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CATALYTIC TREATMENT OF EFFLUENT GASES FROM ASPHALT MANUFACTURING

Results of research conducted on the applicability of the catalytic method for purification of industrial effluent gases from asphalt manufacturing are presented. Commercially available copper-zinc MCA catalyst on γ-Al_2O_3 base-used for industrial effluent gases treatment, was used in this study. Efficiency of catalytic conversion was studied for total hydrocarbons, hydrogen sulphide and mercaptans in the post-oxidation gases as influenced by the temperature, load, contact grain size and the substrate concentration. The research proved full applicability of the MCA catalyst for purification of this type of effluent gases. Based on the results mathematical model for oxidation of hydrocarbons and sulphur compounds in post-oxidation gases was elaborated. The model allows calculation of optimized working parameters for the MCA catalyst in an industrial installation for treatment of gaseous emissions from asphalt manufacturing processes.

1. INTRODUCTION

Hydrocarbons are assigned significant importance in the balance of gaseous emissions to the atmosphere, primarily due to their abundant occurence and their harmful effects to living organisms. Petroleum refining and processing industry is one of the major hydrocarbon emission sources putting out also organic compounds of sulphur and nitrogen. This emission is frequently so extensive that in the vicinity of refineries concentrations of hydrocarbons stay at the level of 100 mg/m^3.

Among the processes employed in refineries one of the most troublesome from the standpoint of air pollution control is the asphalt hardening process resulting from air--oxidation of post-destillation oil residue. The process is conducted in order to improve the properties of artificially obtained asphalts, i.e. in order to obtain a product with determined physico-chemical parameters. The properties of such an asphalt depend primarily on the kind of oil used and also on the method of oxidation process, which in turn influences the quantitative and qualitative composition of the post-oxidation gases.

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The composition of the petroleum post-destillation residue includes, beside various aromatic and aliphatic hydrocarbons, organic oxygen, sulphur and nitrogen compounds and minimal mineral components. Oxygen compounds occur most frequently as phenols and naphtene acids. Sulphur may occur as elementary sulphur, hydrogen sulphide and organic compounds such as thiophens, tioethers and mercaptans, whilst the sulphur content may vary in the range of 0.2–4%. The most frequently occurring nitrogen compounds include alkylated quinolines and isoquinolines. All these compounds are partly washed out from the post-destillation residue and emitted to atmosphere with the post-oxidation gases. It should be added that besides the harmful or toxic influence of the compounds contained in post-oxidation gases on living organisms, most of them are odor producing compounds. Average concentration of individual gaseous elements in the post-oxidation gases occurring during asphalt manufacturing by periodic method is:

- aliphatic compounds   — 2.01–10.4 g/m^3,
- aromatic compounds   — 0.2–4.65 g/m^3,
- hydrogen sulphide   — 0.114–0.37 g/m^3,
- mercaptans expressed as methyl mercaptan   — 0.07–0.15 g/m^3,
- oxygen   — 8.0–13.0% volume,
- nitrogen   — 80.0–75% volume.

Beside the above components post-oxidation gases contain certain amounts of carbon dioxide, phenol and water vapour.

Due to the varied composition of post-oxidation gases the possibility of using the catalytic method was discussed in the view of solutions employed in other industries such as enamel manufacturing, paint and lacquer factories, chemical plants and printing works, etc. For industrial treatment of gaseous pollutants emitted in the above mentioned technologies the noble metal catalysts — platinum and palladium were applied as well as catalysts based on oxides of nickel, chromium, manganese, copper, zinc, iron, cobalt and vanadium [3–5], [12], [14]. The literature on catalytic destruction of sulphur compounds contained in the emissions is much more limited being confined to the compilation of the desulphurization methods based on oxygen catalysts or boxites or zeolites [2], [8], [11].

One well-known process of catalytic treatment of post-oxidation gases has been invented in Soviet Union (a). The method uses a double catalytic insert media. The first with a copper-chromium catalyst on aluminum oxide base, in proportions of 85.95% aluminium oxide, 8.6% copper oxide and 5.45% chromium oxide, serves the gas desulphurization purpose. The second media have the platinum catalyst SzPK-2, containing 0.2% Pt on the aluminum-silica base SzAS — highly active in hydrocarbon post-oxidation. The volumetric ratio of the first to second contact layers is 2:1. High efficiencies of post-oxidation gas treatment reaction were attained when conducting the process at a loading of 5000 h^{-1} and temperature of 723–773 K.

Commercial copper-zinc MCA catalyst on γ-Al_2O_3, granulated and designed for treatment of industrial gaseous emissions, was selected for the feasibility studies on catalytic treatment of post-oxidation gases in our laboratory. The applicability of this catalyst

for removal of hydrocarbon vapours from air has been determined in previous studies [6, 7], [13], where it was compared with other commercially available catalysts in this country. The MCA catalyst proved to be highly active in the post-oxidation of cyclohexanone, gasoline and petroleum vapours in air. The catalyst has also found industrial application in treatment of effluent gases from enamel manufacturer where it proved to be not less efficient than the KAVAG company catalyst [10].

The studies were aimed at determining the resistance of the catalyst against sulphur compounds poisoning and at selection of optimal contact parameters in the investigated process.

2. METHODS AND PROCEDURES

In order for the research to be utilized in the design of contact equipment and calculations of the necessary catalyst loads and process parameters a relationship was to be determined between the rate of the process and the degree of convernion and temperature. Theoretical solution of this problem based on kinetic equation is practically impossible since the process is strongly influenced by diffusion, particularly internal. Due to this fact it is advisable to experimentally determine the rate of reaction on the media grain with normal technical granulation in a dynamic system.

The studies were conducted on real gases, conducting oxidation in a model oxidator designed basing on technology of the asphalt hardening process by the periodic method. The following parameters were applied in the process:

— asphalt quantity   5 kg,
— air flow rate   80 dm^3/h,
— oxygenation time   approx. 36 h,
— temperature in the oxidator 443–543 K.

The fire protection with dry water vapour introduced usually above the asphalt level has not been applied in the experiment due to the difficulties in obtaining water vapour in laboratory conditions.

The layout of the installation for the studies of the catalytic post-oxidation gases treatment is presented in Fig. 1. Asphalt oxidation was conducted in oxidator *1*, made of steel tube equipped with an air sparger which allows the introduction of air necessary for reaction. In order to maintain proper temperature conditions the oxidator was heated electrically. Oxidator effluent gases were cooled, *2*, and the resulting condensate collected in a condenser, *3*. Subsequently, through a mixer, *4*, simultaneously equalizing gas concentrations, the gases were directed to the catalytic reactor, *6*, made of quarz. The lower part of the reactor was filled with Rasching rings and served the role of gas heater, while in the upper, one containing strictly determined quantity of the catalyst, the desired catalytic reaction occured. Both parts of the reactor were independently electrically heated. The

set of pipettes *5* and *7* facilitated gas sampling for analysis, prior to and after the reactor. The air flow rate was measured by a rotameter, *8*.

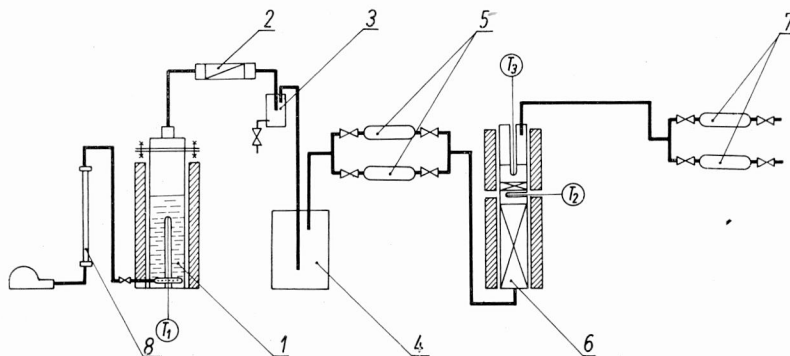Gas temperature before the catalytic bed was measured by the thermal element in

Fig. 1. Layout of laboratory set-up for catalytic treatment of post gases;
1 — oxidator, *2* — condenser, *3* — oil condenser, *4* — mixer, *5* — gas input sampling pipettes, *6* — catalytic reactor, *7* — gas output sampling pipettes, *8* — rotameter, $T_1 T_2 T_3$ — temperature measurements points

Rys. 1. Schemat aparatury laboratoryjnej do badań skuteczności katalitycznego unieszkodliwiania gazów pooksydacyjnych

1 — oksydator, *2* — chłodnica, *3* — odkraplacz olejowy, *4* — mieszalnik, *5* — pipety do poboru prób gazów przed reaktorem, *6* — reaktor katalityczny, *7* — pipety do poboru prób gazów za reaktorem, *8* — rotametr, T_1, T_2, T_3 — punkty pomiaru temperatury

point T_2, while the temperature in the contact layer was measured in point T_3. Process temperature was controlled by means of the thermal element in point T_1.

The efficiencies of after-burning of individual compounds were calculated by comparing their concentration prior to and after the reactor, and by an evaluation of the quality and intensity of gas odors. Concentration analysis was conducted for the following compounds:

— total hydrocarbons,
— hydrogen sulphide,
— mercaptans.

Hydrocarbon analysis was performed by means of the N-503 MERA-ELPO gas chromatograph, performing the quantitative analysis based on n-hexane. Hydrogen sulphide and mercaptans were analyzed according to the modified Wroński's titration method.

In order to delineate the reactions of oxidation of the post-oxidation gases, on MCA catalyst including the diffusion effects it was necessary to study the reaction efficiency as affected by process temperature, contact loading, granulation and substrate concentration. In the studied range of concentrations no change of reaction efficiency was found for the initial concentrations of individual components. The temperature range varied within 573–773 K. Influence of temperature on conversion efficiency has been studied at loadings of 8,000, 12,000, 16,000 and 20,000 h^{-1}. Contact load had been changed by means of altering the thickness of the layer which guaranteed a constant velocity

in the contact layer. All studies were conducted on preselected grain size 2.5 mm. In order to include the effects of diffusion on the deep oxidation process a series of additional measurements were performed on the largest grain size — 6.0 mm for this catalyst.
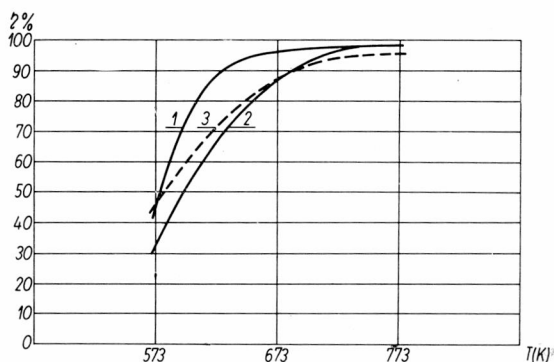
3. RESULTS

The results of conducted studies are presented in Fig. 2. It has been found that in the temperature range of 573–773 K increase of load from 8,000 to 12,000 h^{-1} has not influenced the efficiency of hydrocarbon oxidation reaction. At a loading of 16,000 h^{-1} decrease

Fig. 2. Relationship between the efficiency of conversion of the total hydrocarbons from the post-oxidation gases and the temperature, loading and the contact grain size;

1 — grain size ø 2.5 mm, load 8,000–12,000 h^{-1},
2 — grain size ø 2.5 mm, load 16,000–20,000 h^{-1},
3 — grains size ø 6.0 mm, load 9,300 h^{-1}

Rys. 2. Zależność skuteczności przemiany sumy węglowodorów z gazów pooksydacyjnych od temperatury, obciążenia i wielkości ziarna kontaktu

1 — uziarnienie ø 2,5 mm, obciążenie 8 000–12 000 h^{-1},
2 — uziarnienie ø 2,5 mm, obciążenie 16 000–20 000 h^{-1},
3 — uziarnienie ø 2,5 mm, obciążenie 9 300 h^{-1}

of the process efficiency was observed, whereas further increase of load to 20,000 h^{-1} has not resulted in any further deterioration of the efficiency. Influence of the load is particularly evident at the temperatures below 673 K; e.g. for 623 K — and at 12,000 h^{-1} conversion efficiency was over 85%, while at 20,000 h^{-1} — it amounted to 65%. Above 673 K this difference decreases and the efficiency of the conversion at a temperature of 773 K, in the total load range, was approx. equal to 98%.

Studying the conversion efficiencies of hydrogen sulphide and mercaptans it has been found that their removal at 573 K for all studied loads was equal to 90%, while beginning from the temperature of 623 K, regardless of the load, only traces of these compounds were found in the post-reaction gases.

Periodical control of quality and intensity of odors revealed that beginning with the temperature of 673 K post-reaction gases are free of obnoxious odors.

Based on obtained results a mathematical model was elaborated for oxidation of hydrocarbons and sulphuric compounds in the post-oxidation gases [9], assuming that:

— the process is of the kinetic-diffusion type;
— pollutants concentration in the post-oxidation gases is insignificant, practically not higher than 0.1% vol;
— the contact layer is immobile;
— the pollutants oxidation reaction is irreversible and of first-order.

Constant models were looked for by means of Odra 1304 computer, according to the nonlinear optimization program.

After calculating the research data the hydrocarbons oxidation model has been put in the following form:

$$\ln \frac{c_1}{c_2} = \frac{z \cdot \varepsilon}{G_M \cdot d} \frac{8.6}{5.74 \dfrac{Re^{0.359} \cdot \varepsilon}{G_M} + 1.32 \cdot 10^3 e^{3990/T}}, \tag{1}$$

where

c_1, c_2 — hydrocarbons reactor input and output concentrations (mg/dm³),
z — thickness of contact layer (mm),
d — grain size (mm),
ε — water volume participation in the layer,
G_M — total mass flow rate (mol/cm · s),
Re — Reynolds number.

The model for oxidation of sulphur compounds has a form of:

$$\ln \frac{c_1}{c_2} = \frac{z \cdot \varepsilon}{G_M \cdot d} \frac{8.6}{4.31 \dfrac{Re^{0.359} \cdot \varepsilon}{G_M} + 3.44 \cdot 10^4 e^{1200/T}}, \tag{2}$$

where:

c_1 and c_2 — input and output concentrations of sulphur compounds (mg/dm³).

The calculations have proved that the rate of oxidation of sulphur compounds is higher than the rate of hydrocarbons oxidation in the temperature range of interest 623 to 773 K, thus the optimized parameters for the reactor may be selected based on the hydrocarbon oxidation model. Fig. 3 presents one of the relationships stemming from equation 1: the layer thickness versus total gas flow rate, G_M, for reaction efficiencies of 90 and 95% at a temperature of 773 K. The relationship allows the determination of the thickness of the catalyst layer in the industrial reactor, necessary for conducting reaction with 90 and 95% efficiency, depending on the known mass flow rate and the average grain size in a given catalyst class.
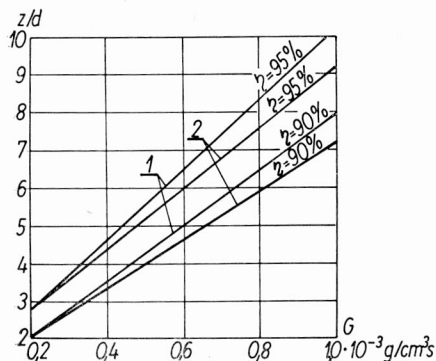

Fig. 3. The layer thickness vs. total gas flow rate and grain size for reaction efficiencies of 90 and 95% at a temperature of 773 K

1 — grain size ø 2.5 mm, *2* — grain size ø 6.0 mm

Rys. 3. Zależność grubości warstwy katalizatora od natężenia przepływu gazu oraz wielkości ziarna kontaktu przy skuteczności przemiany węglowodorów 90 i 95% w temperaturze 773K

1 — uziarnienie ø 2,5 mm, *2* — uziarnienie ø 6,0 mm

4. CONCLUSIONS

The following conclusions may be formulated based on the conducted research:
— MCA catalyst may find application in the industrial process of gas treatment from the asphalt oxidation. The catalyst proved to be highly active in oxidation of organic compounds of sulphur and hydrogen sulphide, attaining, at 573 K oxidation efficiency of 90% and over 99% at the temperature of 623 K, regardless of conctat loading. Hydrocarbon oxidation reaction is more difficult to conduct, attaining the conversion efficiency of 90% and 95% at a temperature of 673 K and 723 K, respectively, at a load of 20,000 h^{-1}. Decrease of the load down to 12,000 h^{-1} allows the respective decrease of reaction temperature down to 623 K at the 90% efficiency and to 673 K at the 95% efficiency level;
— the catalyst exhibits strong resistance to poisoning with sulphur compounds, since after 500 hours of work no efficiency loss occurred;
— based on the obtained results, mathematical models for diffusion-kinetic treatment of the post-oxidation gases on MCA, catalyst were elaborated.

The models describing this process may be applicable in the computation of optimized parameters for industrial reactors.

KATALITYCZNE UNIESZKODLIWIANIE GAZÓW ODLOTOWYCH Z PRODUKCJI ASFALTÓW

W pracy przedstawiono wyniki badań nad możliwością zastosowania metody katalitycznej do unieszkodliwiania przemysłowych gazów odlotowych z produkcji asfaltów. Do badań użyto handlowego katalizatora miedziowo-cynkowego MCA, na nośniku γ-Al$_2$O$_3$, przeznaczonego do oczyszczania przemysłowych gazów odlotowych.

Przebadano skuteczność przemiany katalitycznej węglowodorów, sumarycznie, siarkowodoru oraz merkaptanów w gazach pooksydacyjnych w zależności od temperatury, obciążenia, uziarnienia kontaktu oraz stężenia substratów. Przeprowadzone badania pozwoliły na stwierdzenie pełnej przydatności katalizatora MCA do oczyszczania tego typu gazów odlotowych. Na podstawie uzyskanych wyników wprowadzono model matematyczny utleniania węglowodorów oraz połączeń siarkowych w gazach pooksydacyjnych. Model ten umożliwia wyliczenie optymalnych parametrów pracy katalizatora MCA w przemysłowej instalacji do unieszkodliwiania gazów odlotowych z produkcji asfaltów.

ZUR KATALYTISCHEN NEUTRALISIERUNG DER VON ASPHALTERZEUGUNG STAMMENDEN ABGASE

Die Anwendungsmöglichkeit eines katalytischen Verfahrens zur Neutralisierung der während der Asphalterzeugung entstandenen Abgase ist untersucht. Zu diesem Zweck bediente man sich eines Kupfer--Zink-Handelskatalysators mit Aluminiumdioxidträger. Der Wirkungsgrad der katalytischen Neutrali-

sierung von Kohlenwasserstoff, Wasserstoffsulfit und Merkaptane its in der Abhängigkeit von Temperatur, Belastung, Kontaktkorngrößenverteilung und Trägersubstanz geprüft.

Die Untersuchungen haben gezeigt, daß die auf Kupfer-Zink-Katalysator mit Aluminiumdioxidträger gestützte Neutralisierung der von Asphalterzeugung stammenden Abgase durchführbar ist. Auf Grundlage der Untersuchungsergebnisse wird ein mathematisches Modell für die Oxydierung von Kohlenwasserstoff und Schwefelverbindungen in den Oxydationsabgasen entwickelt. Damit ist die Berechnung der optimalen Leistungsparameter für den untersuchten Katalysator möglich.

КАТАЛИТИЧЕСКОЕ ОБЕЗВРЕЖИВАНИЕ ОТХОДЯЩИХ ГАЗОВ ОТ ИЗГОТОВЛЕНИЯ АСФАЛЬТОВ

Исследовалась возможность применения каталитического метода для обезвреживания промышленных отходящих газов от изготовления асфальтов. Для испытаний употребляли меде-цинковый торговый катализатор МСА, на носителе γ-A₂O₃, предназначенный для очистки промышленных отходящих газов. Исследована эффективность каталитического превращения углеводородов, суммарно — сероводорода и меркаптанов в газах от оксидирования в зависимости от температуры, нагрузки, зернистости, контакта и концентрации субстратов. Результаты исследований показали полную пригодность катализатора МСА для очистки названных отходящих газов. На основе этих результатов введена математическая модель окисления углеводородов и соединений серы в газах от оксидирования, позволяющая перечислить оптимальные параметры работы названного катализатора на промышленной установке для обезвреживания отходящих газов, образующихся при изготовлении асфальтов.

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