

Impact of Catalytic Oxidation Operating Conditions on VOC and CO Conversions on the Pt-Pd/Al₂O₃ Catalyst

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The catalytic oxidation pilot unit with a fixed catalytic bed and Pt-Pd/Al₂O₃ catalyst was implemented before eventual full-scale use of the new catalytic oxidation technology for VOC abatement in the waste gas stream from acrylic acid related production. The pilot unit was used for long-term test, stress test, start-up tests of the catalytic reactor and different technological conditions tests. The long term test proved that chosen catalyst and technological layout can lower operating costs and still meet emission limits for VOC and CO. The estimated payback period of given investment was under 5 years. The stress test showed that unit can be partially overloaded (gas flows exceeding design value). In technological conditions tests, impact of the different gas flow and oxygen concentration levels on conversions of VOC and CO was observed. Such tests can help find out the optimal operating conditions for both pilot plant and full scale plant. It was discovered, that impact of the different oxygen concentration levels and gas flows in quite different for the conversions of VOC and CO. Results of the technological conditions tests and start-up tests are summarised in this contribution.

1. Introduction

In recent years a trend of emission limits tightening for gaseous pollutants within the framework of laws and regulations changes exists. This reflects global efforts to reduce emissions, which is also reflected at the level of EU and national levels. Within these efforts, there is a tightening pressure also on reducing emissions for VOC (Monks et al., 2009). The reason is not only undesirable photochemical oxidation reactions with NO_x, whose products deteriorate the state of the environment, but also the individual VOC exhibits varying degrees of toxicity and carcinogenicity, and have a negative effect on human health and the environment (Meciarova et al., 2014) with various atmospheric lifetimes (Koppmann, 2007). Gaseous wastes are produced mainly by industrial activities. If their production cannot be reduced by primary measures, series of secondary measures that ensure fulfilment of national and international limits must be taken. Volatile organic compounds (VOC) emissions occurs mainly in industry processing the organic material, e.g. various chemical solvents, fuels, cleaning agents, paints and others (Heck et al., 2002).

Chemical manufacturing company Momentive Specialty Chemicals, which products are from field of acrylic acid, its esters and acrylic polymers, produces off-gases streams, containing VOC among other pollutants. In the premises of the company, there are two thermal incineration plants.

At incineration plants are processed waste waters, distillation residues and several types of waste gas. The operation of these units is energetically costly, because its operation consumes large amount of natural gas. Therefore, a search for technologies that would reduce natural gas consumption, while complying with current local emission limits was made by company management. The possibilities to replace the existing incineration plant with a catalytic reactor technology were explored.

Catalytic oxidation is a modern variant of the thermal oxidation, where a catalyst is used, with benefits of combustion temperature decrease (Tungatarova et al., 2014). VOC concentration range of catalytic oxidation application is placed lower than the range for thermal oxidation. If stable flow of gas with a low

concentration of VOC can be reached, the catalytic unit can achieve an economically interesting result with a high efficiency for VOC removal (Schnelle and Brown, 2002).

2. Materials and methods

2.1 Existing technology arrangement and connection of pilot unit

The arrangement of the existing technology with marked connection of the pilot plan is shown in Figure 1. The process off-gas (PVG) is entering the heat exchanger 2E-632, where it receives heat from the exhaust gas. Before entering the combustion chamber 2F-630, the PVG off-gas is mixed with secondary off-gas VG. Natural gas (FG) and air (CA) are fed to the combustion chamber. Combustion gases from the combustion chamber are transported to heat exchangers 2E-630 and 2E-631, where low pressure saturated and medium pressure superheated steam is produced, respectively. Before entering the smokestack, cooled combustion gases preheat the PVG process off-gas in heat exchanger 2E-632.

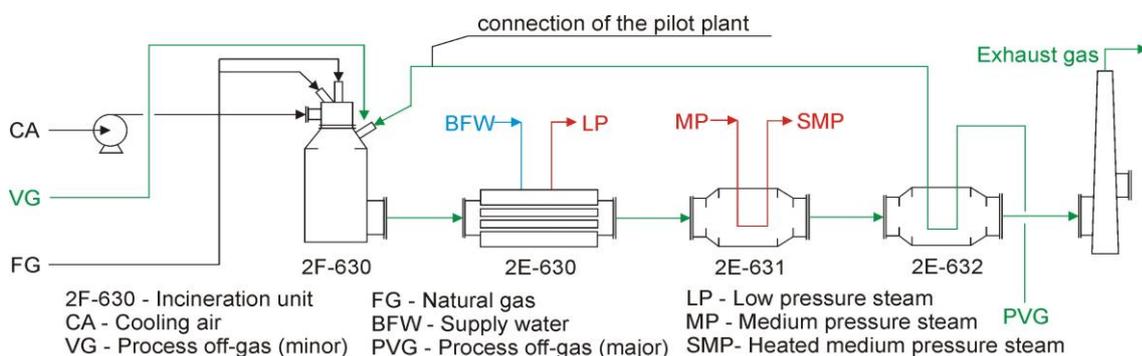


Figure 1: Flow sheet of the incineration unit (existing technology) with marked connection of the pilot plan

2.2 Measurement of the waste gas and other variables

Before the operating conditions tests and start-up tests, the measurement of the composition of waste stream was carried out. The results of the gas composition measurement are shown in Table 1. During operating conditions tests and start-up tests, pressure drop of catalytic bed, inlet pressure of waste stream and cooling air and also inlet and outlet temperature were measured or taken from the online measurements from the control system of a technology. In the waste stream, concentrations of O₂, CO, CO₂, SO₂, NO_x and VOC were monitored. The concentration of VOC was measured by FID analysers. Total VOC concentration fluctuated in the range of 6,000 – 10,000 mg TOC/m_N³ of VOC in wet gas. The content of O₂, CO and CO₂ was measured by IR analysers. Waste gas stream flow was calculated based on the pressure drop on an orifice plate.

Table 1: Composition of process off-gas PVG (humid gas)

Composition	N ₂ , H ₂ O vol. %	VOC vppm	VOC mg TOC/m _N ³	CO, CO ₂ , O ₂ vol. %	vol. %
O ₂				3.576	3.567
N ₂	63.568				63.568
H ₂ O	31.1				31.100
Acrylic acid (AA)		558	897.0		0.056
CO				0.522	0.522
CO ₂				0.524	0.524
Acetic acid (ACA)		1,295	1,388.2		0.130
Propylene		1,058	1,700.8		0.106
Propane		1,108	1,781.2		0.111
Formaldehyde (FAL)		2,763	1,480.4		0.276
Acroleine (ACR)		318	511.2		0.032
SUM	94.668	7,100	7,758.9	4.622	100.000
Temperature; Absolute pressure; Flow rate		73 °C; 106.33 kPa; 18,280 m _N ³ /h			

2.3 The catalytic oxidation experimental pilot unit and used catalyst

The setup and design for the pilot unit was similar as for the planned full scale unit, see Figure 2. For environmental applications of VOC removal from flue gas are most commonly used Pt catalysts or Pt-Pd mixed catalysts (Hermia et al., 1992). The catalyst used was Pt-Pd/Al₂O₃ - EnviCat® VOC-5565 in form of 4-6 mm spheres. Catalysts with precious metals generally have low light-off temperatures (Centi, 2001). Another advantage lies in their better oxidation up to CO₂ with fewer side products (Ojala et al., 2011, Tungatarova et al., 2014) than with use of transition metal oxides.

The catalytic bed was divided at a ratio of 1:3 into two beds, with a total catalytic bed height of 200 mm. In front of each bed, a 100 mm layer of Raschig rings were placed and a pressure air inlet was installed between the beds for cooling.

Operating parameters of the catalyst EnviCat® VOC-5565 are listed in Table 2.

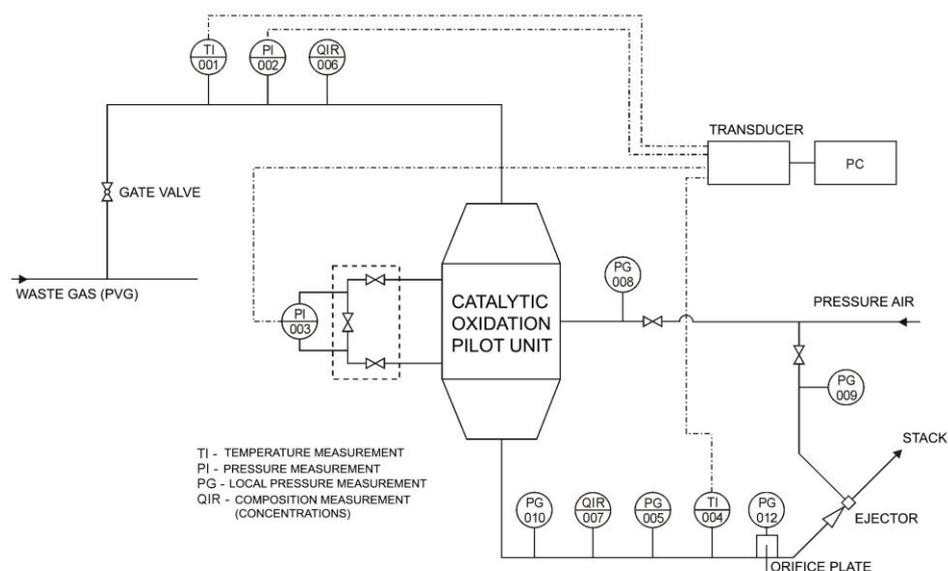


Figure 2: Catalytic oxidation pilot unit flow sheet with measurement and control

Table 2: Operating parameter of catalyst EnviCat® VOC-5565

Oxidation starting temperature	290 - 340 °C
Minimal outlet temperature from catalytic bed	550 °C
Maximum possible working temperature of catalyst	680 °C
Space velocity for design of the catalytic bed	10,000 h ⁻¹
Linear velocity for design of the catalytic bed	0.56 mN.s ⁻¹
Specific gravity of catalyst	600 kg.m ⁻³

3. Results and discussion

3.1 Start-up tests

Start-up of the pilot unit reactor was tested four times in total including one start-up with pre-heated bed. Non-preheated start-up lasted approximately 1 h 30 min, the outlet temperature rose above 600 °C. The steep drop in output concentration of VOC and CO was observed at the time of 15 - 20 min. from the beginning. Start with pre-heated bed was conducted with reactor already preheated to 300 °C.

At the start-up with pre-heated bed was steep drop in output CO and VOC concentration observed after about 5 min and 5 - 7 min. Total time of start-up with pre-heated bed was 40 min. For any full-scale application of catalytic oxidation will be necessary during the start-up to reckon with supply of auxiliary fuel (natural gas) to reduce emissions during this period and preheat the catalyst. Reducing the time required for start-up is important and desired.

It is necessary to avoid contact of the raw gas with the catalyst during the catalyst pre-heating to a required minimum temperature (ca. 300 °C) otherwise there is a threat of the conversion efficiency

reduction. This will be probably the case of our pilot tests, because pilot unit is designed so, it is not possible to preheat the catalyst other way than by waste gas stream. Off-gas flow should be increased after preheating of the catalyst gradually, in order not to violate half-hour emission limits during the start-up. Trends of VOC, CO, O₂ and CO₂ versus outlet temperature during non-preheated pilot unit start-up are showed on Figure 3 and 4.

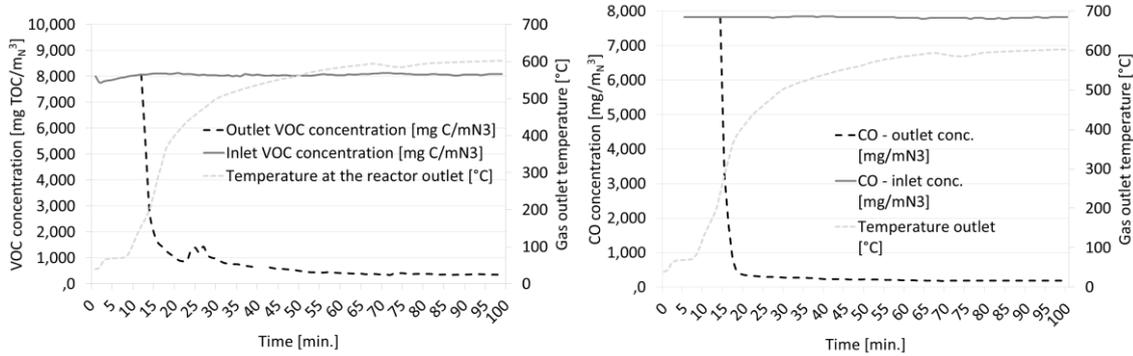


Figure 3: Trends of VOC and CO inlet and outlet concentrations and outlet temperature - pilot unit start-up

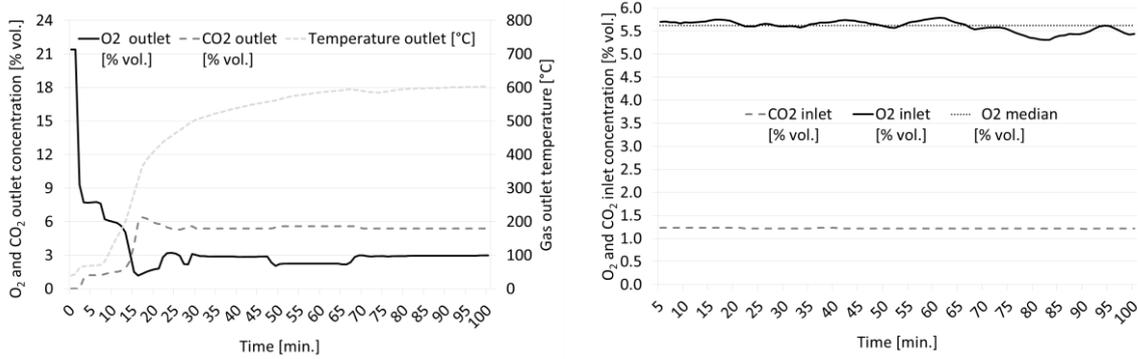


Figure 4: Trends of O₂ and CO₂ inlet and outlet concentrations and outlet temperature - pilot unit start-up

3.2 Technological conditions tests

Various regimes of gas flow through the reactor were tested. The gas flow through the reactor was gradually increased and the response of the technology was monitored after step changes of processed off-gas flow. Increase of the outlet temperature and also pressure drop of the catalytic bed occurred after each step change. Increase of the feed gas flow manifested in the reduction in VOC conversion more than for CO. Dependence of monitored pollutants removal efficiencies on the gas flow through the reactor are shown in Figure 5 (regression equations are valid only for measured range of gas flow). As can be seen on Figure 5 decrease in the conversion of VOC is steeper than for CO when increasing the gas flow through the reactor.

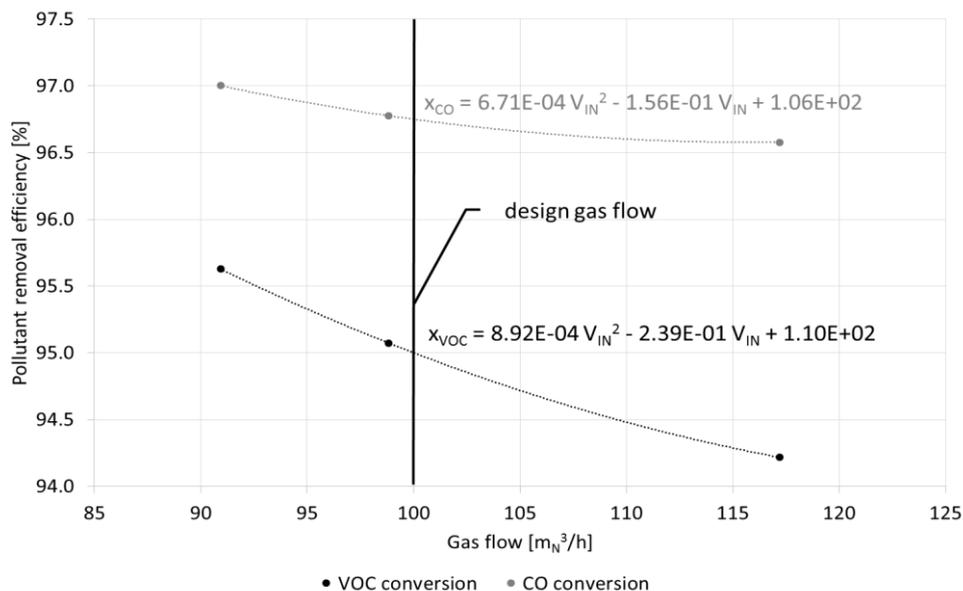


Figure 5: Dependence of monitored pollutants removal efficiencies on the gas flow through the reactor

Furthermore for technological conditions tests, conversion of pollutants when changing the oxygen concentration in the outlet gas was monitored. The catalyst manufacturer recommended to conduct the technology with an excess of oxygen so that the outlet oxygen concentration in raw gas is 2 % vol. (over the stoichiometric required amount). Oxygen concentration was changed by addition of pressure air between of the two catalytic beds. Minimal oxygen concentration was measured without addition of any pressure air.

Dependence of removal efficiencies of the monitored pollutants on the outlet oxygen concentration in dry gas are shown in Figure 6 (regression equations are valid only for measured range of O_2 concentration).

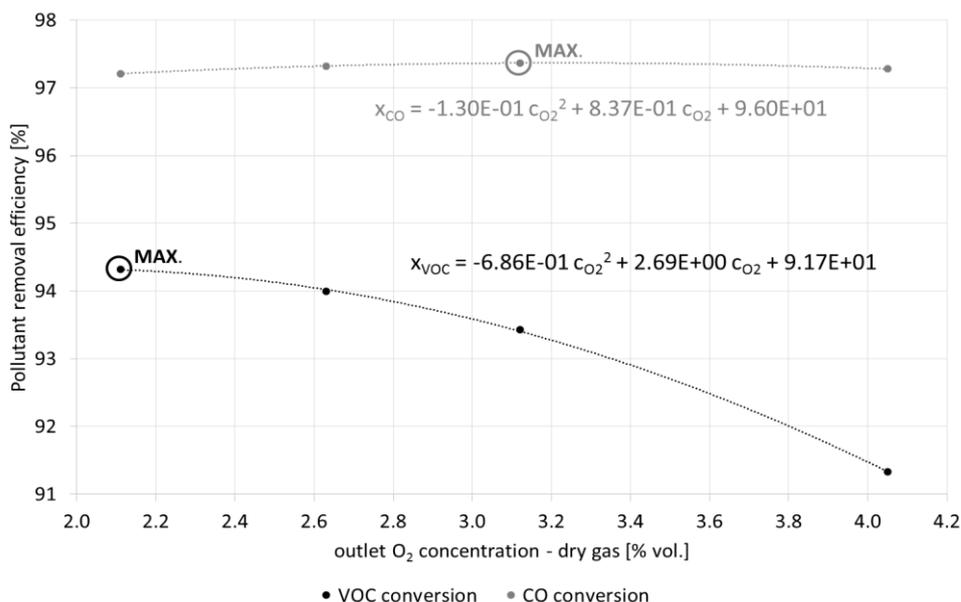


Figure 6: Dependence of removal efficiencies of the monitored pollutants on the outlet oxygen concentration in dry gas

Increase in the input stream oxygen concentration does not contribute to a better combustion of VOC, due to dilution of VOC concentration between catalytic beds and therefore reduction of the stream temperature

that negatively affects conversion of VOC. It was thus verified that for VOC oxidation reactions of this waste stream is more important the higher temperature than substantial stoichiometric excess of oxygen. Therefore any further over-stoichiometric increase in the oxygen concentration higher than 2 % vol. reduces the conversion of VOC. On the other hand, increasing the oxygen concentration contributes to an increase in the CO conversion, the output CO concentration with increasing oxygen concentration decreases. The conversion curve for CO is however quite flat, so there is no big difference in CO conversion resulting from the change of oxygen excess. From the incineration point of view is the appropriate oxygen concentration in the inlet dry gas 3.1 % and 2.1 % for CO and VOC. Because it is more difficult to reach the outlet VOC concentration fulfilling emission limits than in the case of CO, according to the measurement results, it is appropriate to conduct the combustion process with the oxygen concentration in the inlet stream of 2.1 vol. % in the dry gas (1.5 vol. % in the wet gas).

4. Conclusions

Normal and preheated start-up of the pilot unit reactor was tested. Non-preheated start-up lasted approximately 1 h 30 min, preheated took only 40 min, both reaching above 600 °C at steady state. For full-scale application of catalytic oxidation will be necessary to reckon with supply of auxiliary fuel during the start-up. It is necessary to avoid contact of the raw gas with the catalyst during the catalyst pre-heating to a required minimum temperature (ca. 300 °C), otherwise there is a threat of the conversion efficiency reduction. Off-gas flow should be increased after preheating of the catalyst gradually, in order not to violate half-hour emission limits during the start-up. Further, various regimes of the reactor gas flow were tested. Decrease in the conversion of VOC is steeper than for CO when increasing the gas flow through the reactor. Conversion of pollutants when changing the oxygen concentration in the outlet gas was monitored. Any further over-stoichiometric increase in the oxygen concentration higher than 2 % vol. reduces the conversion of VOC. On the contrary, increasing the oxygen concentration contributes to an increase in the CO conversion. Appropriate oxygen concentrations in the inlet dry gas were 3.1 % and 2.1 % for CO and VOC, respectively. It is more difficult to achieve VOC concentrations that meets emission limit in this case than CO, so oxygen concentration in the inlet stream of 2.1 vol. % in the dry gas (1.5 vol. % in the wet gas) is recommended for both pilot and full-scale application.

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