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SHORT COMMUNICATION

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PREVENTION AND CONTROL OF DIMETHYLAMINE VAPORS EMISSION: HERBICIDE PRODUCTION PLANT

The widely used herbicide, dimethylamine salt of 2,4-dichlorophenoxy acetic acid (2,4-D-DMA), is usually prepared by mixing a dimethylamine (DMA) aqueous solution with a solid 2,4-dichlorophenoxy acetic acid (2,4-D). The vapors of the both, reactants and products, are potentially hazardous for the environment. The contribution of DMA vapors in overall pollution from this process is most significant, concerning vapor pressures data of these pollutants. Therefore, the control of the air pollution in the manufacture and handling of methylamines is very important. Within this paper, the optimal air pollution control system in preparation of 2,4-D-DMA was developed for the pesticides manufacturing industry. This study employed the simple pollution prevention concept to reduce the emission of DMA vapors at the source. The investigations were performed on the pilot plant scale. To reduce the emission of DMA vapors, the effluent gases from the herbicide preparation zone were passed through the packed bed scrubber (water - scrubbing medium), and the catalytic reactor in sequence. The end result is a substantially improved air quality in the working area, as well as in the urbanized areas located near the chemical plant.

Key words: herbicide production plant; phenoxy class of herbicides; dimethylamine vapors; pollution prevention; wet scrubber; catalytic treatment.

A pesticide sector comprises many processing units which adopt different technologies, equipments, unit processes and unit operations for manufacturing various products. The manufacturing processes lead to the generation of a wide spectrum of air pollutants, mainly hazardous air pollutants. Some of these pollutants are toxic, responsible for the damage of materials and the creation of malodour.

In order to reduce the air pollutant(s) emissions to an acceptable level, it is necessary to adopt a comprehensive approach considering a possible thermal treatment, recovery of chemicals, good engineering practices and end-of-pipe technology [1,2].

The 2,4-dichlorophenoxy acetic acid (2,4-D) is the active ingredient in several formulations of herbicides widely recommended and used for the control of broadleaf weeds. One of these formulations is the

dimethylamine salt of 2,4-dichlorophenoxy acetic acid (2,4-D-DMA), the phenoxy class of herbicides, which exist on the market under various trade names. The preparation of 2,4-D-DMA is usually performed in the batch reactor by mixing a dimethylamine (DMA) aqueous solution with solid 2,4-D. Both, reactants and product(s) vapors are potentially hazardous for the environment [3-9]. The available data concerning vapor pressures of these pollutants point out that the contribution of DMA in overall pollution from this process is most significant. The vapor pressure of DMA aqueous solution of 197.3 mmHg is significantly higher in comparison with 2,4-D acid vapor pressure of 0.08 mmHg, while volatilization of the 2,4-D-DMA plays only a minor role due to its extremely low vapor pressure of 0.01 mmHg. Therefore, our investigations have been focused on DMA vapor emission reduction.

The four air pollution control methods in the manufacture and handling of DMA are currently in use among the producers and users of DMA [4,9,10].

The most successful and economical method involves the collection of all methylamine vapors into a vent system equipped with an absorber-scrubber unit. When large volumes of amine vapors are absorbed, it

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is often practical to recover the amines by distillation. The amines can also be recovered by using the absorber effluent as an amine solution.

The second method consists of feeding methylamine vapors to a small scrubber column packed with different shaped rings and using diluted sulfuric acid solution as the scrubbing medium. When the acid solution becomes saturated with amine sulfate, it is trickled into a waste treatment sewer. Care must be taken so that the saturated solution does not run into a heavy concentration of sodium hydroxide or other neutralizing solution that will liberate the amine.

The third method removes methylamine vapors by catalytic oxidation [11]. The supported noble metal

EXPERIMENTAL

Experimental system and synthesis procedure

Figure 1 shows the experimental system for the synthesis of 2,4-D-DMA along with the system for DMA vapors removal. A stainless steel batch reactor of 290 mm (Figure 1A, (1)) in diameter and the height of 243 mm, the nominal volume of 16 dm³ equipped with a mechanical agitator (5) with variable rpm. Solid 2,4-D from the reservoir was introduced into the reactor by a screw feeder (6) of 20 mm in diameter.

The synthesis procedure consists of the following steps with the continuous mixing:

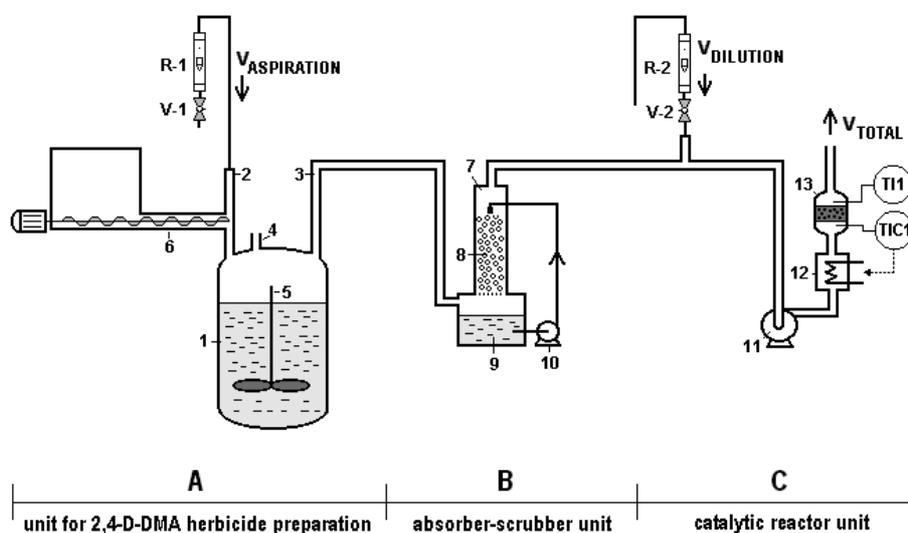


Figure 1. The scheme of the experimental system for DMA vapor removal: (A) unit for 2,4-D-DMA herbicide preparation, (B) absorber-scrubber unit, (C) catalytic reactor unit (1-batch reactor, 2-manifold for air introduction, 3-manifold for output aspiration gases, 4-manifold for liquid components addition, 5-mechanical agitator, 6-screw feeder, 7-scrubber, 8-raschig rings, 9-scrubber reservoir, 10-peristaltic pump, 11-fan, 12-electrical preheater, 13-catalytic reactor, R-1,R-2-gas flowrate indication, V-1,V-2-flowrate regulation valve, T11-temperature indication, TIC1-temperature indication and control).

catalysts are widely used for the complete oxidation of methylamine vapors. Final oxidation products are carbon dioxide, water vapor and nitrogen oxides. A preheater must be used to bring the gases to the reaction temperature of approximately 300 °C.

The last method consists of flaring the gathered amines with fuel gas. The total destruction of the methylamine vapors is accomplished in a properly designed flare stack.

In this paper, we have conducted the preparation of 2,4-D-DMA in the batch reactor with the aim to investigate the optimal air pollution control system. We have restricted our considerations on absorption in a scrubber with pure water as scrubbing medium, catalytic oxidation over Pt supported catalyst and their combination.

Step I: adding settled quantities of the total water amount and of the total DMA aqueous solution.

Step II: feeding batch reactor with the whole amount of solid 2,4-D by a screw feeder and mixing.

Step III: adding the rest of the water and DMA aqueous solution to 100 % of the required amount, the additional mixing and discharging the product.

A void volume above the liquid phase in the reactor was continuously aspirated by a fan through the orifice (3) situated opposite the feeding gap. The contact of DMA vapors with solid 2,4-D in the feeding gap must be prevented in order to avoid clogging.

Catalytic reactor

The catalytic cylindrical stainless steel reactor (Figure 1C, (13)) 70 mm in diameter and the height of

300 mm loaded with the 170 ml Pt/Al₂O₃ catalyst. The mixture of the air and effluent gases was introduced to the reactor over an electric heater (12) at the temperature adjusted by a temperature inlet controller (TIC1). Inlet and outlet temperatures were continuously registered. Through sampling valves the VOCs inlet and outlet concentrations were determined by the gas chromatograph (GC) equipped with FID detector. Through the same sampling valve the NO_x concentration was continuously measured using NO_x chemiluminiscent analyzer. The inlet temperature was kept at about 310 °C and the gas mixture flowrate varied from 3.6 to 8.4 m³/h.

Absorber-Scrubber

The experimental absorber-scrubber unit is a PVC scrubber column (Figure 1B, (7)) 60 mm in diameter loaded with ceramic raschig rings 8 mm in diameter and the height of 8 mm (8), and pure water was used as the scrubbing medium. The height of the scrubber loading was 270 mm. The water with the flux of 18 m³ h⁻¹ m⁻² was recirculated between the scrubber reservoir (9), the nominal volume of 2.5 l, and the packed column by means of peristaltic pump (10), the capacity of 50 l/h. DMA content in scrubbing water was analyzed by the standard volumetric method, titration with 1 M HCl solution with phenolphthalein indicator. The effluent gas flowrate varied between 0.4 and 0.8 m³/h.

RESULTS AND DISCUSSION

The DMA vapour removal methods must satisfy the following conditions that were set up in advance: 1) the water content in the scrubber should be suitable for DMA recycling in the next synthesis step; 2) DMA explosion limits (*LEL* = 2.8 vol.%, *UEL* = 14.4 vol.%) had to be considered; 3) DMA autoignition temperature of 400 °C had to be avoided; 4) a permissible emission level of 10 mg/m³.

In order to evaluate the capability of the proposed methods for DMA vapors removal we conducted two sets of experiments. The first set of experiments involved DMA vapors removal only by catalytic oxidation (Figure 1, A+C), while in the second set the catalytic oxidation was combined with the absorption in water (Figure 1, A+B+C).

Catalytic oxidation

The experimental system is the same as in Figure 1, only without the absorber-scrubber unit (B). The effluent gases from the batch reactor were diluted with ambient air to avoid the explosion limits in the gas mixture. Preheater maintained the inlet gas

temperature to the catalyst bed at approximately 300 °C. Operational parameters are summarized in Table 1.

Table 1. Operational parameters for DMA vapor removal only by catalytic oxidation

Run	$V_{\text{aspiration flow, m}^3 \text{ h}^{-1}}$	$V_{\text{dilution flow, m}^3 \text{ h}^{-1}}$	DMA solution concentration, g/l
1	0.4	5.72	486.0
2	0.4	8.00	486.0
3	0.6	5.40	232.4

Dynamics of preparation steps the in batch reactor and inlet and outlet temperature profiles in a catalytic reactor are presented in Figure 2 in these three runs.

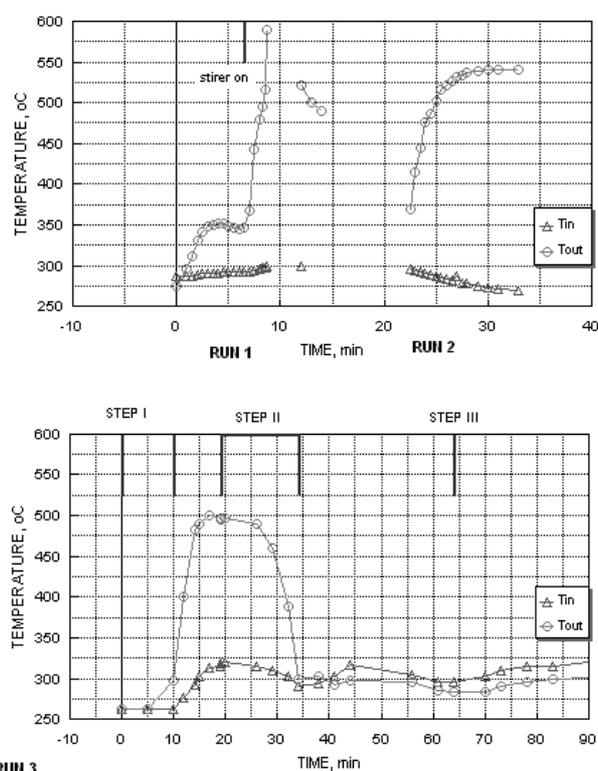


Figure 2. Dynamics of the preparation steps in a batch reactor and corresponding inlet and outlet gas mixture temperature profiles in a catalytic reactor (Step I - adding settled quantities of the total water amount and of the total DMA aqueous solution; Step II - feeding the batch reactor with the whole amount of solid 2,4-D by a screw feeder and mixing; Step III - adding the rest of the water and DMA aqueous solution to 100 % of the required amount, additional mixing and discharging the product; Tin-gas mixture temperature at the inlet of the catalytic reactor (TIC1, Figure 1); Tout-gas mixture temperature at the outlet of the catalytic reactor (T11, Figure 1)).

In Run 1, dilution ratio (ratio of dilution and aspiration flows) was 14.3. Immediately after the introduction of aqueous DMA solution in the batch reactor (Fi-

gure 1, (1)) the temperature rise of about 50 °C was observed in a catalytic reactor (Figure 1, (13)). When the stirrer was turned on, a sharp uncontrolled temperature increase above 600 °C was observed and the run was interrupted due to the safety reasons. Obviously, DMA concentration at the inlet of the catalytic reactor was too high. Therefore, the dilution ratio was increased to 20 in order to lower the temperature in the catalyst bed (Run 2) and the maximum temperature was 550 °C. In order to overcome unsafe conditions in the system, in Run 3, the concentration of feed DMA was decreased. After the start-up of the mechanical mixing in a batch reactor, the temperature rise in the catalytic reactor was about 500 °C. The beginning of the 2,4-D feeding, decreased the catalytic reactor temperature due to DMA spending in the neutralization process. The outlet temperature drop to the value of the inlet temperature after the whole amount of 2,4-D was spent. Further synthesis steps, additional mixing, adding the rest of DMA and water does not affect the temperature profile.

In all runs, the temperature in the catalyst bed overreached DMA autoignition temperature and probably heterogeneous and homogeneous oxidation simultaneously occurred in the catalytic reactor. It is possible to decrease the temperature in the catalyst bed either by increasing the dilution of the batch reactor effluent flow or by decreasing the feed concentration of DMA. The first treatment requires a too high dilution ratio that implicates to high energy consumption for preheating the inlet gas flow to the catalytic reactor and the reactor oversizing. The second treatment should dramatically decrease the productivity of the batch reactor.

The efficiency of the catalyst was very high, confirmed by the gas chromatograph analysis of outlet catalytic reactor gases. Organics concentration at the outlet was below detectability limits of the instrumental method.

Absorption and Catalytic oxidation

The well-known method for methylenes recovering is absorption in acidified water. We tried to utilize the benefits of catalytic oxidation in the combination with the absorption and that represents the second set of DMA vapors removal experiments in the experimental system presented in Figure 1.

The effluent gases from the batch reactor pass through the scrubber, a scrubber outlet gas mixture is diluted with ambient air prior to the catalytic reactor inlet. Operational parameters are summarized in Table 2.

In all runs, hydrocarbons concentrations at the catalytic reactor outlet were not detected by GC ana-

lysis, indicating almost 100 % conversion. Also, in all runs, DMA concentrations were far away from explosive limits, indicated by the moderate temperature rise in a catalytic reactor.

Table 2. Operational parameters for DMA vapor removal by absorption and catalytic oxidation

Run	$V_{\text{aspiration flow}}$ $\text{m}^3 \text{h}^{-1}$	$V_{\text{dilution flow}}$ $\text{m}^3 \text{h}^{-1}$	DMA solution concentration, g/l	Scrubber water loading, l
4	0.6	3.0	486	1.0
5	0.6	3.0	486	1.8
6	0.8	2.8	486	2.0

The scrubber efficiency was calculated on the basis of determined quantity of DMA in the scrubbing water (standard analytical method) and DMA concentrations behind the scrubber estimated by the temperature rise in the catalyst bed. These results are presented in Table 3. High scrubber efficiency enables the recovery of almost 90 % of emitted DMA. This DMA solution can be reused in the next herbicide preparation cycle. Only 10 % of the emitted DMA are fully oxidized over a noble metal catalyst. In this manner two benefits are achieved, the high recovery of DMA and the low undesired NO_x emission.

Table 3. Scrubber efficiency

Run	DMA in scrubbing water, g/l	DMA in scrub- bing water (total), g	DMA behind scrubber (total), g	Scrubber efficiency, %
4	36.00	36.00	9.00	83.11
5	20.25	36.45	4.50	91.19
6	19.00	38.00	3.00	87.11

CONCLUSIONS

This study was conducted in order to investigate the emission reduction of DMA vapors from effluent gasses in a herbicide preparation plant. DMA emissions were reduced by applying proper air pollution control techniques, a wet scrubber and a catalytic oxidation. The benefits of the catalytic oxidation in the combination with the absorption enable a complete removal of DMA vapors from the herbicide production plant. The final result should be a substantially improved air quality within the herbicide plant and in the neighbourhood urbanized areas.

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Nomenclature

2,4-D - 2,4-dichlorophenoxy acetic acid

2,4-D-DMA - dimethylamine salt of 2,4-dichlorophenoxy acetic acid

DMA - dimethylamine

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