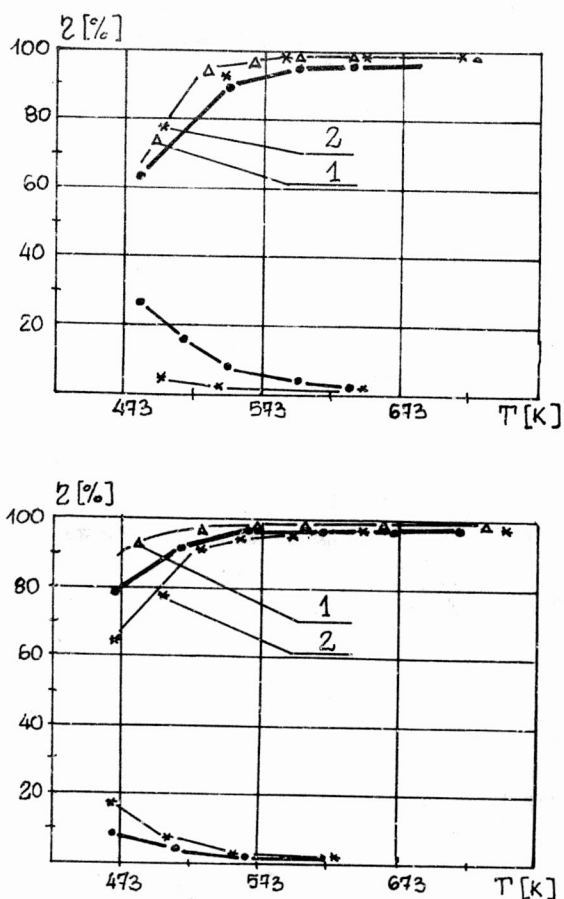
Fig. 5. Destruction efficiency of butanol when combusted separately or in mixtures and the contribution
of butyraldehyde over ZChO-85 0.05 (a) and ZChO-80 (b)
1 − with toluene and n-heptane, *2* − with toluene and methyl ethyl ketone

6. SUMMARY

On the basis of the data obtained, the following generalizations can be made:

1. Of the two platinum catalysts (containing 0.05 or 0.15% Pt and reffered to as ZChO-85 0.05 and ZChO-80, respectively), supported on identical γ-Al_2O_3 carriers, ZChO-80 shows a higher activity in the combustion of all investigated compounds.

2. The reactivity of the investigated compounds depends on the platinum content in the catalyst.

3. The effect of the mixture composition on the destruction of individual compounds depends on the quantity of the active ingredient in the catalyst.
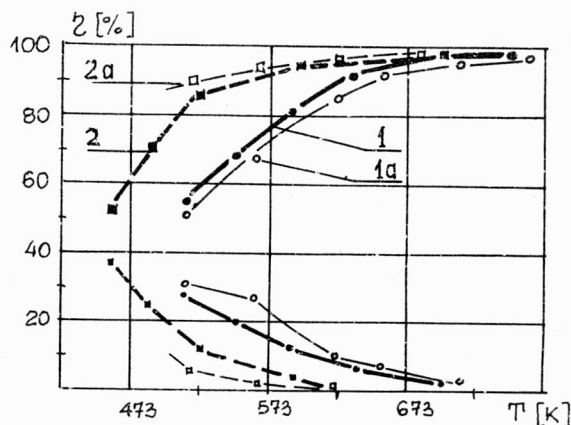
Fig. 6. Destruction efficiency of ethanol when combusted separately or in mixture with toluene and n-heptane, and the contribution of acetaldehyde over ZChO-85 0.05 and ZChO-80 ZChO-85 0.05: *1* – separately, *1*a -- in a mixture, ZChO-80: *2* – separately, *2*a – in a mixture

4. The effect of the presence of other organics in the mixture as well as the effect of the mixture composition on the destruction efficiency were particularly pronounced in the combustion of n-heptane. The destruction of n-heptane was easier when burned separately than in mixtures.

5. A reverse relationship was found to occur during combustion of n-butyl acetate. The presence of other compounds in the reaction mixture generally increases the destruction efficiency.

6. The presence of other organic compounds in the mixture affects not only the efficiency of alcohol destruction, but also the amount of aldehydes, an intermediate product of incomplete combustion.

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KATALITYCZNE SPALANIE PAR ZWIĄZKÓW ORGANICZNYCH

Pary rozpuszczalników stanowią najczęściej spotykane organiczne zanieczyszczenia powietrza emitowane w gazach odlotowych rozmaitych zakładów przemysłowych. Przedstawiono wyniki badań nad spalaniem katalitycznym par związków najczęściej wchodzących w skład typowych rozpuszczalników (toluen, n-heptan, butanol, etanol, octany etylu i n-butylu, aceton, metyloetyloketon) spalanych indywidualnie w powietrzu, a następnie w sześciu mieszaninach trójskładnikowych w różnych kombinacjach jakościowych.

Przebadano dwa katalizatory platynowe zawierające 0,05 i 0,15% platyny na identycznym nośniku γ-Al$_2$O$_3$. Przeanalizowano wpływ zawartości platyny w katalizatorze na reaktywność poszczególnych związków oraz wpływ składników mieszanin na spalanie poszczególnych jej elementów.

КАТАЛИТИЧЕСКОЕ СГОРАНИЕ ПАРОВ ОРГАНИЧЕСКИХ СОЕДИНЕНИЙ

Пары растворителей составляют наиболее часто встречаемые органические загрязнения воздуха, эмиттированные в отходных газах различных промышленных предприятий. Представлены результаты исследований каталитического сгорания паров соединений наиболее часто входящих в состав типичных растворителей (толуон, н-гептан, бутанол, этанол, ацетаты этила и н-бутила, ацетон, метилэтилкетон), сгораемых индивидуально в воздухе, а затем в шести трехкомпонентных смесях разных по составу и качеству. Исследовали два платиновых катализатора, содержащих 0,05 и 0,15% платины на таком же носителе γ-Al$_2$O$_3$. Проанализировано влияние содержания платины в катализаторе на реактивность отдельных соединений, а также компонентов смесей на сгорание ее отдельных элементов.