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INVESTIGATION OF SELECTED OILS AS ABSORBENTS OF THE CHLORINATED HYDROCARBONS

The scope of this investigation was to determine the absorption intensity of selected chloro-organic pollutant as a function of a kind of oil, gas velocity, process temperature and absorbate concentration in gaseous and liquid phases and to compare the absorption abilities of some oils.

The silicone oil, two paraffin oils and vegetable oil as absorbing liquids were investigated in a tubular, wetted-wall column. The highest absorption efficiency was obtained for methyl-silicone oil and the highest absorption ability – for vegetable (soybean) oil. An adverse effect of temperature rise on mass transfer intensity was more significant than an advantageous effect of the decrease in oil viscosity with the rise in temperature. The article is ended with the proposal of a schematic diagram of the exhaust gases cleaning method.

DENOTATIONS

L – sparging density, m^3/m^2h,
C_c – trichloroethylene mass concentration in liquid at the inlet of column, g/m^3,
C_{g1} – trichloroethylene mass concentration in gas at the inlet of column, mg/m^3,
C_{g2} – trichloroethylene mass concentration in gas at the outlet of column, mg/m^3,
T_l – liquid temperature, K,
T_g – gas temperature, K,
v – gas velocity, m/s,
η – absorption efficiency, %.

1. INTRODUCTION

Chlorinated hydrocarbons belong to a great group of aliphatic and aromatic organic compounds that are widely used in industry. For example, they have application

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in varnish, glue and paste industry, for the production of polyurethane froths, aerosol confections, anti-insect agents, refrigerating agents, degrease agents and as some intermediate products in chemical synthesis. Therefore, the necessity of limiting the emission of chlorinated hydrocarbons is caused not only by their toxicological effects[1], but also by economical losses that are due to their wastage in technological process. In addition, some of them are responsible for destroying an ozone layer in the atmosphere and for photochemical smog.

Catalytic combustion combined with absorption of some undesirable reaction by-products and adsorption are most often used for removal of chlorinated hydrocarbon vapours from exhaust gases. The first method is disadvantageous because of the necessity of preliminary dedusting and heating up of gases, destructing of some valuable substances and producing of secondary pollutants, especially chloric compounds. The second method allows us to recover the compounds being removed, but it also requires a fine preliminary dedusting and drying of gases. These methods are expensive and can be applied in multistage installations only.

2. SELECTION OF OIL ABSORBENTS

As absorbing liquids the following substances were chosen: silicone oil, two paraffin oils and vegetable oil. Silicone oil was chosen because of its high resistances to oxidation, stableness to heat, low surface tension, lacking of odour, physiological indifference, insolubility in water and dissolubility in some chlorinated hydrocarbons

Table

Selected features of oils and their prices

Oil type	Kinematic viscosity	Density	Ignition temperature	Solidifying temperature	Price*
	m^2/s	kg/m^3	K	K	zł/kg
Methylosilicone oil – POLSIL OM-10, Organika Sarzyna, Poland [1]	$10 \cdot 10^{-6}$ (298 K)	940	423	188	33.70
Paraffin oil – WINOG 7.5, Hansen a. Rosenthal KG, Germany [2]	$14.4 \cdot 10^{-6}$ (293 K)	835	423	258	5.40
Paraffin oil – WINOG 70 Hansen a. Rosenthal KG, Germany [2]	$225 \cdot 10^{-6}$ (293 K)	864	lack of data	lack of data	5.40
Vegetable oil – OLVIT, Z.P.T. OLVIT, Gdańsk, Poland [3]	$55 \cdot 10^{-6}$ (293 K)	914	613	lack of data	3.62

* 1 USD = 3.8 zł, January, 2001.

[1] They cause parenchymatous organ destruction and cancer.

(e.g. trichloroethylene, methylene chloride and tetrachloromethane). The choice of paraffin oils mainly results from their comparatively low price, nontoxic features, lacking of smell and insolubility in water. Vegetable oils, which belong to the linoleic acid group (e.g. soybean, linen, herm oils) and to the erucic acid group (e.g. rape, charlock oils), are competitive because of their price, availability, low toxity and high ignition temperature. However, their resistance to oxidation is lower[2].

The characteristic of the oils tested is given in table.

3. EXPERIMENTAL SETUP

The investigations were carried out using a laboratory model plant [4] consisting of an empty, double-coat, thermostatic, wetted-wall tubular column, 1 m high and 0.012 m diameter, an absorbate steam generator with dispenser, a system of feeding and receiving of absorption liquid, a system of temperature stabilization and standard measuring instrumentation, including hydrocarbon analyzer with FID detector.

Tubular columns offer the following advantages: the possibility of phrenic heat recuperation, low flow resistances, easy way of specifying an interfacial surface, simple construction, insusceptibility to blocking, cleaning easiness, the possibility of mass transfer intensity due to application of packing and a scale enlarging simplicity.

Model exhaust gases in the form of a mixture of preliminary cleaned (by active carbon) air and the steams of selected chlorinated organic compound (trichloroethylene) were introduced into the column bottom and contacted in countercurrent with oil.

Trichloroethylene absorption intensity in selected oils versus gas velocity, process temperature and trichloroethylene concentration in gaseous and liquid phases were measured. Intensity of absorption was determined as a standard absorption efficiency according to the following formula:

$$\eta = 100 \cdot \frac{C_{g1} - C_{g2}}{C_{g1}} \quad [\%].$$

The following ranges of parameters were tested: v from 0.5 to 1.5 m/s, $L = 10$ m^3/m^{2}h, T_g and T_l from 293 to 343 K, C_{g1} from 100 to 900 mg/m^3 and C_c from 0 to 530 g/m^3.

4. RESULTS AND DISCUSSION

The preliminary test of some selected oils applicability to trichloroethylene removal from exhaust gases was its absorption efficiency, depending on a gas veloc-

[2] It can be improved by using antioxidising agents, chelating agents, polysilicates or by oil hydrogenation.

ity. The following parameters were established during experiments: sparging density, gas and liquid temperature and trichloroethylene concentration in a gaseous phase. The column was continuously fed by fresh oil due to application of an open liquid circulation. In the investigated range of gas velocity, the absorption efficiency decreases with the increase in gas velocity (figure 1), which is due to cutting down a contact time. The highest absorption efficiency was obtained for the POLSIL OM-10 oil, which was by about 10% higher than that for the WINOG 7.5 oil and by 20% higher than these for the WINOG 70 and OLVIT oils at the gas velocity of 1 m/s. These differences were caused by various solubility of trichloroethylene in the oils investigated, various viscosities of oils which in consequence caused differences in liquid film thickness and various wetting abilities of tubular materials.

The results obtained proved that the intensity of mass transfer decreases with the increase in liquid viscosity.

Next, the sorption ability of oils was investigated in a closed cycle of liquid. The circulating liquid volume, velocities of media as well as temperature and inlet trichloroethylene concentration in gaseous phase were established. In equal time intervals (every two minutes), the outlet trichloroethylene concentration in gaseous phase was registered. Based on the results obtained we were able to establish a trichloroethylene mass balance and to find out the relationship between trichloroethylene absorption efficiency and trichloroethylene concentration in liquid phase (figure 2).

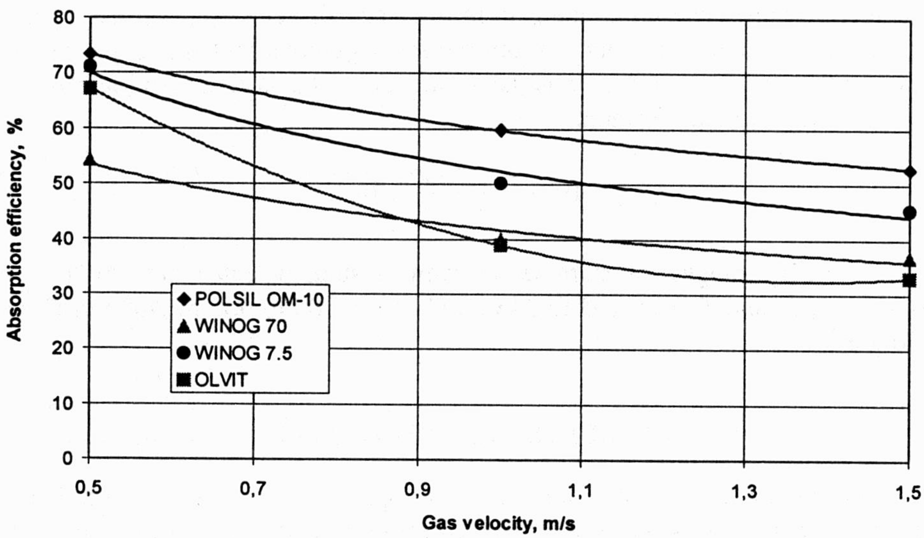

Fig. 1. Absorption efficiency as a function of gas velocity in empty column; $L = 10\ m^3/m^2h$, $C_{g1} = 400\ mg/m^3$, $T_l = T_g = 293$ K, $C_c = 0\ g/m^3$

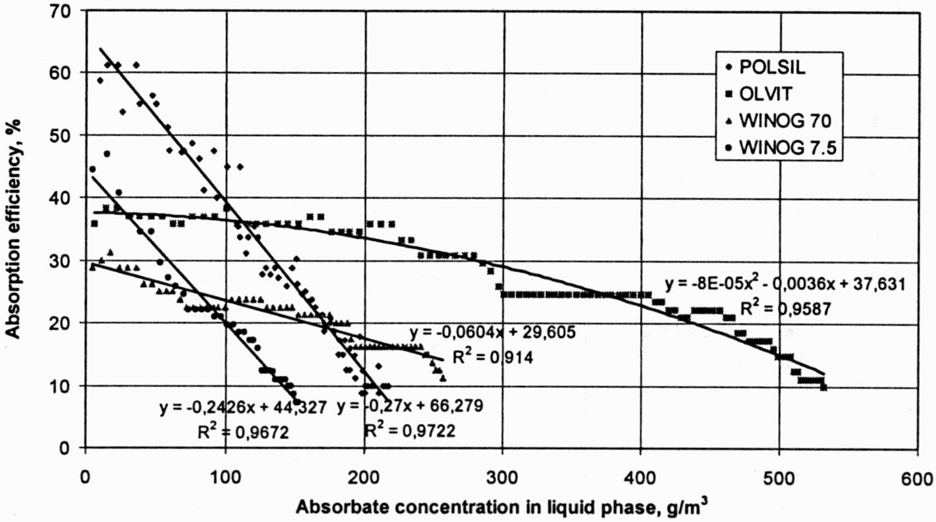

Fig. 2. Absorption efficiency as a function of trichloroethylene concentration in liquid phase; C_{g1} = 400 mg/m^3, L = 10 m^3/m^{2}h, v = 1 m/s, $T_l = T_g$ = 293 K

An increase of absorbate concentration in liquid causes a decrease of process motive modulus, thus a decrease of mass transfer. The differences in the sorption abilities of the oils tested are caused by various trichloroethylene solubility in these oils (in an available literature there are no equilibrium constants for the system examined).

On the basis of the investigation results we can construct the hypothesis that the absorption efficiency decreases more quickly with the increase of absorbate concentration in liquid for oils of low viscosity (e.g. POLSIL OM-10 and WINOG 7.5). So, the usage of low-viscosity oils increases the mass transfer intensity, but simultaneously a larger liquid volume is indispensable for absorbing the same absorbate quantity. Therefore, the cost of oil regeneration may increase. However, oils of higher viscosity require a larger mass transfer surface (consequently, absorber costs are higher).

In order to obtain the same absorption efficiency of trichloroethylene in the WINOG 7.5 oil as that in the POLSIL OM-10 oil, trichloroethylene concentration in liquid phase should be 1.5 times lower. Therefore, the WINOG 7.5 oil volume should be adequately larger. In this consideration, the OLVIT oil seems to be more profitably. Its advantage is more pronounced for trichloroethylene concentration in liquid higher than 110 g/m^3.

Analysis of the results obtained allows us to restrict our tests to two kinds of oils: the first of the highest absorption efficiency and the highest stability (POLSIL OM-10) and the second of the highest absorption capability and the lowest price (OLVIT). The dependencies of the absorption efficiency upon the trichloroethylene concentration in a gaseous phase (figure 3) and liquid temperature (figure 4) (under established other process parameters) were determined.

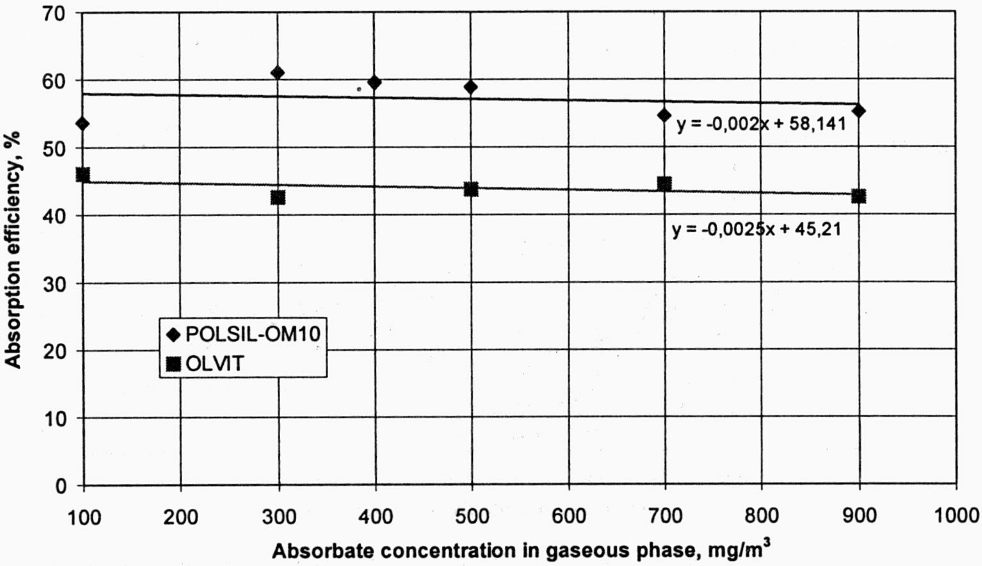

Fig. 3. Absorption efficiency as a function of trichloroethylene concentration in gaseous phase; $L = 10\ m^3/m^2h$, $v = 1$ m/s, $T_l = T_g = 293$ K, $C_c = 0\ g/m^3$

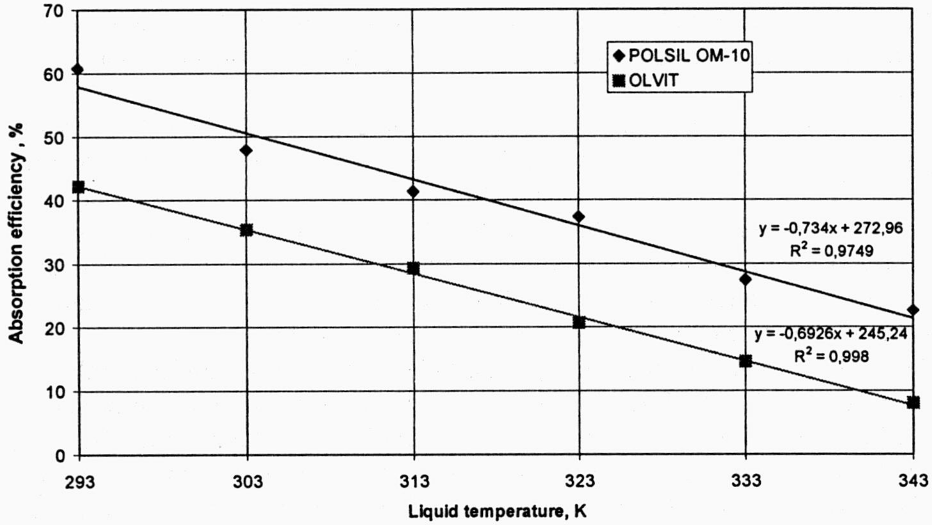

Fig. 4. Absorption efficiency as a function of temperature; $L = 10\ m^3/m^2h$, $C_{g1} = 400\ mg/m^3$, $v = 1$ m/s, $T_g = 293$ K, $C_c = 0\ g/m^3$

In the investigated ranges of parameters, the absorption efficiency of trichloroethylene does not practically depend on its concentration in gaseous phase, but notably decreases with a temperature rise (figure 4). Unprofitable influence of temperature rise on a mass transfer intensity (associated with the decrease of trichloroethylene solubility) is more significant than a profitable oil viscosity decrease with a temperature rise.

5. SCHEME OF THE CLEANING OF EXHAUST GASES

The idea of the method of purifying exhaust gases (figure 5) consists in chloroorganic pollutants absorption by oil and a subsequent absorbent regeneration associated

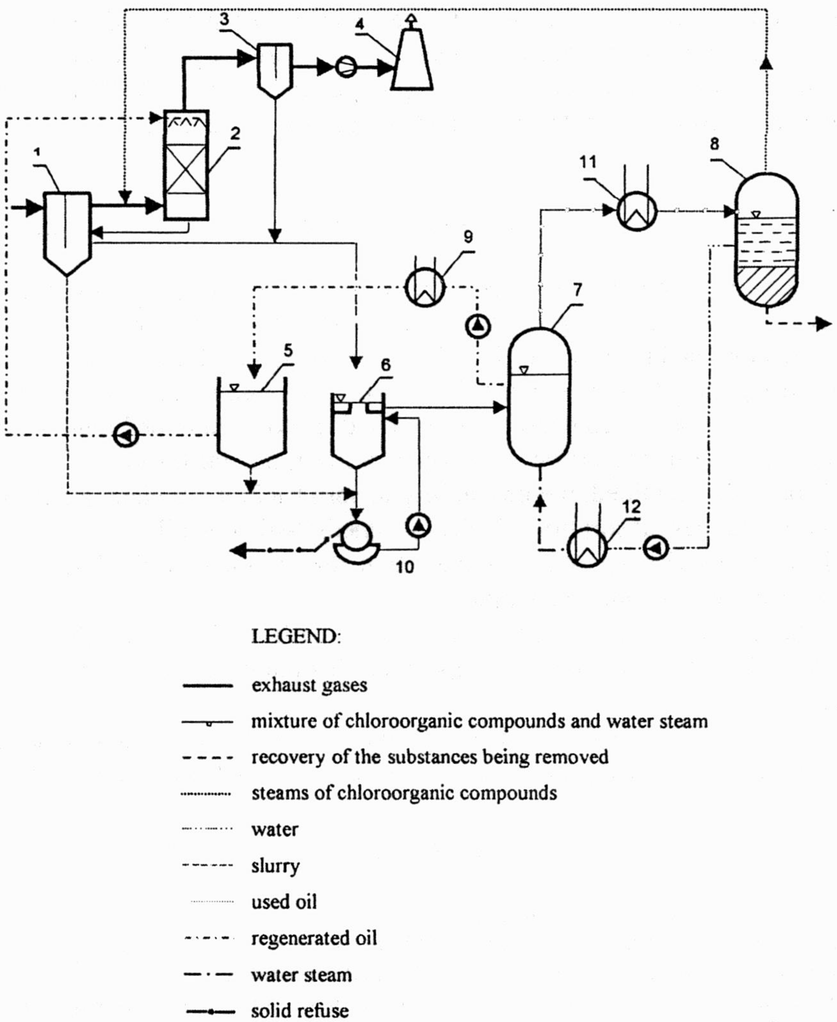

Fig. 5. Idea scheme of the waste cleaning technology

with the recovery of the compounds being removed [4], [5]. Exhaust gases, after possible preliminary cooling, dedusting and absorbing in the first stage of cleaning (*1*), are directed to absorption column (*2*), where they are contacted in a countercurrent with oil, and – through a demister (*3*) and a chimney (*4*) – are removed into the atmosphere. The oil is pumped to the top of the column (*2*) from the tank (*5*) and flows gravitationally – after the first stage of treatment (*1*) – to the sedimentation tank (*6*). Clarified oil is directed to the desorber (*7*), which is fed with water steam from the steam generator (*12*). The slurry from the first stage (*1*) and tanks (*5*), (*6*) is carried away to a drum-type filter (*10*). Desorbed substances, together with the water steam, are directed to the condenser (*11*), and then to the gravitational distributor (*8*). The mixture of condensed solvents is reused. The water from separator (*8*) feeds the steam generator (*12*). Tail gases from the condenser (*11*) are recycled to the column (*2*). Regenerated oil, through the cooler (*9*), is pumped to the tank (*5*). Water and oil circulate in a semi-closed cycle. Heat demand is minimized due to heat pump effect.

6. CONCLUSIONS

1. The method proposed enables both the reuse of valuable substances removed from exhaust gases and absorbent regeneration. This technology is not sensitive to gas concentration fluctuations and interruptions in pollutant inflows, it enables simultaneous removal of miscellaneous pollutants (including dust), does not cause secondary hazards to environment (in comparison to combustion methods), does not require preliminary drying and duplicating devices (in comparison to the standard adsorption methods).

2. Of four oils examined, the best ability to sorb trichloroethylene exhibits vegetable oil and the highest absorption efficiency – methyl-silicone oil.

3. Oils of a low viscosity enhance mass transfer, but they require larger volume of absorbent or more efficient regeneration.

4. At the trichloroethylene concentration ranging from 0.1 to 1.0 g/m^3, absorption efficiency of the oils tested does not depend on this pollutant concentration in a gaseous phase.

5. At the temperature range of 293–343 K, trichloroethylene absorption in the oils tested decreases lineary with the temperature rise (the slope of a straight line is equal to 0.7).

REFERENCES

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[5] GAJ K. et. al., Patent application No. P346668, 2001.

BADANIA WYBRANYCH OLEJÓW JAKO ABSORBENTÓW WĘGLOWODORÓW CHLOROWANYCH

Celem badań było określenie intensywności absorpcji wybranego zanieczyszczenia chloroorganicznego w wybranych olejach w zależności od ich rodzaju, prędkości gazu, temperatury, w jakiej zachodzi proces, stężenia absorbatu w fazie gazowej i ciekłej oraz porównanie zdolności sorpcyjnych analizowanych olejów. Przebadano olej silikonowy, dwa oleje parafinowe i olej roślinny, stosując laboratoryjną kolumnę rurkową ze zwilżonymi ściankami.

Najwyższą skuteczność absorpcji uzyskano dla oleju metylosilikonowego, a najwyższą zdolność sorpcyjną – dla oleju roślinnego (sojowego). Niekorzystny wpływ wzrostu temperatury na intensywność wymiany masy okazał się bardziej znaczący od korzystnego wpływu zmniejszenia lepkości oleju ze wzrostem temperatury. Końcowym efektem pracy jest schemat ideowy metody oczyszczania gazów odlotowych.